

# The age and accretion of the Earth

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## Abstract

Culminating a long series of effort, the monumental work of Patterson [Geochim. Cosmochim. Acta 10 (1956) 230] showed that the age of the earth was close to that of most meteorites at 4.55 Ga. Later refinements have consistently arrived at a younger age for the earth, shedding light on the accretion history of the earth. A review of progresses after Patterson's work is presented on ages for core formation, Xe closure, and formation of the earliest crust using U–Pb, Hf–W, I–Pu–U–Xe, Sm–Nd, and Nb–Zr systems; consistency among the systems is examined; and discrepancies are decoded. The combination of U–Pb and Hf–W systems can rule out some models of rapid earth accretion (at  $\sim 4.55$  Ga) followed by smooth and continuous core formation, but allow at least two different models. I–Pu–U–Xe systematics reveals a consistent and young age of  $4.45 \pm 0.02$  Ga for Xe closure. The systematics also allows an estimation of primordial  $^{130}\text{Xe}$  concentration in the bulk silicate earth to be  $0.034 \pm 3$  ppt, and I concentration to be  $15.5 \pm 2.8$  ppb. Earliest crustal formation age constrained by U–Pb ages of detrital zircon, coupled Sm–Nd system, and Nb–Zr system is about  $4.45 \pm 0.05$  Ga. The combination of all the isotopic constraints shows that they are consistent with either one of the following two scenarios for the accretion and differentiation of the earth: (i) A single age of  $4.45 \pm 0.02$  Ga for all events in the context of instantaneous differentiation, younger than Patterson's 4.55 Ga by about 100 Myr. This age would most likely represent the time of the last giant impact by an impactor of the size of Mars or greater, from which the earth was rehomogenized and reborn. The age would probably also signify the time when the earth reached about 80–90% of its present mass. In this scenario, the history of the proto-earth before 4.45 Ga was obliterated by the giant impact at  $\sim 4.45$  Ga. (ii) Continuous earth accretion and simultaneous core formation with a mean age of 4.53 Ga (mean accretion time of 30 Myr). The continuous accretion was infrequently disrupted by giant impacts that were not powerful enough to rehomogenize the whole earth. The last of such impacts (by a body the size of the moon or greater) occurred at about 4.45 Ga, which stripped the atmosphere from the earth and remelted the crust of the earth. In this scenario, some history of the proto-earth before 4.45 Ga is still preserved in the isotopic records. If the measurement precision of  $^{182}\text{W}/^{184}\text{W}$  ratio can be improved by a factor of 10, or if earliest crust formation age can be further constrained, it will be possible to rule out one of the scenarios and further constrain the accretion history of the earth.

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## 1. Introduction and overview

The age of the earth has intrigued mankind for a long time. The discovery of radioactivity near the end of 19th century led to the rise of isotope geochronol-

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ogy to determine ages of geologic events. High-quality Pb isotopic data (Nier, 1938; Nier et al., 1941; Patterson et al., 1953) allowed the estimation of the age of the earth, which was gradually refined from about 3 Ga to about 4.5 Ga (Holmes, 1946, 1947; Houtermans, 1946a,b, 1953). Patterson (1956) established that the earth and meteorites have a similar age of 4.55 Ga through Pb–Pb isotopic isochron (Fig. 1). Since then, there have been improvement and refinement of the age of meteorites and the earth, all of which point to slightly younger ages for the earth than primitive meteorites (Wetherill, 1975; Staudacher and Allegre, 1982; Allegre et al., 1995; Lee and Halliday, 1995, 1996; Galer and Goldstein, 1996; Zhang, 1998; Halliday and Lee, 1999; Ozima and Podosek, 1999; Halliday, 2000; Shearer and Newsom, 2000). In this work, I review the developments in refining the age and accretion history of the earth after Patterson's work, decode apparent problems and inconsistencies, and combine various isotopic systems to examine which models can be ruled out and which are allowed.

The age of the earth depends somewhat on its definition. The age of a person, for example, could be defined as the time of birth, or conception, or some other critical event in human development. The definition of the age by birth is satisfying because it is well defined, basically instantaneous, and easily deter-

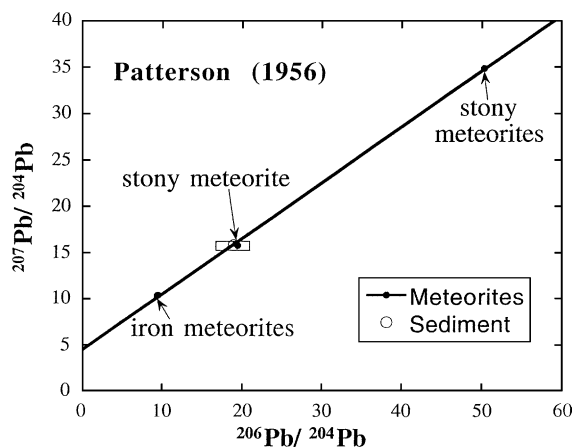


Fig. 1. Patterson's isochron (1956) to determine the age of the earth and meteorites. Pb isotopic ratios of two iron meteorites, three stony meteorites, and terrestrial oceanic sediment are shown. The boxed area is enlarged in Fig. 2.

minable. For the earth, if the earth formed simply by the collision of two planetesimals of roughly equal size, the timing of this event would be a good definition for the age of the earth. Because the earth is still growing at a rate of  $40,000 \pm 20,000$  tons a year owing to meteoroid bombardment (Ozima et al., 1984; Maurette et al., 1986, 2000; Takayanagi and Ozima, 1987; Esser and Turekian, 1988; Love and Brownlee, 1993), there is some degree of arbitrariness in the definition of the age of the earth. The approach used in many works is to define the age of the earth through a critical event in the accretion and differentiation history of the earth even though there would always be pitfalls. Such a critical event must be well defined, datable, and significant enough to be called the birth or rebirth of the earth. Some major events related to the formation of the earth are as follows.

### 1.1. The formation of the first minerals in meteorites

The ages of meteorites have been refined after Patterson's work. The age of first minerals (refractory inclusions) in primitive meteorites is well known, 4.56–4.57 Ga with the most precise Pb–Pb age of CAI's being  $4.566 \pm 0.002$  Ga (e.g., Chen and Wasserburg, 1981; Swindle and Podosek, 1988; Tilton, 1988; Allegre et al., 1995; Swindle et al., 1996). Since then, particles collided to form small planetesimals, which, in turn, collided to form larger planetesimals and eventually planets. There were no planet-sized bodies when the first meteoritic minerals formed. Although one may still define this to be the age of the earth and all planetary bodies because these minerals (as well as minerals formed later) contributed to the formation of planets and the sun, doing so would obscure the accretion process and the difference in the accretion history of different planetary bodies.

### 1.2. The first recognition of an earth-like planet

If continuous pictures were taken during early solar system evolution, there would be a time when a large planetary body was recognizably earthlike. Such recognition could be based on, for example, that near the current earth orbit (e.g.,  $1.0 \pm 0.1$  AU) there was one body that was significantly larger than the rest and with mass  $>50\%$  of the earth's present mass. (One cannot simply define the largest planetesimal at any

given time near the present earth orbit to be the proto-earth because collision of other smaller planetesimals may form a planetesimal larger than the first largest planetesimal.) The timing for a planetesimal to be recognizably earth-like may be the best definition for the age of the earth. However, this event cannot be dated at present.

### 1.3. *The earth roughly reached its present mass*

In his classic work on the age of the earth, Patterson (1956) interpreted the age that he obtained to mean the time when the earth roughly reached its present mass. Whether his interpretation is correct or not, defining the age as the time of roughly reaching its present mass is satisfying. Because the earth is still growing, roughly reaching the present mass must be more specific to be meaningful: such as reaching 90% of the present mass. Strictly speaking, this event cannot be dated because isotopic systems only date specific fractionation events. However, as will be seen next, it may be argued that the age is that of the last giant impact.

### 1.4. *The last giant impact*

Giant impacts during the accretion of the earth are almost a certainty (Hartman and Davis, 1975; Cameron and Ward, 1976; Wetherill, 1985, 1994; Stevenson, 1987; Cameron, 2001). A giant impact by an impactor of the size of the moon ( $\sim 1\%$  of the mass of the earth) may strip the atmosphere from the earth (e.g., Ahrens, 1993) and melt a significant portion of the earth. A Martian-sized ( $\sim 10\%$  of the mass of the earth) or greater impact would completely melt the earth and might be able to rehomogenize the earth. Because the impacts would restart isotopic systems, some of the isotopic ages likely date impact events. Furthermore, an impact by a body of the size of Mars or greater would significantly change the mass of the earth and hence the last giant impact might correspond to the time when the earth roughly reached its present mass (such as 90% of the present mass, allowing for 10% of the mass coming as late veneers (Wanke, 1981; Drake, 2000).

### 1.5. *Xe retention*

Because Xe is the heaviest gas in the atmosphere, the ability to keep Xe from loss to outer space

signifies that the earth was beginning to keep its atmosphere, reaching a critical stage in its accretion. Xe closure age can be determined using I-Pu-U-Xe system (Wetherill, 1975; Staudacher and Allegre, 1982; Allegre et al., 1995; Zhang, 1998; Ozima and Podosek, 1999). Barring catastrophic events such as giant impact, a proto-planet of the size of Moon (about 1/81 of earth's mass), and certainly the size of Mars, was already able to keep Xe in its atmosphere (Walker, 1977). However, Xe closure turned out to be fairly late in the accretion history of the earth ( $\sim 100$  Myr after the formation of primitive meteorites). The late Xe closure age is best explained by erosion of the atmosphere by giant impacts (e.g., Ahrens, 1993) unless one is willing to argue that at 4.45 Ga, the proto-earth only reached a small fraction of its present mass.

### 1.6. *Core formation*

Core formation defines the most major differentiation of the earth, during which 1/3 of the mass of the earth (siderophile elements) went to the core and 2/3 of the mass of the earth (lithophile elements) stayed in the mantle (Ringwood, 1960; Oversby and Ringwood, 1971; Jones and Drake, 1986; Li and Agee, 1996; Walker, 2000). Core formation would release heat, leading to higher temperature of the interior of the earth, which in turn leads to more rapid core growth. Hence, core formation is a process with strong positive feedback and could release enough heat to melt the whole earth (Birch, 1965; Flasar and Birch, 1973; Pollack, 1997). Therefore, much of earth differentiation likely occurred at this time. In addition to earlier works on Pb isotopes (e.g., Stacey and Kramers, 1975; Wetherill, 1975; Doe and Zartman, 1979; Duncan, 1985; Allegre et al., 1995; Galer and Goldstein, 1996), tremendous progress has been made recently on core formation age using Hf–W system (Lee and Halliday, 1996; Halliday and Lee, 1999; Halliday, 2000).

### 1.7. *Formation of the earliest crust*

The formation of the earliest crust marks the beginning of mantle–crust differentiation, another critical event in the evolution of the earth. Earliest crust formation likely occurred soon after core for-

mation and the time difference between core formation and first crust formation may be too small to be resolved. The age for the earliest crust formation has been elusive for some time. Extraordinary progress has been made in the last several years to constrain the age of the earliest crustal formation using Pb isotopes in detrital zircon, Sm–Nd and Nb–Zr systems (Mojzsis et al., 2001; Wilde et al., 2001; Harper and Jacobsen, 1992; Sharma et al., 1996a,b; Munker et al., 2000).

From the above discussion, not only the age itself is important, the meaning of the age is equally important, if not more so, for the understanding of the accretion and evolution history of the earth. Because an isotopic system can only date events that reset the isotopic clock, ages from different isotopic systems may have different meanings. Hf–W system can be used to date core formation that fractionates Hf from W (W is siderophile and preferentially goes to the core; and Hf is lithophile and stays in the mantle). I–Pu–U–Xe system can be used to determine the Xe closure age of the earth, similar to Ar closure age of a mineral or rock (Dodson, 1973). Sm–Nd coupled system and Nb–Zr system can be used to date earliest crustal formation that fractionates Sm from Nd and Nb from Zr (Nd/Sm and Nb/Zr ratios in the crust are greater than those in the mantle). The meaning of U–Pb age of the bulk silicate earth is more complicated but probably reflects the core formation age (Galer and Goldstein, 1996). Other systems (such as K–Ar) have not played a main role in constraining the age of the earth.

## 2. Pb isotopic age, and core formation age from Hf–W system

### 2.1. Pb isotopic age

Pb isotopic system is the first being used to determine the age of the earth and is also the system that later showed that the earth must be younger than 4.55 Ga. Three of the four stable Pb isotopes ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) are radiogenic:  $^{206}\text{Pb}$  receive contribution from  $^{238}\text{U}$ ,  $^{207}\text{Pb}$  from  $^{235}\text{U}$ , and  $^{208}\text{Pb}$  from  $^{232}\text{Th}$ . Because two U isotopes decay to two Pb isotopes, the U–Pb system is a coupled system and is very powerful in many applications (such as the

determination of model ages of the earth, Pb–Pb isochrons, U–Pb concordia, determination of zircon formation ages, etc.).

Initial work on the age of the earth focused on common lead (or conformable lead), referring to past Pb isotopes measured in minerals with negligible U/Pb and Th/Pb ratios so that their Pb isotopic compositions reflect those at the time of their formation (Aston, 1927; Nier, 1938; Nier et al., 1941). Holmes (1946) and Houtermans (1946a,b) independently formulated the model for Pb isotopic evolution for the U–Pb coupled system and derived the following equation:

$$\frac{(^{207}\text{Pb}/^{204}\text{Pb}) - (^{207}\text{Pb}/^{204}\text{Pb})_0}{(^{206}\text{Pb}/^{204}\text{Pb}) - (^{206}\text{Pb}/^{204}\text{Pb})_0} = \frac{(e^{\lambda_{235}t} - e^{\lambda_{235}t_1})}{137.88(e^{\lambda_{238}t} - e^{\lambda_{238}t_1})}, \quad (1)$$

where  $\lambda_{235}$  and  $\lambda_{238}$  are the decay constants of  $^{235}\text{U}$  and  $^{238}\text{U}$ , the subscript “0” means the initial state,  $1/137.88$  is the present  $^{235}\text{U}/^{238}\text{U}$  ratio,  $t$  is the model age of the earth and  $t_1$  is the age of conformable lead mineral formation ( $t_1 < t$ ). This model assumes that each common lead sample experienced a three-stage evolution: In the first stage (before  $t$ ),  $\mu$  (the present equivalent of  $^{238}\text{U}/^{204}\text{Pb}$  ratio) was small and there was negligible Pb isotopic growth. At the end of the first stage, Pb isotopic ratios were still similar to the primordial Pb isotopic ratios. In the second stage (between  $t$  and  $t_1$ ),  $\mu$  was high and constant. In the third stage (after  $t_1$ ),  $\mu$  was small and Pb isotopic growth was negligible. That is, Pb isotopic ratios only grew in the second stage and the growth was characterized by a constant  $\mu$ . The model has been known as the Holmes–Houtermans model. If the primordial  $(^{206}\text{Pb}/^{204}\text{Pb})_0$  and  $(^{207}\text{Pb}/^{204}\text{Pb})_0$  ratios were known (which were not until 1953; Patterson et al., 1953; Houtermans, 1953), from each pair of measured Pb isotopic ratios ( $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$ ) in a single common Pb sample, an age ( $t$ ) can be calculated from Eq. (1) if the age of the common Pb sample ( $t_1$ ) is known. This calculated age is called the model age of the earth. Besides the uncertainties of model assumptions, the calculation for the age of the earth was further hampered by the imprecise isotopic ratio determination, and uncertainties in  $(^{206}\text{Pb}/^{204}\text{Pb})_0$ ,

$(^{207}\text{Pb}/^{204}\text{Pb})_0$ , the decay constants, and the age of each ore deposit. Nevertheless, the estimated model age of the earth was gradually refined from about 3 Ga to about 4.5 Ga (Holmes, 1946, 1947; Houtermans, 1946a,b, 1953).

Patterson et al. (1953) determined  $^{206}\text{Pb}/^{204}\text{Pb}_0$ ,  $(^{207}\text{Pb}/^{204}\text{Pb})_0$ , and  $^{208}\text{Pb}/^{204}\text{Pb}_0$  ratios by measuring Pb isotopic ratios in troilite in Canyon Diablo (an iron meteorite). The sample contains negligible amount of U and the effect of decay can be corrected (Tatsumoto et al., 1973; Chen and Wasserburg, 1983). It is assumed that Pb was isotopically uniform at the beginning of the solar system. The determination of these primordial ratios provided the critical data to Houtermans (1953) to refine the model age of the earth. Later, Patterson (1956) used the Pb–Pb isochron and investigated the age of meteorites and the earth. He found that three stony meteorites, two iron meteorites, and terrestrial ocean sediment (a clever choice of average Pb isotopic composition of surface rocks on the earth) almost fall on a single  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  isochron (Fig. 1). He hence concluded that the earth and these meteorites all have this age of 4.55 Ga. This work has become a classic: the 4.55-Ga isochron has since been termed the geochron; and the 4.55-Ga age of the earth has become widely known.

Since the work of Patterson, the decay constants of  $^{238}\text{U}$  and  $^{235}\text{U}$  have been refined (Jaffey et al., 1971), and new and more accurate isotopic data have been obtained. Meteorite ages have also been refined. Refractory (CAI) inclusions in chondrites are about 4.56–4.57 Ga, and chondrites and most differentiated meteorites (angrites, eucrites, iron meteorites, etc.) have a narrow age spread, ca. 4.54–4.57 Ga (Tatsumoto et al., 1973; Allegre et al., 1975; Wetherill, 1975; Birck and Allegre, 1978; Chen and Wasserburg, 1981; Swindle and Podosek, 1988; Tilton, 1988; Wasserburg, 1987; Lugmair and Galer, 1992; Allegre et al., 1995; Tera et al., 1997; Lugmair and Shukolyukov, 1998; Quitte et al., 2000). For terrestrial samples, on closer inspection of new and high precision Pb isotopic data displayed on the same  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram of Patterson (Fig. 2A is a close-up of Fig. 1), two features unknown to Patterson (1956) are clear: (i) most terrestrial Pb isotopic ratios do not fall on the 4.55-Ga geochron, but lie to the right-hand (younger) side (Fig. 2A; Doe and Zartman, 1979; Zindler et al., 1982; Zindler and

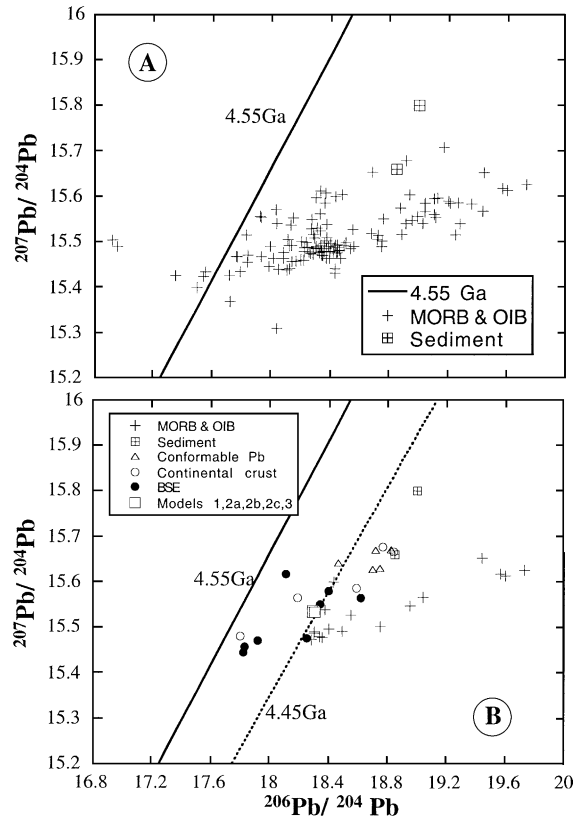


Fig. 2. Pb isotopic data compared with the 4.55- and 4.45-Ga geochrons (a close-up view of the small box in Fig. 1). (A) Individual measurements of some mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). (B) Various estimated averages of different reservoirs by different authors. The model results (squares) are discussed in the text. The various isochrons have different slopes. Data are from Cohen and O’Nions (1982), Zindler et al. (1982), Dupre and Allegre (1983), Hamelin et al. (1984), Staudigel et al. (1984), Hamelin and Allegre (1985), Zindler and Hart (1986), Allegre et al. (1986/87a) and Galer and Goldstein (1996). One of the points for sediment is from Patterson (1956).

Hart, 1986); and (ii) the data form a trend with a slope smaller than the 4.55 Ga. The trend with smaller slope can be attributed to various processes in the mantle such as mixing and differentiation, but that the average Pb isotopic ratios do not lie on the 4.55-Ga geochron is difficult to reconcile with the age of 4.55 Ga. If the bulk silicate earth (referred to as BSE hereafter, meaning crust plus mantle plus oceans plus the atmosphere) formed at 4.55 Ga, the average Pb isotopic data must lie on the 4.55-Ga geochron. That it does not is a problem called Pb paradox,

extensively discussed by Zindler and Hart (1986), among others. A search for a silicate reservoir with Pb isotopes lying to the left of the “geochron” so that BSE lies on it has not been successful (e.g., Rudnick and Goldstein, 1990; Galer and Goldstein, 1996). The paradox disappears if the time of U/Pb fractionation in the earth was younger than 4.55 Ga. That is, the Pb paradox implies that U/Pb differentiation age of the earth is younger than 4.55 Ga.

Many workers (Wetherill, 1975; Doe and Zartman, 1979; Duncan, 1985; Rudnick and Goldstein, 1990; Allegre et al., 1995; Galer and Goldstein, 1996) further quantified the Pb age of the earth using isotopic data similar to those shown in Fig. 2, as well as common Pb data in lead ore deposits as shown above. Often, a two-stage model is assumed for a modern sample: In the first stage, there was negligible Pb isotopic growth. At the end of the first stage, Pb isotopic ratios were still similar to the initial Pb ratios in the solar system at 4.56 Ga. In the second stage,  $\mu$  was high and constant. Hence, Pb isotopic ratios only grew in the second stage and the growth is characterized by a constant  $\mu$ . Thus, the model age ( $t$ ) of the earth can be solved from the following equation:

$$\frac{(^{207}\text{Pb}/^{204}\text{Pb}) - (^{207}\text{Pb}/^{204}\text{Pb})_0}{(^{206}\text{Pb}/^{204}\text{Pb}) - (^{206}\text{Pb}/^{204}\text{Pb})_0} = \frac{(e^{\lambda_{235}t} - 1)}{137.88(e^{\lambda_{238}t} - 1)}, \quad (2)$$

where the initial isotopic ratios of  $(^{207}\text{Pb}/^{204}\text{Pb})_0$  and  $(^{206}\text{Pb}/^{204}\text{Pb})_0$  are taken to be the primordial ratios in the solar system at 4.56 Ga (Patterson et al., 1953; Tatsumoto et al., 1973; Chen and Wasserburg, 1983; see Table 1 for values). Using Eq. (2), from each pair of measured Pb isotopic ratios in a single modern terrestrial sample, a model age ( $t$ ) can be calculated assuming there was no complicated evolution history for the sample (Wetherill, 1975; Doe and Zartman, 1979; Duncan, 1985; Allegre et al., 1995). Because the geologic history of most rocks is complicated, each model age does not necessarily have any meaning. Nevertheless, the weighted average of all model ages of the earth must be the same as the age of the earth.

Wetherill (1975) used the model age approach and estimated from modern Pb isotopic ratios that the

Table 1

Selected data for U–Th–Pb, Hf–W, and I–Pu–U–Xe systems

<i>Decay constants</i>	
$^{129}\text{I}$	$44.15 \times 10^{-9} \text{ yr}^{-1}$
$^{182}\text{Hf}$	$77 \times 10^{-9} \text{ yr}^{-1}$
$^{232}\text{Th}$	$0.04948 \times 10^{-9} \text{ yr}^{-1}$
$^{235}\text{U}$	$0.98485 \times 10^{-9} \text{ yr}^{-1}$
$^{238}\text{U}$	$0.155125 \times 10^{-9} \text{ yr}^{-1}$
$^{244}\text{Pu}$	$8.664 \times 10^{-9} \text{ yr}^{-1}$
<i>Fraction of parent that undergoes fission to a specific daughter (Ref. 1)</i>	
$^{244}\text{Pu}$ to $^{136}\text{Xe}$ ( $Y_{136}$ )	$(7.00 \pm 0.75)10^{-5}$
$^{244}\text{Pu}$ to $^{134}\text{Xe}$	$6.57 \times 10^{-5}$
$^{244}\text{Pu}$ to $^{132}\text{Xe}$	$6.20 \times 10^{-5}$
$^{244}\text{Pu}$ to $^{131}\text{Xe}$	$1.72 \times 10^{-5}$
$^{238}\text{U}$ to $^{136}\text{Xe}$ ( $X_{136}$ )	$(3.43 \pm 0.22)10^{-8}$
$^{238}\text{U}$ to $^{134}\text{Xe}$	$2.85 \times 10^{-8}$
$^{238}\text{U}$ to $^{132}\text{Xe}$	$2.04 \times 10^{-8}$
$^{238}\text{U}$ to $^{131}\text{Xe}$	$0.26 \times 10^{-8}$
<i>Concentrations in BSE</i>	
K	$240 \pm 40$ ppb (Ref. 2)
I	$10 \pm 3$ ppb (Ref. 3); $15.5 \pm 2.8$ ppb (this work)
$^{130}\text{Xe}$	$0.034 \pm 2.8$ ppt, or $2.6 \times 10^{-13} \pm 2.8$ mol/kg (this work)
Hf	$283 \pm 28$ ppb (Ref. 2)
W	$16 \pm 5$ ppb (Ref. 4)
Pb	$150 \pm 30$ ppb (Ref. 2)
U	$20.3 \pm 4.0$ ppb (Ref. 2)
Th	$79.5 \pm 12$ ppb (Ref. 2)
<i>Initial ratios</i>	
$^{129}\text{I}/^{127}\text{I}$ in Bjurböle	$0.000110 \pm 0.000003$ (Ref. 5)
$^{244}\text{Pu}/^{238}\text{U}$ in Bjurböle	$0.0068 \pm 0.0010$ (Ref. 6)
$^{182}\text{Hf}/^{180}\text{Hf}$ in Forest Vale	$0.000187 \pm 0.000016$ (Ref. 7)
$^{206}\text{Pb}/^{204}\text{Pb}$	$9.3066$ (Ref. 8)
$^{207}\text{Pb}/^{204}\text{Pb}$	$10.293$ (Ref. 8)
$^{208}\text{Pb}/^{204}\text{Pb}$	$29.475$ (Ref. 8)
<i>Elemental ratios</i>	
$^{180}\text{Hf}/^{184}\text{W}$ (atomic) in Chondrites	$1.30$ (Ref. 2)
$^{180}\text{Hf}/^{184}\text{W}$ (atomic) in BSE	$20.8$ (Refs. 2,4)
$^{127}\text{I}/^{130}\text{Xe}$ (atomic) in BSE	$4.7 \times 10^5$ (this work)
<i>Isotopic ratios at present day</i>	
$^{182}\text{W}/^{184}\text{W}$ in Chondrites	$0.864985 \pm 0.000025$ (Ref. 9)
$^{182}\text{W}/^{184}\text{W}$ in BSE	$0.865000 \pm 0.000018$ (Ref. 9)
$^{235}\text{U}/^{238}\text{U}$	$1/137.88$
<i>Mass of bulk silicate earth</i>	
	$4.1 \times 10^{24}$ kg

References: 1. Ozima and Podosek, 1983; 2. McDonough and Sun, 1995; 3. Deruelle et al., 1992; 4. Newsom et al., 1996; 5. Swindle and Podosek, 1988; 6. Hudson et al., 1989; 7. Lee and Halliday, 2000a; 8. Chen and Wasserburg, 1983; 9. Halliday, 2000.

earth was  $4.43 \pm 0.07$  Ga. He further showed that this age was consistent with model ages of common leads (conformable leads) as far back in time ( $\sim 3.7$  Ga) as data were available. Similar approaches were used by others (Stacey and Kramers, 1975; Doe and Zartman, 1979; Duncan, 1985). Allegre et al. (1995) used Eq. (2) to calculate the model ages of individual mid-ocean ridge basalts (MORB). They averaged the model ages for Pacific, Atlantic, and Indian MORBs to obtain an age of  $4.45 \pm 0.03$  Ga. Galer and Goldstein (1996) developed a model to treat both modern lead and old lead. Their best estimate of the Pb age of the earth is  $4.48 \pm 0.04$  Ga. Although these model ages are consistently younger than the isochron age obtained by Patterson (1956) by about 100 Myr, they have not been widely accepted, probably because the meaning of model ages is ambiguous because most rocks likely experienced a complex history.

Another approach is to estimate the Pb isotopic ratios in the present BSE, and then estimate the Pb age (Rudnick and Goldstein, 1990; Galer and Goldstein, 1996). (That is, rather than finding the model age first and then average the model ages, this method first averages Pb isotopic ratios of BSE and then finds a single age.) This method assumes that BSE is a closed system and hence Pb isotopic evolution in the BSE can be treated as a two-stage model in this context (Fig. 3a). (Nevertheless, there are other ambiguities as will be clear below.) The average Pb ratio in the BSE may be estimated from the average ratios in the two complementary reservoirs: the depleted mantle and continental crust. Average Pb isotopic ratios in the depleted mantle can be obtained from those in MORB. Average Pb isotopic ratios of the continental crust can be obtained from the weighted average of upper and lower continental crusts. The average Pb isotopic composition of the upper continental crust may be estimated from sediment, but the characterization of the lower continental crust remains an uncertainty. Rudnick and Goldstein (1990) estimated Pb isotopic compositions of lower crustal xenoliths. Galer and Goldstein (1996) summarized Pb isotopic ratios in various earth reservoirs (including BSE). Comparing these estimates with the various “geochrons” in the enlarged Pb–Pb isotopic diagram gives the Pb age of the earth (Fig. 2b). Clearly, estimated average Pb isotopic ratios in the BSE do not plot on

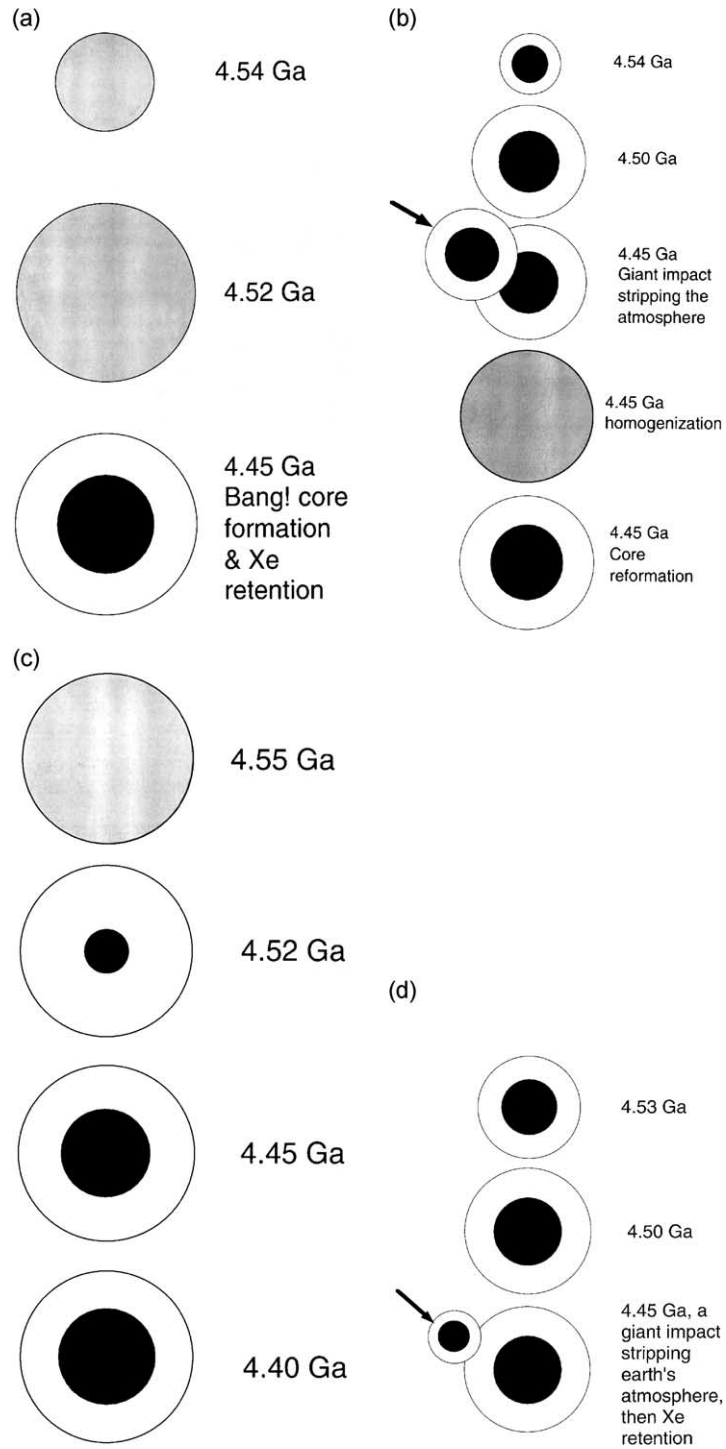
the 4.55-Ga isochron. The various estimates indicate a Pb age of 4.51–4.41 Ga.

The exact meaning of the Pb–Pb age has been debated. U is refractory and lithophile and hence behaves simply: it is not lost during condensation and does not go to the core. However, Pb is both volatile and chalcophile, and could be lost during condensation. Whether or not Pb goes to the core is not straightforward. The Pb content in iron meteorites is low (e.g., Gopel et al., 1985), arguing against Pb going to the core at low pressures. However, Pb can follow sulfur to the core (Oversby and Ringwood, 1971) or might go to the core at high pressures. U and Pb could hence be fractionated either by core formation, or by volatile loss during condensation, or both. Most authors assume that the Pb–Pb age means core formation age (e.g., Ringwood, 1960; Oversby and Ringwood, 1971; Allegre et al., 1995; Halliday, 2000). Jacobsen and Harper (1996) argued that Pb isotopes do not date core formation. Galer and Goldstein (1996) assessed the effect of volatile loss vs. core formation to Pb isotopic system, and estimated that volatile loss increased  $\mu$  in the earth from 0.14 to 0.67 and core formation increased  $\mu$  in BSE to  $\sim 9$ . They hence concluded that the Pb–Pb age is core formation age. If volatile loss occurred during a giant impact that also caused the reformation of the core (the preferred model in this work; see below), then ambiguity is removed since the two events (volatile loss and core formation) occurred roughly at the same time. Hence, U/Pb fractionation would roughly date both volatile loss and core formation during or right after the giant impact.

In addition to the uncertainty in estimating Pb isotopic ratios in the BSE and the above ambiguity of the meaning of the age, the same Pb isotopic data allow different physical models of core formation, leading to various ages. These subtleties and various interpretations will be discussed later, together with Hf–W constraints.

## 2.2. Hf–W system

The extinct nuclide  $^{182}\text{Hf}$  decays to  $^{182}\text{W}$  with a half-life of 9 Myr. Both Hf and W are refractory. W goes to the core but Hf stays in the mantle. Because of this fractionation, Hf/W ratio is  $\sim 1.11$  in CI chondrites and hence the whole earth (McDonough





and Sun, 1995), and 17.7 in BSE (Newsom et al., 1996). Hence, the Hf–W system can be used to constrain the core formation age. Harper et al. (1991) reported the first indication of the presence of  $^{182}\text{Hf}$  in the early solar system. Lee and Halliday (2000a) demonstrated the presence of  $^{182}\text{Hf}$  in the early solar system. Lee and Halliday (1995, 1996, 2000a,b), Lee et al. (1997), Halliday (2000), Halliday and Lee (1999), Halliday et al. (1996), and other workers (Horan et al., 1998; Quitte et al., 2000) discussed Hf–W systematics in meteorites, terrestrial rocks, and lunar rocks. Iron meteorites and the metal portion of ordinary chondrites have smaller  $^{182}\text{W}/^{184}\text{W}$  ratio than the bulk chondrites or the stone portion of ordinary chondrites, demonstrating very early metal–silicate segregation of meteorite parent bodies ( $\sim 4.55$  Ga). The initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio in the meteorite Forest Vale is  $(1.87 \pm 0.16) \times 10^{-4}$  (Lee and Halliday, 2000a). As with other extinct nuclides, it is assumed that the  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio in the early solar system is uniform from place to place and depends only on time. The age of Forest Vale is roughly 4.55 Ga, younger than that of Bjurbole (4.56 Ga; reference meteorite for I–Xe and Pu–Xe systems) by  $10 \pm 10$  Myr (Lee and Halliday, 2000a; Swindle and Podosek, 1988). For the discussion of  $^{182}\text{Hf}$ – $^{182}\text{W}$  system, this reference age of 4.55 Ga will be used instead of 4.56 Ga when other systems (U–Pb and I–Pu–Xe) are discussed.

Lee and Halliday (1995, 1996) and Lee (2000, personal communication) showed that all terrestrial rocks studied (including MORB, ocean island basalt, etc.) have an identical  $^{182}\text{W}/^{184}\text{W}$  ratio, that is the same as the ratio in carbonaceous chondrites within uncertainty. Because W goes to the core, Hf/W ratio in BSE is  $\sim 16$  times that in carbonaceous chondrites or

in the whole earth (Newsom et al., 1996). Hence,  $^{182}\text{W}/^{184}\text{W}$  ratio in the BSE is expected to be greater than that in carbonaceous chondrites if there was still live  $^{182}\text{Hf}$  after core formation. The similarity in  $^{182}\text{W}/^{184}\text{W}$  ratio between terrestrial rocks and carbonaceous chondrites and among different terrestrial rocks implies that core formation occurred after  $^{182}\text{Hf}$  in the earth decayed to a negligible level. Let  $\Delta(^{182}\text{W}/^{184}\text{W}) = (^{182}\text{W}/^{184}\text{W})_{\text{BSE}} - (^{182}\text{W}/^{184}\text{W})_{\text{CHON}}$  where subscript “BSE” and “CHON” mean bulk silicate earth and chondrites. If the core formed instantaneously, one can relate  $\Delta(^{182}\text{W}/^{184}\text{W})$  with core formation time as:

$$\begin{aligned} \Delta(^{182}\text{W}/^{184}\text{W}) = & [(^{180}\text{Hf}/^{184}\text{W}) \\ & - (^{180}\text{Hf}/^{184}\text{W})_{\text{CHON}}] \\ & \times (^{182}\text{Hf}/^{180}\text{Hf})_{\text{FV},0} e^{-\lambda_{182} \Delta t}, \quad (3) \end{aligned}$$

where  $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{FV},0}$  is the initial ratio in Forest Vale,  $\lambda_{182}$  is the decay constant of  $^{182}\text{Hf}$ , and  $\Delta t$  is the time interval between the earth’s core formation and formation of Forest Vale. Using values given in Table 1,  $\Delta(^{182}\text{W}/^{184}\text{W}) = (1.5 \pm 3.1) 10^{-5}$  (Halliday, 2000), and  $\Delta t$  can be calculated to be 71 Myr. Considering the uncertainty,  $\Delta t$  ranges from 57 Myr to infinity. Hence, core formation age is  $\leq 4.49$  Ga (Lee and Halliday, 1995). This is consistent with the Pb age. Therefore, Hf–W isotopic systematics supports (but does not prove) that major U–Pb fractionation occurred at core formation.

The absence of  $^{182}\text{W}$  anomaly in terrestrial rocks only provides a limit on core formation age. For example, W isotopic data cannot distinguish whether core formation was 4.49 Ga or 0.001 Ga. If the small

Fig. 3. (a) An unlikely scenario for earth accretion, core growth and Xe retention. The core is shown in darkened central region and the mantle is in white. Homogeneous “sphere” without a darkened core means that the core did not segregate. In this scenario, the earth roughly reached its present mass early on or before 4.50 Ga. Then at 4.45 Ga, suddenly there was core formation and Xe retention. This corresponds to the two-stage model in the text. (b) A likely scenario for earth accretion, core growth and Xe retention. The core is darkened. In this scenario, the earth reached about 70% of its present mass before 4.45 Ga (it could be about 4.50 Ga with little growth between 4.50 and 4.45 Ga). Then at 4.45 Ga, a Martian-sized planetesimal collided with the earth, adding >15% of the mass, stripped the earth its atmosphere, and rehomogenized the earth. Then the core regrew rapidly. Another 10% of the mass to the earth might have been added later as late veneers. (c) Another unlikely scenario for rapid earth accretion, and continuous and gradual core growth and Xe retention, corresponding to Models 2a, 2b and 2c in Section 3. In this scenario, the earth accreted and reached its present mass early at 4.55 Ga. Then there was continuous core growth lasting about 100 Myr. (d) A possible scenario for earth accretion, core growth and Xe retention. In this scenario, the earth accreted continuously and the core formed simultaneously. The mean age of earth accretion (and core formation) is 4.53 Ga. At 4.45 Ga, there was a lunar-sized giant impact, stripping earth’s atmosphere. Afterwards, Xe is retained. Hence, Xe retention age reflects the timing of impact.

difference in  $^{182}\text{W}/^{184}\text{W}$  isotopic ratio between terrestrial samples and CI chondrites can be resolved in the future with improved precision, Hf–W system would be able to provide a much more stringent constraint on core formation time.

### 2.3. More models on core formation ages

The above estimation of ages assumes a two-stage model with a sharp transition in between, explainable by a late and rapid core formation at 4.45 Ga (Fig. 3a). The simple model is physically unlikely because (i) core formation in small planetary bodies was early as evidenced by the old ages of iron meteorites and (ii) there is no known mechanism to delay core formation in the earth. Many other physical and mathematical models for core formation may be constructed and tested using the combined constraints of U–Pb and Hf–W systems. In these models, U–Pb fractionation is assumed to be simultaneous with Hf–W fractionation. It will be shown that the combined constraints can indeed rule out some models. Unfortunately, the combined constraints do not yet lead to a unique model: two models below can satisfy them. Another feature is that different models can lead to different

mean core formation ages for the same isotopic data. These intricacies are discussed below.

#### 2.3.1. Instantaneous core formation by a giant impact

One scenario is to assume that the earth grew smoothly but with some giant impacts that brought a significant fraction of mass to the proto-earth. If the most energetic giant impact is able to rehomogenize the earth (mixing the core back to the mantle), leading to instantaneous core reformation soon after the impact (see Fig. 3b), then Pb and W isotopes would date such a giant impact. For Pb system, let  $\mu$  vary as follows (Galer and Goldstein, 1996):

$$\mu = \begin{cases} 0.67 & \text{first stage } (0 \leq t \leq \tau) \\ 9 & \text{second stage } (t > \tau) \end{cases}, \quad (\text{Model 1})$$

where  $\tau$  is the time of core–mantle fractionation. This is referred to as model 1 shown in Fig. 4. Mathematically, the net result of this model is equivalent to a two-stage evolution model in which the parent/daughter ratio was low in the first stage and high (the present ratio) in the second stage. Hence, core formation age with this model is  $4.46 \pm 0.05$  Ga from Pb

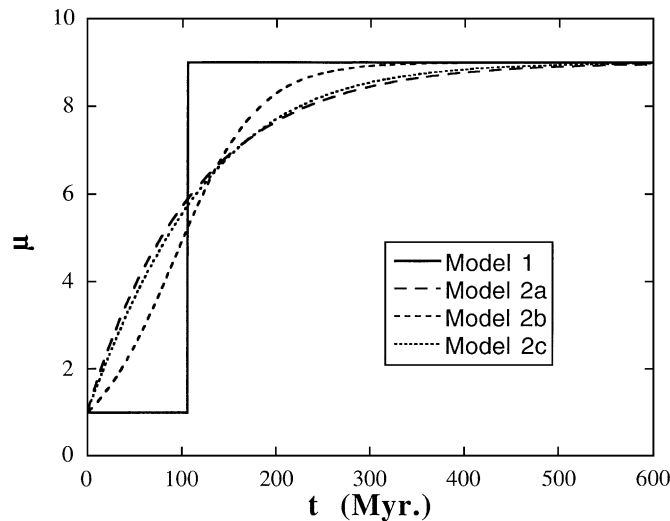


Fig. 4. Evolution of  $\mu$  in the BSE as a function of time ( $t=0$  means 4.56 Ga) in different models. Every model roughly satisfies the present-day  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios in the BSE (shown as squares in Fig. 2B). For Model 1, instantaneous core formation was 102 Myr after primitive meteorites. For Models 2a, 2b and 2c, mean core formation times are 107, 37, and 89 Myr, respectively. See text for discussion. For simultaneous accretion and core formation,  $\mu$  in the BSE is always 9 (not shown in this figure).

isotopes as derived above from the simple method (Fig. 2b). Similarly, core formation age from  $^{182}\text{Hf}$ – $^{182}\text{W}$  system (Lee and Halliday, 1995) is  $\leq 4.49$  Ga as derived above. Combining the two constraints, the core formation age is  $4.45 \pm 0.04$  Ga in the context of the instantaneous core formation model.

### 2.3.2. Rapid earth accretion followed by continuous core formation

In the second class of models, it is assumed that the earth accreted rapidly and formed at 4.56 Ga (or 4.55 Ga) as a homogeneous body and then the core grew smoothly (Fig. 3c). Although this scenario is physically unlikely, it has been a popular way to construct simple continuous evolution models for core formation and degassing (e.g., Galer and Goldstein, 1996; Jacobsen and Harper, 1996a,b). This group of models is discussed here also because of previously unrealized interesting consequences depending on the assumed evolution function. Three representative evolution models for  $\mu$  can be constructed under this scenario (others can also be constructed; Galer and Goldstein, 1996). In Model 2a,  $\mu$  is assumed to depend on time as (Galer and Goldstein, 1996),

$$\mu = 0.67 + (9 - 0.67)(1 - e^{-t/\tau}), \quad (\text{Model 2a})$$

where  $\tau$  is the time scale for core formation and  $t=0$  means the beginning of core formation at 4560 Ma. Knowing how  $\mu$  varies with time, Pb isotopic evolution can be calculated as:

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_t = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \int_0^t \mu e^{\lambda_{238}(4560-t')} \lambda_{238} dt',$$

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_t = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \int_0^t \frac{\mu}{137.88} e^{\lambda_{235}(4560-t')} \lambda_{235} dt'$$

where the unit of  $t$  is in million years (Myr). Varying  $\tau$  in Model 2a so that the calculated Pb isotopic ratios match the mean Pb isotopic data at present (Fig. 2B),  $\tau$  is constrained to be about  $107 \pm 50$  Myr; or core formation age is  $4.45 \pm 0.05$  Ga. The variation of  $\mu$  with time for  $\tau = 107$  Myr is shown in Fig. 4, and the

resulting Pb isotopic ratios are shown as a square in Fig. 2B. For  $^{182}\text{Hf}$ – $^{182}\text{W}$  system, a similar relation is assumed:

$$^{180}\text{Hf}/^{184}\text{W} = 1.3 + (20.8 - 1.3)(1 - e^{-t/\tau}) / (1 - e^{-4560/\tau}),$$

where the  $1/(1 - e^{-4560/\tau})$  term is necessary so that the present  $^{180}\text{Hf}/^{184}\text{W}$  is 20.8 (because  $\tau$  turns out to be large from numerical results). A  $\tau$  of  $\geq 1500$  Myr (or mean core formation age  $\leq 3.05$  Ga) would be required to generate  $^{182}\text{W}/^{184}\text{W} \leq 0.865018$  in the present BSE. Because it is expected that Pb and W would go to the core on a similar time scale, the large difference in  $\tau$  of the two isotopic systems ( $107 \pm 50$  Myr vs.  $\geq 1500$  Myr) implies that this model cannot reconcile the two isotopic systems and can be ruled out.

In Model 2b of the continuous evolution of  $\mu$ , it is assumed that  $1/\mu$  ratio decreases with time exponentially,

$$1/\mu = 1.5 + (1/9 - 1.5)(1 - e^{-t/\tau}), \quad (\text{Model 2b})$$

so that  $\mu=0.67$  initially and  $\mu=9$  at present. Varying  $\tau$  so that the calculated Pb isotopic data match the estimated mean Pb isotopic data at present (Fig. 2B),  $\tau$  is constrained to be about  $37 \pm 20$  Myr; or core formation age is  $4.52 \pm 0.02$  Ga. The variation of  $\mu$  with time for this  $\tau$  is shown in Fig. 4. For  $^{182}\text{Hf}$ – $^{182}\text{W}$  system, if a similar relation is assumed:

$$^{184}\text{W}/^{180}\text{Hf} = (1/1.3) + (1/1.3 - 1/20.8) \times (1 - e^{-t/\tau}) / (1 - e^{-4560/\tau}),$$

then a  $\tau$  of  $\geq 102$  Myr (or mean age of  $\leq 4.45$  Ga for core formation) is necessary for  $^{182}\text{W}/^{184}\text{W}$  in the present BSE to be  $\leq 0.865018$ . Hence, this model cannot reconcile the two isotopic systems.

In Model 2c, it is assumed that the mass of the core increased as  $F_{\text{core}} = 0.314(1 - e^{-t/\tau})$  where  $F_{\text{core}}$  is the mass fraction of the core (and currently  $F_{\text{core}} = 0.314$ ), and U and Pb partition between the core and BSE with

constant partition coefficients. Hence, the expression for  $\mu$  is:

$$\mu = \mu_0(D + F - DF)/F,$$

$$F = 1 - 0.314(1 - e^{-t/\tau}), \quad (\text{Model 2c})$$

where  $\mu_0 = 0.67$ ,  $F = F_{\text{mantle}} = 1 - F_{\text{core}}$ , partition coefficient for U between the core and BSE is assumed to be zero, and  $D$  is that for Pb between the core and BSE and is adjusted to 27.3 so that  $\mu = 9$  when  $F = 0.686$ . With this model, varying  $\tau$  so that the calculated Pb isotopic ratios match the mean Pb isotopic data at present,  $\tau$  is about  $89 \pm 40$  Myr; or core formation age is  $4.47 \pm 0.04$  Ga. The variation of  $\mu$  with time for this model and this  $\tau$  is shown in Fig. 4. For  $^{182}\text{Hf}$ – $^{182}\text{W}$  system, if a similar relation is assumed, then a  $\tau$  of  $\geq 1000$  Myr (or mean age of  $\leq 3.55$  Ga for core formation) would be required for  $^{182}\text{W}/^{184}\text{W}$  in the present BSE to be  $\leq 0.865018$ . Hence, this model cannot reconcile the two isotopic systems.

Three points can be made from the above models. (i) By combining U–Pb and  $^{182}\text{Hf}$ – $^{182}\text{W}$  systems, it is possible to rule out all three versions of continuous core formation models as presented above. (ii) Although the mathematical difference between Models 2a, 2b, and 2c appears to be small, the difference in constrained  $\tau$  (by Pb isotopic data, or by W isotopic data) is large. (iii) The variable  $\tau$  values coupled with the different functions result in relatively small different evolution history for  $\mu$  as shown in Fig. 4. For example,  $\mu$  reaches 6.5 at about the same  $t$  (130 Myr) in all three models (2a, 2b and 2c) for the  $\tau$  values given above. If  $\tau$  was the same for the three models, different function of  $\mu(t)$  would lead to large difference in the growth of Pb isotopes. This explains why very different  $\tau$  values are necessary for the different functions. That is, the mean ages can differ significantly simply due to the choice of the functional forms of  $\mu(t)$ . Therefore, caution is necessary in interpreting the significance of mean ages or mean times for core formation unless a priori knowledge is available for choosing an evolution function. By analogy, caution should be exercised for interpreting the physical meaning of mean degassing ages when modeling mantle degassing (e.g., Staudacher and Allegre, 1982; Sarda et al., 1985; Allegre et al., 1986/87b; Zhang and Zindler, 1989).

### 2.3.3. Continuous accretion and simultaneous core formation

Another model is continuous earth accretion and simultaneous core formation over time (Lee and Halliday, 1995; Halliday, 2000). In this scenario, the accretion is continuous and homogeneous (i.e., incoming planetesimals are homogeneous with metal/rock ratio similar to that in the present earth, instead of metal first and rock later). The mass fraction of the core is assumed to be constant (at 31.4%). As new materials with low  $\mu$  ( $\sim 0.67$  but the exact value does not matter as long as it is small) were added to the earth, the new materials were mixed into the mantle (hence altering Pb isotopic ratios in the mantle) with subsequent and “instantaneous” metal segregation from the mantle into the core. It is also assumed that there was no Pb flux from the core to the BSE. Assuming the mass of the earth grew as

$$M/M_0 = 0.001 + 0.999(1 - e^{t/\tau}), \quad (\text{Model 3})$$

where  $M_0$  is the present-day mass of the earth and  $\tau$  is the mean accretion time of the earth, Pb isotopic evolution in the BSE can be calculated. To satisfy the observed modern Pb isotopic data in Fig. 2b,  $\tau$  is found to be about  $30 \pm 5$  Myr (Halliday and Lee, 1999; Halliday, 2000), leading to a mean age of the earth of  $4.53 \pm 0.01$  Ga. (This is called the mean age of the earth, instead of mean age for core formation, because Model 3 deals with accretion of the earth with simultaneous core formation, whereas Models 2a to 2c deal with core formation in a fully grown earth.) In the context of continuous accretion model as defined in Model 3, there is no single age for the earth, and there was no major event at 4.53 Ga. According to the equation of Model 3, the mean age represents the time when the mass of the earth reached 63% of its present mass. The earth would have reached 86% of its present mass at 4.50 Ga ( $2\tau$  after 4.56 Ga), 95% of its present mass at 4.47 Ga, and 98% of its present mass at 4.44 Ga.

Using the same simultaneous accretion and core formation model for the  $^{182}\text{Hf}$ – $^{182}\text{W}$  system, mean time for earth accretion is  $\geq 24$  Myr (Lee and Halliday, 1996; Halliday and Lee, 1999; Halliday, 2000) to satisfy measured  $^{182}\text{W}/^{184}\text{W}$  ratio of  $\leq 0.865018$  in the present BSE, consistent with Pb isotopic data. W isotopic evolution in this model is shown in Fig. 5.

Earlier publications on W isotopes by Harper and Jacobsen (1996) and Jacobsen and Harper (1996a,b)

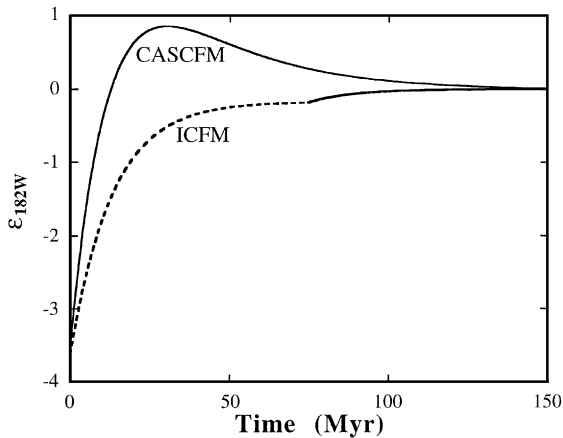


Fig. 5. Calculated evolution of W isotopic ratio in the BSE as a function of time for two models, where  $\epsilon_{182W} = 10,000[(^{182}\text{W}/^{184}\text{W})/0.865 - 1]$ . CASC FM = continuous accretion and simultaneous core formation model; ICFM = instantaneous core formation model (the same as two-stage model). The first part ( $t < 74.5$  Myr) of the ICFM evolution is dashed because it is not constrained by this model (there could be core formation before the last core formation). See Halliday and Lee (1999).

arrived at different mean times for core formation,  $\leq 10$  Myr. The reason for the apparent inconsistency is that Harper and Jacobsen (1996) and Jacobsen and Harper (1996a,b) assumed that chondritic  $^{182}\text{W}/^{184}\text{W}$  was about the same as that in the iron meteorite Toluca, an assumption that has been shown to be incorrect by the work of Lee et al. Hence, there is no inconsistency.

The effect of giant impacts can also be incorporated if the timing and mass of the giant impacts are known assuming the giant impacts only rehomogenized the impactor with the mantle of the proto-earth (no flux from the core to the mantle, otherwise it would result in Model 1). There are numerous combinations, and Halliday (2000) explored some of them. He concluded that W and Pb isotopic composition of BSE can be explained by a relatively late impact (such as  $\geq 70$  Myr after primitive meteorites). If the impact occurred at or before 50 Myr after the start of the solar system, there would have to be significant subsequent accretion, including possibly more giant impacts.

#### 2.3.4. Summary of model results

From the above discussion, the combined constraints from U–Pb and  $^{182}\text{Hf}$ – $^{182}\text{W}$  systems do not support rapid homogeneous earth accretion followed

by smooth and continuous core formation (Models 2a, 2b and 2c above). The ability to rule out some earth accretion and evolution models demonstrates the power of combining U–Pb and Hf–W systems. The U–Pb and  $^{182}\text{Hf}$ – $^{182}\text{W}$  data allow either of the following two scenarios: (i) the instantaneous core formation with an age of  $4.45 \pm 0.04$  Ga; and (ii) continuous accretion and simultaneous core formation with a mean age of the earth of  $4.53 \pm 0.01$  Ga. Conformable lead isotopic ratios as a function of geologic time do not provide much additional constraint.

Although the instantaneous core formation age and the mean age of the earth have different meanings, it is noteworthy that the two ages (4.45 vs. 4.53 Ga) based on the same combined U–Pb and Hf–W isotopic data depend so much on the details of accretion and growth models. Improving the precision of W isotopic measurement in the future may place more stringent limit on core formation and may remove the ambiguity. For instantaneous core formation with an age of 4.45 Ga,  $\Delta(^{182}\text{W}/^{184}\text{W})$  would be about  $10^{-6}$ . On the other hand, for simultaneous accretion and core formation with a mean age of 4.53 Ga,  $\Delta(^{182}\text{W}/^{184}\text{W})$  would be at about  $10^{-5}$ . Currently, the best measurement for  $\Delta(^{182}\text{W}/^{184}\text{W})$  (Eq. (13)) is  $(1.5 \pm 3.1)10^{-5}$  (Halliday, 2000), consistent with both models. If the measurement precision of  $^{182}\text{W}/^{184}\text{W}$  ratio could be improved to resolve whether  $\Delta(^{182}\text{W}/^{184}\text{W})$  is  $10^{-5}$  or  $10^{-6}$ , then it would be possible to distinguish between the two end-member models. (However, there would still be uncertainties related to complicated combination models of continuous accretion and giant impacts.) The above analysis further shows the power of the Hf–W system in constraining earth accretion and core formation.

### 3. Xe closure age using I–Pu–U–Xe system

#### 3.1. Data and general consideration of Xe closure age

It is now generally believed that earth's atmosphere originated from degassing of the earth (plus modifications by photosynthesis and other surface processes). This hypothesis is supported by observations. For example,  $^3\text{He}$  measurement in ocean water and in mid-ocean ridge basalt indicates that mantle degassing

is still occurring at mid-ocean ridges (Craig et al., 1975; Lupton, 1983). The high abundance of  $^{40}\text{Ar}$  (0.93 vol.%) in the atmosphere can only be derived from degassing  $^{40}\text{Ar}$  produced by decay of  $^{40}\text{K}$  inside the earth. Not long ago, it was argued that comets delivered most of ocean water (and presumably other volatiles) to the earth (e.g., Chyba, 1990). This hypothesis has been shown to be inconsistent with recent discovery of high  $^2\text{H}/^1\text{H}$  ratio ( $\sim 0.00032$ ; Meier et al., 1998) in ice in all three comets that have been analyzed. From  $^2\text{H}/^1\text{H}$  ratio in comets, in ocean water (0.0001558) and in the mantle (0.0001433), if one assumes that ocean water is a mixture of water from the mantle and from comets, cometary contribution to ocean water is about 7%. If one incorporates the fractionation effect between magma and water vapor and assumes the fractionation factor between water vapor and magma is 1.03 (Dobson et al., 1989), contribution to ocean water from comets decreases to  $\sim 5\%$ . If there was hydrodynamic escape that would have increased  $^2\text{H}/^1\text{H}$  ratio in surface water relative to mantle water, cometary contribution to ocean water would be  $< 5\%$ . Hereafter, the radiogenic components of Xe are assumed to be completely derived from the earth's interior, the same as  $^{40}\text{Ar}$ .

Xenon has nine stable isotopes. The isotopes  $^{124}\text{Xe}$ ,  $^{126}\text{Xe}$ ,  $^{128}\text{Xe}$  and  $^{130}\text{Xe}$  are nonradiogenic. The isotope  $^{129}\text{Xe}$  receives a radiogenic contribution from the extinct nuclide  $^{129}\text{I}$  (half-life = 15.7 Myr), and negligible contribution from fission. The isotopes

$^{136}\text{Xe}$ ,  $^{134}\text{Xe}$ ,  $^{132}\text{Xe}$  and  $^{131}\text{Xe}$  receive fissionogenic contribution from the extinct nuclide  $^{244}\text{Pu}$  (half-life = 80 Myr), and minor contribution from  $^{238}\text{U}$  (half-life = 4468 Myr). The minor contribution from  $^{238}\text{U}$  can be accounted for in quantitative treatment (Zhang, 1998), but ignoring it does not produce a significant error. Pepin (1991) estimated the nonradiogenic Xe isotopic composition of the terrestrial atmosphere. Hence, the amount of radiogenic Xe can be calculated (Table 2).

Many authors have quantified the I-Pu-U-Xe system to obtain the age of the earth. Wetherill (1975) used the I-Xe system to estimate the age of the earth to be 113 Myr younger than that of primitive meteorites. Staudacher and Allegre (1982) concluded that Earth was 50–70 Myr younger than the meteorites. Ozima and Podosek (1983) obtained 133 Myr for  $^{129}\text{I}$ – $^{129}\text{Xe}$  and 227 Myr for  $^{244}\text{Pu}$ – $^{136}\text{Xe}$ . The difference between these results is owing to differences in input parameters. Subsequent progress in geochemistry has improved some of the input data significantly (Hudson et al., 1989; Deruelle et al., 1992; McDonough and Sun, 1995). Revisiting the  $^{129}\text{I}$ – $^{129}\text{Xe}$  method, Allegre et al. (1995) concluded that the absolute age of Earth is 4.46 Ga, about 100 Myr younger than that of the meteorite Bjurböle. Zhang (1998) used the total inversion technique to treat all radiogenic Xe isotopes and obtained a Xe closure age of  $4.45 \pm 0.02$  Ga. Ozima and Podosek (1999), on the other hand, modeled Xe escape and obtained a for-

Table 2  
Radiogenic Ar and Xe isotopes

	$^{40}\text{Ar}$	$^{129}\text{Xe}$	$^{131}\text{Xe}$	$^{132}\text{Xe}$	$^{134}\text{Xe}$	$^{136}\text{Xe}$
Parent	$^{40}\text{K}$	$^{129}\text{I}$		$^{244}\text{Pu}$ and $^{238}\text{U}$		
Half life (Myr)	1250	15.7		80, 4468		
Contemporary atmospheric ratio	296	$6.4958 \pm 0.0116$	$5.2127 \pm 0.0118$	$6.6068 \pm 0.0106$	$2.5628 \pm 0.0074$	$2.1763 \pm 0.0044$
Nonradiogenic ratio	0.0003	$6.053 \pm 0.058$	$5.1873 \pm 0.0142$	$6.518 \pm 0.026$	$2.470 \pm 0.026$	$2.075 \pm 0.026$
Amount of radiogenic daughter in air ( $10^9$ mol)	$1.64 \times 10^9$	$277 \pm 36$	$15.9 \pm 8.8$	$55.6 \pm 16.4$	$58.1 \pm 16.4$	$63.4 \pm 16.4$
Total production in BSE ( $10^9$ mol) if BSE were 4.55 Ga	$(3.5 \pm 0.7)10^9$	$23,000 \pm 3$	$76 \pm 21$	$279 \pm 75$	$298 \pm 80$	$320 \pm 86$
Total production in BSE ( $10^9$ mol) if BSE were 4.45 Ga	$(3.3 \pm 0.7)10^9$	$276 \pm 3$	$33 \pm 10$	$121 \pm 36$	$131 \pm 38$	$141 \pm 41$

Ar data are from Ozima and Podosek (1983). Xe data are from Pepin (1991). The Ar isotopic ratio is for  $^{40}\text{Ar}/^{36}\text{Ar}$ , and the Xe isotopic ratios are relative to  $^{130}\text{Xe}$ . I concentration in present BSE used here for  $^{129}\text{Xe}$  production is  $10 \pm 3$  ppb (Deruelle et al., 1992), not the concentration derived in this work ( $15.5 \pm 2.8$  ppb) which would make the numbers more consistent. K and U concentrations are  $240 \pm 50$  ppm and  $20.3 \pm 4$  ppb (McDonough and Sun, 1995). Errors are given at the  $2\sigma$  level.

mation age of 4.49 Ga or older for the earth. Although on the surface, there is a significant difference between the result of Ozima and Podosek (1999) and the results of others, it will be shown later that the difference is owing to the different definition of the ages (Zhang, 2000).

Before going into quantitative calculations of the Xe closure age of the earth, the I–Pu–Xe constraints are summarized. Briefly, there is not enough radiogenic Xe in the earth, meaning that Xe closure age must be younger than 4.55 Ga. Because the amount of noble gases in the mantle cannot be directly determined, and because atmospheric composition is well known, it is necessary to understand the relation between radiogenic noble gases in the atmosphere and total radiogenic production in the BSE. This is done best with the  $^{40}\text{K}$ – $^{40}\text{Ar}$  system because (i) nonradiogenic  $^{40}\text{Ar}$  is negligible and hence the amount of radiogenic  $^{40}\text{Ar}$  in the atmosphere is the same as total  $^{40}\text{Ar}$  in the atmosphere ( $1.64 \times 10^{18}$  mol); and (ii)  $^{40}\text{K}$  (the parent of  $^{40}\text{Ar}$ ) has a long half-life of 1.25 billion years, meaning that small difference (4.55 Ga vs. 4.45 Ga) in the age of the earth does not significantly affect the calculated amount of  $^{40}\text{Ar}$  production. K content in the BSE has been estimated well to be about 240 ppm (McDonough and Sun, 1995). The estimated amount of total  $^{40}\text{Ar}$  production in the BSE over the earth history is  $3.3 \times 10^{18}$  to  $3.5 \times 10^{18}$  mol (Table 2). That is,  $\sim 50\%$  of total  $^{40}\text{Ar}$  production is now in the atmosphere and the other 50% is in the mantle (Table 2). The average degree of degassing of the whole mantle for  $^{40}\text{Ar}$  is hence 50%, less than that of the degassed mantle ( $\sim 80\%$ , Allegre et al., 1986/87b; Zhang and Zindler, 1989).

With  $^{40}\text{Ar}$  as the reference, global budgets of radiogenic and fissionogenic Xe isotopes are compared in Table 2. The amount of radiogenic  $^{129}\text{Xe}$  in the atmosphere ( $2.77 \times 10^{11}$  mol) would represent only 0.78% of total radiogenic  $^{129}\text{Xe}$  production, ( $3.55 \times 10^{13}$  mol, if the earth were 4.56 Ga (1.2% if the age were 4.55 Ga), far less than the degree of degassing for  $^{40}\text{Ar}$ . The amount of fissionogenic  $^{136}\text{Xe}$  in the atmosphere ( $63 \times 10^9$  mol) would represent only 18% of total fissionogenic  $^{136}\text{Xe}$  production if the earth were 4.56 Ga (20% if the earth's age were 4.55 Ga). The degree of degassing for radiogenic  $^{129}\text{Xe}$  is expected to be roughly the same as that of  $^{136}\text{Xe}$ ,

and the degree of degassing for Xe is expected to be slightly greater, rather than significantly smaller, than that for  $^{40}\text{Ar}$  (Zhang and Zindler, 1989; Zhang, 1998). This is because of smaller solubility of Xe than Ar (Jambon et al., 1986; Zhang and Zindler, 1989; Zhang, 1998) and because  $^{40}\text{Ar}$  is gradually produced in the mantle, whereas  $^{129}\text{Xe}$  and  $^{136}\text{Xe}$  were rapidly produced.  $^{40}\text{Ar}$  produced more recently may not have degassed. The large difference (1.2% vs. 20% vs. 50%) implies that there is a major problem in the assumption that the earth's age was 4.55 Ga. If the age of the earth is instead younger, the production of  $^{136}\text{Xe}$  would be less and that of  $^{129}\text{Xe}$  would be much less. Hence, qualitatively, the degree of degassing for these nuclides might become similar by a younger Xe closure age of the earth, eliminating the problem above (Table 2). The analyses below show that quantitative reconciliation can be achieved if the Xe closure age is  $\sim 4.45$  Ga. The different geochronometers in the I–Pu–U–Xe system are discussed first before the quantitative analyses.

### 3.1.1. Different geochronometers in the I–Pu–U–Xe system

There are several geochronometers in the I–Pu–U–Xe system to quantitatively extract Xe closure age, including  $^{129}\text{Xe}$ – $^{136}\text{Xe}$ ,  $^{129}\text{I}$ – $^{129}\text{Xe}$ ,  $^{244}\text{Pu}$ – $^{238}\text{U}$ – $^{136}\text{Xe}$ – $^{134}\text{Xe}$ – $^{132}\text{Xe}$ – $^{131}\text{Xe}$  (although each of  $^{244}\text{Pu}$ – $^{238}\text{U}$ – $^{136}\text{Xe}$ ,  $^{244}\text{Pu}$ – $^{238}\text{U}$ – $^{134}\text{Xe}$ ,  $^{244}\text{Pu}$ – $^{238}\text{U}$ – $^{132}\text{Xe}$ , and  $^{244}\text{Pu}$ – $^{238}\text{U}$ – $^{131}\text{Xe}$  can be used separately, they are usually treated together), and  $^{136}\text{Xe}^*1$ – $^{136}\text{Xe}^*2$  ( $^{136}\text{Xe}^*1$  is fissionogenic  $^{136}\text{Xe}$  derived from  $^{244}\text{Pu}$ ,  $^{136}\text{Xe}^*2$  is fissionogenic  $^{136}\text{Xe}$  derived from  $^{238}\text{U}$ ) methods. Some are more reliable than others.

For the  $^{129}\text{Xe}$ – $^{136}\text{Xe}$  method, one first obtains the ratio of radiogenic  $^{129}\text{Xe}$  to fissionogenic  $^{136}\text{Xe}$  in the atmosphere (Table 2). This ratio (4.4) is assumed to be the same as that in the BSE (assuming the same degree of degassing for  $^{129}\text{Xe}$  and  $^{136}\text{Xe}$ ). Then the initial  $^{129}\text{I}/^{244}\text{Pu}$  ratio in the earth at the time of Xe closure can be calculated as:

$$\left( \frac{^{129}\text{I}}{^{244}\text{Pu}} \right)_{\text{BSE},0} = Y_{136} \frac{^{129}\text{Xe}^*}{^{136}\text{Xe}^*1} \approx 3 \times 10^{-4}, \quad (4)$$

where  $Y_{136}$  represents the fraction of  $^{244}\text{Pu}$  that undergoes fission into  $^{136}\text{Xe}$ . The initial  $^{129}\text{I}/^{244}\text{Pu}$  ratio in

the BSE is related to Xe closure age of the earth as follows:

$$\left(\frac{^{129}\text{I}}{^{244}\text{Pu}}\right)_{\text{BSE},0} = \left(\frac{^{129}\text{I}/^{127}\text{I}}{^{244}\text{Pu}/^{238}\text{U}}\right)_{\text{B},0} \left(\frac{\text{I}}{^{238}\text{U}}\right)_{\text{BSE},0} \times \exp[-(\lambda_{129} - \lambda_{244} + \lambda_{238})\Delta t], \quad (5)$$

where  $I_{\text{BSE},0} = (^{127}\text{I})_{\text{BSE}}$  is the amount (mol) of I in the BSE, the subscript “B,0” means initial Bjurbole and  $\Delta t$  is time interval between Bjurbole formation and BSE formation. The advantage of this chronometer is that it does not require knowledge of the degree of degassing as long as the two radiogenic isotopes ( $^{129}\text{Xe}^*$  and  $^{136}\text{Xe}^*$ ) have the same degree of degassing. From the available data (Tables 1 and 2),  $\Delta t$  can be found to be  $90 \pm 25$  Myr (the uncertainty is largely due to the large uncertainty in the estimated I concentration in the BSE; Deruelle et al., 1992). Jacobsen and Harper (1996a,b) used the same approach but obtained a  $\Delta t$  of 70 Myr. It is not clear what caused the small difference. With the younger age of the earth by about 90 Myr, the total radiogenic production for  $^{129}\text{Xe}$  is decreased. Calculations show that radiogenic  $^{129}\text{Xe}$  in the atmosphere would represent 41% of total  $^{129}\text{Xe}$  production in the BSE, and fissionogenic  $^{136}\text{Xe}$  in the atmosphere would represent 40% of total  $^{136}\text{Xe}$  production in the BSE. These two fractions are similar and are not too different from that for  $^{40}\text{Ar}$ . Hence, a younger age for Xe closure than 4.56 Ga can bring consistency among the radiogenic noble gases.

$^{129}\text{I}$ – $^{129}\text{Xe}$ , and  $^{244}\text{Pu}$ – $^{238}\text{U}$ – $^{136}\text{Xe}$ – $^{134}\text{Xe}$ – $^{132}\text{Xe}$ – $^{131}\text{Xe}$  systems provide more constraints on the Xe closure age of the earth. To apply these constraints quantitatively, the degree of degassing of radiogenic Xe must be estimated. The half-life of  $^{40}\text{K}$  is 1.25 billion years, meaning that  $^{40}\text{Ar}$  is continuously produced. Recently produced  $^{40}\text{Ar}$  in the mantle is less degassed than  $^{40}\text{Ar}$  produced in the early history of the earth. On the other hand,  $^{129}\text{Xe}$  and  $^{244}\text{Pu}$ –fissionogenic  $^{136}\text{Xe}$  were produced very early in the earth’s history. Therefore, the degree of degassing for  $^{129}\text{Xe}$  from the whole mantle should be greater than that for  $^{40}\text{Ar}$ . Hence, the degree of degassing for Xe from the whole mantle is estimated (Zhang and Zindler, 1989) to be 60%, but changing this fraction

from 30% to 100% does not change the following results significantly. Knowing the percentage of total radiogenic Xe production that is in the atmosphere, one can obtain total  $^{129}\text{Xe}^*$  production, and hence initial  $^{129}\text{I}$  in the BSE. Then using I concentration in the BSE, one can obtain the initial  $^{129}\text{I}/^{127}\text{I}$  ratio of the BSE. Then the Xe closure age of the earth can be calculated from the following equation:

$$(^{129}\text{I}/^{127}\text{I})_{\text{initial earth}} = (^{129}\text{I}/^{127}\text{I})_{\text{B},0} e^{-\lambda_{129}\Delta t}, \quad (6)$$

where  $\Delta t$  is the time difference between Bjurbole formation and Xe closure age of the earth and is found to be 100 Myr.

Similarly,  $^{244}\text{Pu}$ – $^{136}\text{Xe}$ – $^{134}\text{Xe}$ – $^{132}\text{Xe}$ – $^{131}\text{Xe}$  system can be applied. On the basis of the amount of radiogenic  $^{136}\text{Xe}$ ,  $^{134}\text{Xe}$ ,  $^{132}\text{Xe}$ , and  $^{131}\text{Xe}$  in the atmosphere, one can estimate the required initial amount of  $^{244}\text{Pu}$ . Then the Xe closure age of the earth can be calculated from:

$$\left(\frac{^{244}\text{Pu}}{^{238}\text{U}}\right)_{\text{initial earth}} = \left(\frac{^{244}\text{Pu}}{^{238}\text{U}}\right)_{\text{B},0} e^{-(\lambda_{244} - \lambda_{238})\Delta t}, \quad (7)$$

Such Xe closure age of the earth is about 130–140 Myr younger than primitive meteorites depending on which isotope is considered.

The last geochronometer, which is currently highly uncertain, is the  $^{136}\text{Xe}^*1$ – $^{136}\text{Xe}^*2$  method. Because both  $^{244}\text{Pu}$  and  $^{238}\text{U}$  undergo fission to form  $^{136}\text{Xe}$ , the ratio of  $^{244}\text{Pu}$ –fissionogenic  $^{136}\text{Xe}$  to  $^{238}\text{U}$ –fissionogenic  $^{136}\text{Xe}$  can be used to calculate the initial ratio of  $^{244}\text{Pu}/^{238}\text{U}$  in BSE, which can be used to calculate the age of BSE. For example, if the age of BSE is 4.45 Ga, the ratio  $^{244}\text{Pu}$ –fissionogenic  $^{136}\text{Xe}$  to  $^{238}\text{U}$ –fissionogenic  $^{136}\text{Xe}$  would be 10.9, meaning only 8.4% of fissionogenic  $^{136}\text{Xe}$  is from  $^{238}\text{U}$ . However, currently, it is difficult to constrain the ratio of  $^{136}\text{Xe}^*1/^{136}\text{Xe}^*2$  and hence difficult to apply this geochronometer.

### 3.1.2. Reconciliation of all the geochronometers

Because all the geochronometers in the I–Pu–U–Xe system date the same event of Xe closure, they should all give one age. The slightly different Xe closure ages using I–Xe clock (4.46 Ga), Pu–U–Xe clock (4.43 Ga), and  $^{129}\text{Xe}$ – $^{136}\text{Xe}$  clock (4.47 Ga) are due to



uncertainties in the input parameters. The different ages can be reconciled by considering uncertainties in I and U concentration in BSE, initial  $^{129}\text{I}/^{127}\text{I}$  and  $^{244}\text{Pu}/^{238}\text{U}$  ratios, branch fission constants, and the amount of radiogenic Xe isotopes in the atmosphere (see Tables 1 and 2 and references therein).

Zhang (1998) considered I-Pu-U-Xe clocks together. Using total inversion (a regression method being able to handle uncertainties in input parameters; Tarantola and Valette, 1982), he treated all the radiogenic isotopes of Xe in the I-Pu-U-Xe system to constrain the Xe closure age. The following equations can be written (correcting an error in Zhang, 1998):

$$^{129}\text{Xe}^* = F_{129} (^{127}\text{I})_{\text{BSE}} \times (^{129}\text{I}/^{127}\text{I})_{T_0} \exp[-\lambda_{129}\Delta t], \quad (8)$$

$$^{136}\text{Xe}^* = Y(^{244}\text{Pu})_{T_0} F_1 \exp[-\lambda_{244}\Delta t] + X(^{238}\text{U})_{T_0} F_2 [\exp(-\lambda_{238}\Delta t) - \exp(-\lambda_{238}T_0)], \quad (9)$$

$$^{134}\text{Xe}^* = R_{134} Y(^{244}\text{Pu})_{T_0} F_1 \exp[-\lambda_{244}\Delta t] + Q_{134} X(^{238}\text{U})_{T_0} F_2 [\exp(-\lambda_{238}\Delta t) - \exp(-\lambda_{238}T_0)], \quad (10)$$

$$^{132}\text{Xe}^* = R_{132} Y(^{244}\text{Pu})_{T_0} F_1 \exp[-\lambda_{244}\Delta t] + Q_{132} X(^{238}\text{U})_{T_0} F_2 [\exp(-\lambda_{238}\Delta t) - \exp(-\lambda_{238}T_0)], \quad (11)$$

$$^{131}\text{Xe}^* = R_{131} Y(^{244}\text{Pu})_{T_0} F_1 \exp[-\lambda_{244}\Delta t] + Q_{131} X(^{238}\text{U})_{T_0} F_2 [\exp(-\lambda_{238}\Delta t) - \exp(-\lambda_{238}T_0)], \quad (12)$$

where  $^{129}\text{Xe}^*$  is the amount (mol) of radiogenic  $^{129}\text{Xe}$  in the atmosphere,  $F_{129}$  is the fraction of BSE-derived

$^{129}\text{Xe}^*$  that is in the atmosphere,  $^{129}\text{Xe}^*/F_{129}$  means the amount of initial  $^{129}\text{I}$  in the earth at the time of Xe closure,  $(^{127}\text{I})_{\text{BSE}}$  is the amount (mol) of I in the BSE, and  $(^{129}\text{I}/^{127}\text{I})_{T_0}$  is the initial isotopic ratio in the meteorite Bjurbole,  $T_0$  equals 4.56 Gyr,  $Y$  is the fraction of  $^{244}\text{Pu}$  that goes to  $^{136}\text{Xe}$ ,  $X$  is that of  $^{238}\text{U}$ ,  $R_{134}$  is the yield of  $^{134}\text{Xe}$  from  $^{244}\text{Pu}$  normalized to the yield of  $^{136}\text{Xe}$ , and  $Q_{134}$  is the yield of  $^{134}\text{Xe}$  from  $^{238}\text{U}$  normalized to the yield of  $^{136}\text{Xe}$ ,  $F_1$  is the fraction of  $^{244}\text{Pu}$ -fissionogenic  $^{136-131}\text{Xe}^*$  that is in the atmosphere and  $F_2$  is the fraction of  $^{238}\text{U}$ -fissionogenic  $^{136-131}\text{Xe}^*$  that is in the atmosphere. Eq. (5) is a combination of Eqs. (8) and (9) and hence not independent. From all the equations,  $\Delta t = 110 \pm 20$  Myr and the closure age of Xe is  $4.45 \pm 0.02$  Ga. The model of Ozima and Podosek (1999) will be discussed in a later section because it involves a fine point in the definition of the age.

### 3.1.3. Meaning of the I-Pu-U-Xe age

The meaning of the Xe closure age is similar to the closure age definition by Dodson (1973) and is explained in Fig. 6. The scale of the horizontal axis in the figure is such that  $^{136}\text{Xe}^*$  growth (for Fig. 6a) or  $^{129}\text{Xe}^*$  growth (for Fig. 6b and c) is linear with “scaled time”. If radiogenic Xe accumulation started at 4.56 Ga, the present amount of radiogenic  $^{136}\text{Xe}$  in the atmosphere (indicated as the long-dashed line intersecting the time “now”) would be about three times the actual amount, and that of radiogenic  $^{129}\text{Xe}$  would be 128 times the actual amount (hence, the actual amount of radiogenic  $^{129}\text{Xe}$  is tiny in the Fig. 6b and a close-up view in Fig. 6c is necessary). Regardless of the actual loss history, the closure age is always well defined by extrapolating the present amount back to the time of zero radiogenic Xe according to the radiogenic growth law. Furthermore, the Xe closure age is based on the total amount of  $^{129}\text{Xe}^*$ ,  $^{136}\text{Xe}^*$ , etc. in the earth, and it is less model dependent compared to the core formation age using Pb isotopic constraint. (Xe isotopic data in the mantle are not used to avoid complication and confusion.) Furthermore, precision for the Xe closure age is greater than that for core formation. The essence of the argument can be recapitulated as follows: the amount of  $^{129}\text{Xe}^*$  isotopes in the earth is so small that Xe closure age of the earth must be younger than primitive meteorites. The consistency between the I–

Xe system and Pu–UXe system provides independent check to the results.

### 3.2. Some apparent problems and inconsistencies

#### 3.2.1. Missing Xe “problem”

When nonradiogenic noble gas in the terrestrial atmosphere is compared to the chondritic pattern, Ne,

$^{36}\text{Ar}$  and  $\text{Kr}$  are depleted by a uniform factor, but Xe is depleted by an additional factor of about 20 (Ozima and Podosek, 1983). This additional depletion of Xe was often referred to as the missing Xe problem. It is critical to know whether there is a hidden Xe reservoir in the earth that can compensate for the missing Xe in understanding Xe geochemistry. For some time, it was believed that missing Xe is stored in sediment or some other reservoirs (e.g., Canalas et al., 1968; Finale and Cannon, 1971). Subsequently, authors have made measurements to show that Xe in shales and in glacial ice is not enough to account for missing Xe (e.g., Bernatowicz et al., 1984, 1985).

Possible missing Xe can be addressed using radiogenic Xe isotopes. Total  $^{136}\text{Xe}^*$  production in the BSE can be calculated from initial  $^{244}\text{Pu}$  and  $^{238}\text{U}$ . The maximum amount of  $^{136}\text{Xe}^*$  production can be obtained by assuming an age of 4.56 Ga and is  $3.43 \times 10^{11}$  mol (about 24% relative error). At present, total radiogenic  $^{136}\text{Xe}^*$  in BSE is about  $1.06 \times 10^{11}$  mol. Hence, using the constraint of  $^{136}\text{Xe}^*$  alone, missing radiogenic Xe can be at most three times the current amount of radiogenic Xe. However, considering  $^{136}\text{Xe}^*$  alone, assuming an age of 4.56 Ga would produce large inconsistencies with  $^{129}\text{Xe}^*$ . By considering both radiogenic  $^{129}\text{Xe}^*$  and radiogenic  $^{136}\text{Xe}^*$  and constraining the proportion of missing  $^{129}\text{Xe}^*$  and that of  $^{136}\text{Xe}^*$  to be the same, the amount of missing radiogenic Xe can be further constrained. That a closure age of 4.45 Ga can reconcile both radiogenic  $^{129}\text{Xe}^*$  and  $^{136}\text{Xe}^*$  (Zhang, 1998) is consistent with no missing radiogenic xenon in any terrestrial reservoir. In fact, output from the total inversion algorithm (Zhang,

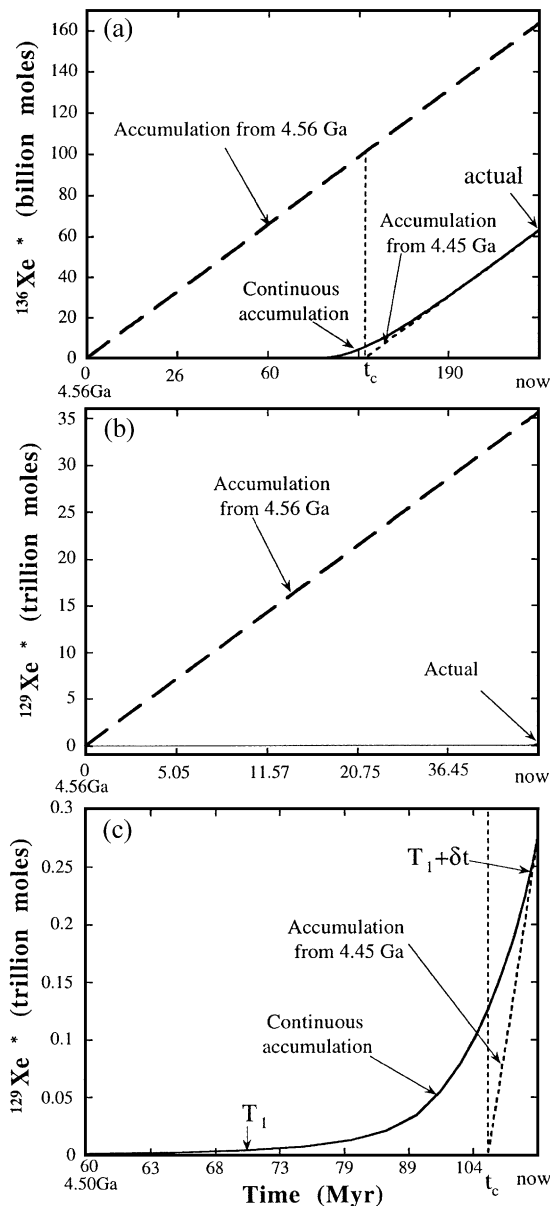


Fig. 6. (a) Meaning of Xe closure age  $t_c$  (Dodson, 1973) of  $^{136}\text{Xe}$ . The horizontal axis (time) is such that  $^{136}\text{Xe}^*$  growth is linear in this figure. The loss of Xe could be a step function (short-dashed lines), or smooth and continuous (solid curve), or any scenario in between. Regardless of the details of the loss process, the closure age is obtained by extrapolating from the present amount along a line parallel to the long-dashed line back to zero amount of  $^{136}\text{Xe}^*$ , leading to  $t_c$  of 110 Myr. (b) The same figure for  $^{129}\text{Xe}^*$  growth but the present amount of  $^{129}\text{Xe}^*$  is so small that a close-up view is necessary. (c) Close-up view of  $^{129}\text{Xe}^*$  growth. Assuming continuous loss (solid curve), the closure age is between that of the beginning of Xe retention (“formation” age  $T_1$  of Ozima and Podosek, 1999, see text) and that for complete Xe retention ( $T_1 + \delta t$ ).

1998) constrains the amount of missing radiogenic Xe to be  $(-3 \pm 13)\%$  relative. That is, there is essentially no missing radiogenic Xe. Hence, Xe closure ages obtained above is not affected by this problem.

Because there is little missing radiogenic Xe, a missing Xe reservoir that is 20 times the atmospheric reservoir is impossible unless Xe in the hidden reservoir is entirely nonradiogenic. Since no known terrestrial Xe is less radiogenic than atmospheric Xe and there is no reason to expect otherwise, the missing Xe is almost certainly a whole earth phenomenon and cannot be hidden in some earth reservoir. Furthermore, it is almost certain that missing Xe can only be nonradiogenic Xe escaped to outer space at very early times, and the loss could have been either from the proto-earth (before or at 4.45 Ga during a giant impact), or from planetesimals that later came of the earth. That is, “missing Xe” should be treated in the same category as “missing K” or “missing Na” in the earth budget due to their volatility.

Since missing Xe from the BSE can be ruled out, atmospheric  $^{130}\text{Xe}$  represents roughly 60% of total  $^{130}\text{Xe}$  in BSE. Hence, using the amount of  $^{130}\text{Xe}$  in the atmosphere (Ozima and Podosek, 1983),  $^{130}\text{Xe}$  concentration in the present undegassed mantle (or mantle plus crust plus atmosphere) is estimated as  $2.6 \times 10^{-13}$  mol/kg (or  $0.034 \pm 3$  ppt). According to the output from the total inversion results of Zhang (1998), I concentration in BSE is  $15.5 \pm 2.8$  ppb. This estimate agrees with the estimate of Deruelle et al. (1992). The  $^{127}\text{I}/^{130}\text{Xe}$  ratio in BSE is about  $4.7 \times 10^5$ .

### 3.2.2. Concerns on the validity of $^{129}\text{I}-^{244}\text{Pu}-^{129}\text{Xe}$ clock

In a review paper, Azbel and Tolstikhin (1993) claimed that the  $^{129}\text{I}-^{129}\text{Xe}$  clock is meaningless because iodine is volatile. This claim does not have merit. Because the Xe clock is based on the amount of radiogenic Xe isotopes, it dates the Xe closure time. Loss of iodine does not matter as long as iodine was also closed at the same time or an earlier time. (In the unlikely scenario that there was significant iodine loss after Xe closure, the Xe closure age would be even younger than inferred above.) Furthermore, Pu–Xe age is consistent with I–Xe age (Zhang, 1998; Ozima and Podosek, 1999) and Pu is refractory. Hence, the

claim of Azbel and Tolstikhin (1993) can be dismissed.

To avoid complexity and confusion, models for Xe and other gas degassing from the mantle are not considered. A detailed understanding of degassing is not necessary for understanding Xe closure age, and including such models only complicates the issue and causes confusion. Furthermore, a perfect understanding of mantle Xe and other gases is elusive (Staudacher and Allegre, 1982; Allegre et al., 1983, 1986/87b; Sarda et al., 1985, 2000; Zhang and Zindler, 1989, 1993; Patterson et al., 1990, 1991; Honda et al., 1991a,b; Staudacher et al., 1991; Poreda and Farley, 1992; Farley and Poreda, 1993; Moreira et al., 1995, 1998; Porcelli and Wasserburg, 1995a,b; Zhang, 1997; Kunz et al., 1998; van Keken and Ballentine, 1998, 1999; Caffee et al., 1999; Meshik et al., 2000). Caffee et al. (1999) and Meshik et al. (2000) presented new ideas about isotopic systematics of mantle Xe. Because the Xe closure age of the earth discussed here is mainly based on atmospheric Xe and largely independent of mantle Xe systematics, their new results on mantle Xe do not affect the inferred Xe closure ages above.

### 3.2.3. Apparent inconsistencies

Inconsistencies between Xe closure ages published before 1992 are not discussed here because they used various input data. These input data have been updated. Among the new age estimates, the results of Allegre et al. (1995) and Zhang (1998) are similar (4.46 Ga vs. 4.45 Ga). Jacobsen and Harper (1996a,b) estimated the age of the earth using Eq. (5) and obtained a  $\Delta t$  of 70 Myr (corresponding to an age of 4.49 Ga), different from 90 Myr obtained above (Eq. (5)). They then argued that the Xe closure age of the earth must be older than 4.49 Ga but no justification was provided. My assessment is that their conclusion is not justified.

Ozima and Podosek (1999) discussed Xe loss to outer space and the “formation” age of the earth. They obtained a “formation” age of 4.49 Ga or older, apparently inconsistent with other recent results (Allegre et al., 1995; Zhang, 1998). Fig. 6c compares the “formation” age of Ozima and Podosek (1999) and the Xe closure age, and decodes the apparent “inconsistency”. Ozima and Podosek (1999) defined that the earth “formed” at a time  $T_1$ , and after another  $\delta t$ ,

“most of the atmospheric inventory of Xe is lost, taking with it the radiogenic  $^{129}\text{Xe}$  and  $^{136}\text{Xe}$ ”. Hence, in the context of their continuous Xe loss model,  $T_1$  is the incipient time for Xe retention, and  $T_1 + \delta t$  is the time for complete Xe retention. Clearly, both  $T_1$  and  $T_1 + \delta t$  are poorly defined because they are highly model dependent and they depend on data resolution (Dodson, 1973; Zhang, 1994). Ozima and Podosek (1999) obtained  $T_1$  to be 4.49 Ga and  $T_1 + \delta t$  is 4.43 Ga. By definition, the mean age of atmosphere retention (or formation), which would roughly correspond to the definition of the atmosphere closure age, must lie between the two ages. If the middle value of  $T_1$  and  $T_1 + \delta t$  is taken, the closure age would be about 4.46 Ga (Fig. 6c), consistent with other works (Allegre et al., 1995; Zhang, 1998). Hence, there is no inconsistency except that Ozima and Podosek (1999) used a non-conventional definition of the “closure” or “formation” age. Furthermore, continuous escape of Xe from the earth when the earth was substantially grown as modeled by Ozima and Podosek (1999) is much less likely than catastrophic loss due to a giant impact. Hence, the result from the continuous escape model of Ozima and Podosek (1999) is probably less meaningful than the simple Xe closure age.

### 3.3. More complicated degassing models?

To model Xe isotopic evolution beyond the closure age, various detailed models, such as continuous gas escape model similar to those of Ozima and Podosek (1999), or a simple two-stage evolution model, can be used. In a two-stage model, there would be a first stage with low and constant  $^{127}\text{I}/^{130}\text{Xe}$  ratio in the BSE. At the end of the first stage, there would be a giant impact, stripping atmospheric Xe and hence increasing  $^{127}\text{I}/^{130}\text{Xe}$  ratio in the BSE. In the second stage, the  $^{127}\text{I}/^{130}\text{Xe}$  ratio is the present ratio. These models can be similar to the models for Pb and W isotopes. However, there is an additional complexity: the fractionated nature of Xe isotopic composition in the atmosphere compared to solar Xe (or U–Xe; Pepin, 1991) means that there was isotopic fractionation during Xe loss. Xe isotopic fractionation during escape depends on the gravity field and other details of hydrodynamic escape (e.g., Walker, 1977; Ozima and Podosek, 1983; Hunten, 1990; Pepin, 1991). For continuous escape, one has to assume a quantitative

relation between Xe isotopes and Xe content in BSE to model Xe isotopic evolution, which is beyond the scope of this review. With the two-stage evolution model, it may be assumed that the Xe isotopes in the first stage are U–Xe (Pepin, 1991), and that I/Xe, Pu/Xe and U/Xe ratios were sufficiently low so that Xe isotopic ratios did not increase significantly with time in the first stage. Then with a giant impact, significant Xe escaped so that Xe isotopic ratio fractionated to earth-like, and that I/Xe, Pu/Xe and U/Xe ratios increased so that Xe isotopic ratios grew rapidly with time in the second stage.

As shown earlier,  $^{127}\text{I}/^{130}\text{Xe}$  ratio in the present BSE is estimated to be  $4.7 \times 10^5$ . In the context of the

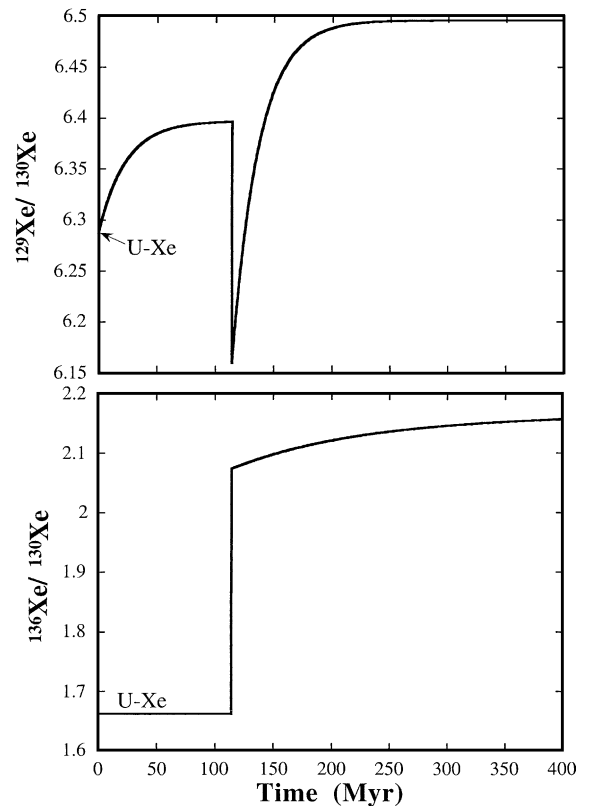


Fig. 7. Calculated evolution of  $^{129}\text{Xe}/^{130}\text{Xe}$  and  $^{136}\text{Xe}/^{130}\text{Xe}$  isotopic ratios in the BSE (including the atmosphere) in the two-stage model. In the calculation, in the first stage, the  $^{127}\text{I}/^{130}\text{Xe}$  ratio was 1000. In the second stage, the  $^{127}\text{I}/^{130}\text{Xe}$  ratio is  $4.7 \times 10^5$  (see text). The fractionation at the boundary of the two stages is constrained by the fractionation of nonradiogenic isotopes (such as  $^{124}\text{Xe}/^{130}\text{Xe}$ ) from U–Xe to the present atmospheric Xe.

two-stage evolution model, if  $^{127}\text{I}/^{130}\text{Xe}$  ratio in the first stage is less than 1000, then the two-stage model gives the same results as the Xe closure age. Fig. 7 shows calculated isotopic ratio evolution in such a two-stage model. If  $^{127}\text{I}/^{130}\text{Xe}$  ratio in the first stage is more than 1000, then  $\Delta t$  would be greater than 110 Myr, meaning a Xe closure age younger than 4.45 Ga. Using the two-stage evolution model, one can also show that  $^{127}\text{I}/^{130}\text{Xe}$  ratio in the first stage cannot be  $\geq 5000$ , otherwise the resulting  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio would be greater than that in air no matter how other parameters are adjusted within uncertainties. Therefore, in the context of the two-stage evolution model, the earth (or in planetesimals that predate the earth) likely lost  $\geq 99\%$  [ $1 - (5000/470,000)$ ] of  $^{130}\text{Xe}$  during the fractionation process that produced air Xe from U–Xe.

#### 4. Age of the earliest crust–mantle differentiation

Formation of continental crust (i.e., differentiation of the silicate earth into crust and mantle) is a continuous process. Some crustal rocks are young and some are old. The oldest known crustal rocks have been dated to be 4.00–4.03 Ga (Bowring and Williams, 1999). Both the mean age of crust formation and the age of earliest crust formation are of interest. Below, I discuss only the formation age of the earliest crust because it is related to the age of the earth. Obviously, the record for the first (earliest) crust–mantle differentiation is difficult to preserve and might have been erased owing to erosion, subduction, metamorphism, remelting, etc. Hence, estimation of such an age is not straightforward. Nevertheless, giant progress has been made recently in estimating the earliest crust–mantle differentiation age using the coupled U–Pb geochronometer in detrital zircon crystals, the coupled Sm–Nd geochronometer ( $^{147}\text{Sm}$ – $^{143}\text{Nd}$  and  $^{146}\text{Sm}$ – $^{142}\text{Nd}$ ), and  $^{92}\text{Nb}$ – $^{92}\text{Zr}$  geochronometer. All of these systems point to very early formation of the first crustal rocks.

##### 4.1. Zircon ages

Some detrital zircon grains have crystallization age older than 4.0 Ga, providing evidence for the antiquity of the continental crust. All these old zircon grains

come from metasedimentary belt (Jack Hills and Mount Narryer) in Western Australia. Because zircon takes U but not much Pb, and because zircon is resistant to post-crystallization perturbations, the growth of Pb isotopes in zircon is especially powerful in determining the crystallization age of the spot of zircon under consideration. One test for possible post-growth alteration is to check whether  $^{206}\text{Pb}/^{238}\text{U}$  vs.  $^{207}\text{Pb}/^{235}\text{U}$  data lie on the concordia curve.

The formation ages of detrital zircon grains have crept up gradually (Compston and Pidgeon, 1986; Mojzsis et al., 2001; Wilde et al., 2001). The oldest zircon spot that has been dated so far has reached  $4.404 \pm 0.008$  Ga (Wilde et al., 2001). Furthermore, this oldest age is almost perfectly concordant. Other spots in the same zircon grain have U–Pb ages ranging from 4.267 to 4.364 Ga, but some of these younger ages are discordant. The oldest zircon age of  $4.404 \pm 0.008$  Ga provides the lower limit for the time of the earliest crust–mantle differentiation, and it is very close to the Xe closure age of  $4.45 \pm 0.02$  Ga. Hence, the first piece of crust probably formed immediately after the Xe loss event.

##### 4.2. Coupled Sm–Nd system

The coupled Sm–Nd system is similar to the coupled U–Pb system:  $^{147}\text{Sm}$  decays to  $^{143}\text{Nd}$  with a half-life of 106 billion years and  $^{146}\text{Sm}$  decays to  $^{142}\text{Nd}$  with a half-life of 103 Myr. The presence of  $^{146}\text{Sm}$  in the early solar system was demonstrated by Lugmair et al. (1983). Nevertheless, the system is not as useful as the U–Pb coupled system because the half-lives of  $^{147}\text{Sm}$  and  $^{146}\text{Sm}$  differ by three orders of magnitude, whereas the half-lives of  $^{238}\text{U}$  and  $^{235}\text{U}$  differ by only a factor of 6.3. All  $^{146}\text{Sm}$  but only 3% of  $^{147}\text{Sm}$  has decayed away in the history of the earth. The use of Nd–Nd isochrons (similar to Pb–Pb isochrons in Figs. 1 and 2) to terrestrial rocks is hence very difficult, if not impossible.

Sm/Nd ratio is fractionated during partial melting of the mantle. Nd preferentially goes to the melt and continental crust. The ratio by weight is 0.32 in BSE, about 0.18 in the upper continental crust, and 0.36 in mid-ocean ridge basalt (McDonough and Sun, 1995; Wedepohl, 1995). Hence, if there is  $^{142}\text{Nd}$  anomaly in any terrestrial rocks, it would imply that the earliest crust formed when there was still live  $^{146}\text{Sm}$ . Harper

and Jacobsen (1992) reported such an anomaly (albeit small) in a felsic gneiss from 3.8 Ga Isua Supracrustals in West Greenland. From this, they concluded that the earliest crust formed at  $4.47 \pm 0.05$  Ga. Because of the importance of the issue, others have tried to reproduce the result using either the same rock or similar rocks (Goldstein and Galer, 1992; McCulloch and Bennett, 1993; Regelous and Collerson, 1996; Sharma et al., 1996a,b; Jacobsen and Harper, 1996a,b). So far, two rocks have been reported to have this anomaly but there is still debate (Sharma et al., 1996a,b; Jacobsen and Harper, 1996a,b). Nevertheless, measurements by both Harper and Jacobsen (1992) and Sharma et al. (1996a) show similar magnitude of  $^{142}\text{Nd}$  anomaly (Jacobsen and Harper, 1996a,b) although the precisions claimed by the two groups are different. Hence, my own assessment is that the small anomaly is likely real and hence it does constrain the age of the earliest crustal formation. Improved precision in  $^{142}\text{Nd}/^{144}\text{Nd}$  measurement will further constrain the age of crustal formation.

#### 4.3. Nb–Zr system

The nuclide  $^{92}\text{Nb}$  decays to  $^{92}\text{Zr}$  with a half-life of 36 Myr. Harper (1996) reported the first indication for  $^{92}\text{Zr}$  anomaly in meteoritic rutile, possibly indicating the presence of initial  $^{92}\text{Nb}$  in the early solar system. Yin et al. (2000) reported both low  $^{92}\text{Zr}/^{91}\text{Zr}$  in zircon and high  $^{92}\text{Zr}/^{91}\text{Zr}$  in rutile, further supporting the presence of initial  $^{92}\text{Nb}$ . Sanloup et al. (2000) reported Zr isotopic anomalies in chondrites and attributed them to both pre-solar nucleosynthetic processes and decay of extinct  $^{92}\text{Nb}$ . Munker et al. (2000) reported  $^{92}\text{Zr}/^{91}\text{Zr}$  isotopic data in meteorites, refractory inclusions and terrestrial samples. Although they did not measure other Zr isotopes and hence did not demonstrate  $^{92}\text{Zr}$  anomaly is entirely due to the decay of  $^{92}\text{Nb}$  instead of some contribution from nucleosynthetic heterogeneities; their main conclusion is the absence of  $^{92}\text{Zr}/^{91}\text{Zr}$  anomaly and is hence not affected. The correlation between  $^{92}\text{Zr}/^{91}\text{Zr}$  anomaly and Nb/Zr ratio in a single sample (i.e., internal isochron) has yet to be presented to demonstrate the initial presence of  $^{92}\text{Nb}$  and to derive the initial ratio of  $^{92}\text{Nb}/^{93}\text{Nb}$ .

Nb/Zr ratio is fractionated during partial melting of the mantle. Nb is more incompatible during mantle

partial melting and preferentially goes to the melt and continental crust. In the BSE, Nb/Zr ratio by weight is about 0.063 (McDonough and Sun, 1995). The ratio in the upper continental crust is roughly 0.11 and the average ratio in mid-ocean ridge basalt (derived from the depleted mantle) is roughly 0.03 (McDonough and Sun, 1995; Wedepohl, 1995). Hence, if there is  $^{92}\text{Zr}$  anomaly, it would imply that the earliest crust formed when there was still live  $^{92}\text{Nb}$ . Munker et al. (2000) showed that there is no significant  $^{92}\text{Zr}$  anomaly in terrestrial samples. More quantitatively, the isotopic anomaly is less than 0.7 epsilon unit (see Notation list), or

$$\Delta(^{92}\text{Zr}/^{91}\text{Zr}) = (^{92}\text{Zr}/^{91}\text{Zr})_{\text{crust}} - (^{92}\text{Zr}/^{91}\text{Zr})_{\text{CI}} < 1.1 \times 10^{-4} \quad (13)$$

Although Munker et al. (2000) suggested that crust–mantle fractionation occurred more than 50 Myr after the primitive meteorites, my calculation using the above data and a two-stage model shows that crust–mantle fractionation occurred more than 70 Myr after CAI inclusions in Allende meteorite (Fig. 8). The inclusions were dated at  $4.566 \pm 0.002$  Ga (Allegre et al., 1995). Therefore, earliest crust formation is

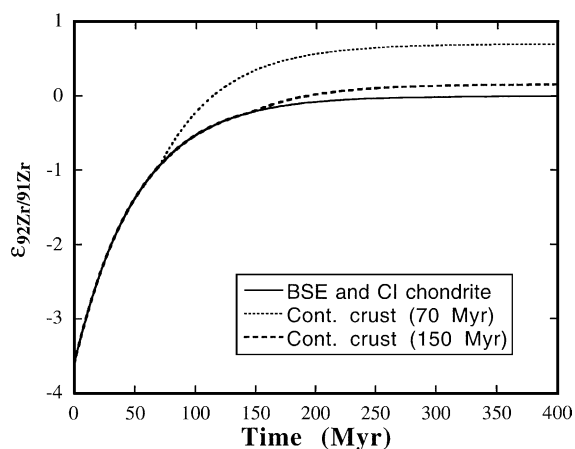


Fig. 8. Modeled evolution of  $^{92}\text{Zr}/^{91}\text{Zr}$  in carbonaceous chondrite (CI) and in continental crust. Seventy and 150 Myr in the parentheses mean the time of formation of the crust. For the continental crust to have  $\epsilon_{92\text{Zr}/91\text{Zr}} < 0.7$ , the crust must have been separated from the mantle no earlier than 70 Myr after CAI formation.

younger than 4.496 Ga. Hence, the use of this system is very similar to that of  $^{182}\text{Hf}$ – $^{182}\text{W}$  system, providing a limit on the age. The reported data in Munker et al. (2000) allow some slight variation of terrestrial  $^{92}\text{Zr}/^{91}\text{Zr}$  ratio, which may be noise but may also be real. Future directions include (i) the use of internal isochrons to demonstrate the initial presence of  $^{92}\text{Nb}$  and to determine the initial  $^{92}\text{Nb}/^{93}\text{Nb}$  ratio, and (ii) the improvement of measurement precision to determine whether there are resolvable variations in  $^{92}\text{Zr}/^{91}\text{Zr}$  of terrestrial rocks. Such understandings will further constrain the formation age of the earliest crust.

Schönbächler et al. (2002) showed that the initial  $^{92}\text{Nb}/^{93}\text{Nb}$  ratio is about  $10^{-5}$ , much lower than  $10^{-3}$  assumed by Munker et al. (2000). Hence the absence of a measurable  $^{92}\text{Zr}/^{91}\text{Zr}$  anomaly (meaning an anomaly  $<10^{-4}$ , Eq. (13)) in the earth's crust does not provide any constraint on the age of crustal formation.

#### 4.4. Earliest crustal formation age

None of the three systems discussed above is yet able to provide a firm age for the formation of the earliest crust. Nevertheless, the collective weight of the three systems ( $>4.404$  Ga from zircon ages,  $<4.496$  Ga from the  $^{92}\text{Nb}$ – $^{92}\text{Zr}$  system, and  $4.47 \pm 0.05$  Ga from the coupled Sm–Nd system) brackets a rough age of  $4.45 \pm 0.05$  Ga for the earliest crustal formation using the simple two-stage evolution model. This age is similar to the Xe closure age and the instantaneous core formation age. Because this age is for the formation of the earliest crust, continuous crustal formation models (lasting for billions of years) do not affect the interpretation of such an age.

### 5. The age of the moon

The most widely accepted model for the formation of the moon is the impact model (Hartman and Davis, 1975; Cameron and Ward, 1976; Stevenson, 1987; Cameron, 2001; Canup and Asohaug, 2001). Oldest known lunar rocks have ages of  $4.51 \pm 0.01$  Ga (Hanan and Tilton, 1987),  $4.44 \pm 0.02$  Ga (Carlson and Lugmair, 1988), and  $4.562 \pm 0.068$  Ga (Alibert et al., 1994).

These ages of crustal rocks provide a lower limit for the age of the giant impact that produced the moon. Hence, the giant impact must be older than 4.50 Ga if the ages are reliable. Hf–W systematics in lunar rocks has the potential to further constrain the age of the moon.

Initial measurements showed that  $^{182}\text{W}/^{184}\text{W}$  ratio in lunar rocks is highly variable and ranges up to 7 epsilon units (Lee et al., 1997). Interpreted as due to in situ decay of  $^{182}\text{Hf}$ , the high  $^{182}\text{W}/^{184}\text{W}$  ratios would indicate old age of the moon (such as 4.52 Ga). Later work shows that most of the variability is due to cosmogenic  $^{182}\text{W}$  and not due to in situ decay of  $^{182}\text{Hf}$  (Leya et al., 2000; Lee et al., in press). The anomaly due to in situ  $^{182}\text{Hf}$  decay is likely small (up to  $1.3 \pm 0.4$  epsilon unit). Nevertheless, the presence of such a resolvable anomaly constrains the age of the moon to about  $4.49 \pm 0.01$  Ga, 60 million years after Forest Vale (Lee et al., 1997; Lee and Halliday, 2000a). This age estimate is consistent with the results of Hanan and Tilton (1987) and Alibert et al. (1994), and older than the Xe closure age of the earth ( $4.45 \pm 0.02$  Ga).

### 6. Conclusions

Among the four scenarios discussed in Fig. 3, two scenarios (Fig. 3b and d) are consistent with all the isotopic data and physical considerations, and the other two (Fig. 3a and c) are unlikely. Fig. 3a shows the scenario of continuous homogeneous earth accretion (for the first 90% of its mass) lasting for about 100 Myr. In this scenario, the core did not grow until 4.45 Ga, at which time the core suddenly grew and Xe suddenly could be retained. On the basis of the antiquity of iron meteorites and because there is no physical basis to delay core formation, this scenario is physically unlikely (although it is mathematically equivalent to the scenario in Fig. 3b and can hence account for all isotopic data). Fig. 3c shows the case of rapid earth accretion with subsequent continuous and gradual core formation and Xe loss until 4.40 Ga, leading to a mean age of  $\sim 4.45$  Ga for both core formation and Xe closure. Earlier, I showed that the combination of Pb and Hf–W isotopic systems does not allow this scenario. Furthermore, it is physically unlikely since (i) core formation releases energy to heat up the earth and is expected to be a runaway process and hence very

rapid, and (ii) Xe retention is largely dependent on the mass of the protoplanet (except when there is giant impact) and independent of core growth.

Ruling out these two scenarios, U–Pb and Hf–W systems can be interpreted in two different kinds of core formation models (Fig. 3b and d). All the other isotopic data can also be interpreted in either of these two scenarios: (i) continuous earth accretion and simultaneous core formation, plus a lunar-size giant impact at 4.45 Ga, and (ii) a single age of 4.45 Ga, best explained by a Martian-sized (or greater) giant impact at about 4.45 Ga. Some combination of the two models can also be constructed to satisfy the isotopic data.

With the continuous earth accretion and simultaneous core formation model (Fig. 3d), the mean core formation age is about  $4.53 \pm 0.02$  Ga. Continuous earth accretion and simultaneous degassing model is almost certainly untenable for Xe closure because once the earth was more massive than the moon, the earth should be able to keep Xe in its atmosphere (Walker, 1977) except for catastrophic events such as giant impacts. Hence, the younger Xe closure age and younger age for the earliest crust are best explained by a Moon-sized giant impact that eroded the atmosphere (e.g., Ahrens, 1993) and remelted the crust. Hence, in this scenario, much of the earth accreted continuously with a mean time of 30 Myr and the core formed and grew simultaneously as the earth grew. There were infrequent giant impacts (one of which produced the moon), but these did not remix the core back to the mantle and hence did not significantly affect the U–Pb and Hf–W systems. At  $\sim 4.45$  Ga, an impactor the size of the moon (or slightly greater) collided with the earth, and restarted the Xe clock and crustal formation.

The single age scenario in the context of instantaneous reformation model after a giant impact is my preferred model. In this model, the estimates of Xe closure age, core formation age, and earliest crustal formation age are all similar ( $4.45 \pm 0.02$  Ga; Fig. 9), and are explainable by a giant impact of Martian size (or greater) planetesimal at  $\sim 4.45$  Ga. In addition to its simplicity, giant impacts were almost a certainty in the late stage of earth accretion (Wetherill, 1985, 1994), and Xe closure age almost demands a giant impact (although not necessarily one that was large enough to rehomogenize the core and mantle) at that time. Hence, such a simple model is appealing. In this

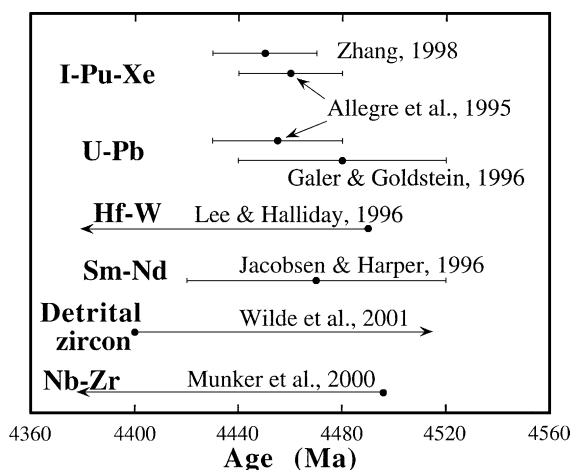


Fig. 9. Summary of age constraints. Included are Xe closure ages, core formation age based on U–Pb and Hf–W systems assuming instantaneous core formation, and earliest crustal formation ages based on Sm–Nd and Nb–Zr systems and U–Pb in detrital zircons. The arrow means that the age is constrained at the end point but not constrained at the arrow direction. Primitive meteorite ages are at 4560 Ma (the vertical axis on the right-hand side).

scenario (Fig. 3b), in the later stage of earth accretion, the earth did not grow smoothly, but rather grew episodically and catastrophically through giant impacts (Wetherill, 1985, 1994). The giant impacts added significant mass to the earth. (In between the infrequent giant impacts, it was possible that the earth grew continuously, with simultaneous core growth and proto-atmosphere formation.) The greatest of these giant impacts is hypothesized to have occurred at about 4.45 Ga, and to have enough energy to rehomogenize the whole earth (Halliday et al., 1996; Harper and Jacobsen, 1996; Zhang, 1998). The energy delivered by a Martian-sized impact may increase the temperature of the earth by 7500 K, and is about three times the energy released by core formation (Birch, 1965; Flasar and Birch, 1973; Pollack, 1997). A larger planetesimal would deliver even more energy. Hence, there is no difficulty in terms of energetics although the dynamics must be worked out. This giant impact might not be the same as the impact that presumably produced the moon, since the moon is older than 4.45 Ga. (This is not a problem for the model since it is not unreasonable to expect two or more giant impacts in the late accretion history of the earth; Wetherill, 1985,



1994). Under this scenario (Fig. 3b), a giant impactor that is able to remix the core and mantle would have a mass >15% of the mass of the earth. If this mass was added to the earth, the impact would have increased the mass of the earth significantly. It might also be possible that the mass of the earth was reduced by the impact. Either way, the last greatest impacting event probably marked the time when the earth reached 80–90% of its present mass. Subsequent growth would have included late veneers (Wanke, 1981; Drake, 2000). Therefore, 4.45 Ga probably also marks the time when the earth roughly reached its present mass, in addition to almost complete atmosphere removal, remixing of core and mantle, and melting of the whole earth. After the impact, the core formed again (leading to the young core formation age), a new atmosphere was degassed from the mantle (the mean age of gases in the atmosphere ranges from 4.43 to 4.15 Ga since mean degassing time is about 20–300 Myr; Allegre et al., 1986/87b; Zhang and Zindler, 1989) and retained, the first crust formed, and the earth was reborn. Although the details of the accretion history discussed above are necessarily speculative and incomplete, all isotopic systems are consistent with the conclusion that the age of 4.45 Ga marks a main defining point for the rebirth of the earth.

The ambiguity of two possible accretion models may be resolved in the future. One is by improving measurement precision of W isotopic ratios by about a factor of 10; this would improve the core formation age and hence constrain the accretion model. The second is by further constraining the age of the earliest crust formation. For example, if the earliest crust formation age can be shown to be 4.50 Ga, then Xe closure is best explained by an impact of the size of Moon, instead of Mars. In such a case, continuous earth accretion and simultaneous core formation would be much more likely and instantaneous core formation at  $4.45 \pm 0.02$  Ga due to an impact greater than Mars would be ruled out since no crust would have survived such an impact.

#### Notation, terms and acronyms

BSE	Bulk silicate earth (including the mantle, crust, oceans and atmosphere).
CAI	Calcium–aluminum-rich inclusions.
CHON	Chondrites.

**Concordia** A curve on a  $^{206}\text{Pb}^*/^{238}\text{U}$  vs.  $^{207}\text{Pb}^*/^{235}\text{U}$  diagram for closed system evolution. The concordia curve can be used to verify whether there was disturbance in the isotopic system.

**Isochron** For several minerals formed at the same time from the same isotopic reservoir, the plot of the ratio of radiogenic to nonradiogenic isotopes vs. the ratio of parent nuclide to nonradiogenic isotope (e.g.,  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $^{87}\text{Rb}/^{86}\text{Sr}$  where  $^{87}\text{Rb}$  decays to  $^{87}\text{Sr}$ , and  $^{86}\text{Sr}$  is a stable and nonradiogenic isotope of Sr) is a straight line. This straight line is called the isochron. From the slope of an isochron, one can obtain the age. Some examples are given in Figs. 1 and 2.

**Geochron** A special isochron in  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram for an age of 4.55 Ga (Fig. 1). Other younger geochrons can also be drawn (Fig. 2).

**Model age** There are different kinds of model ages. Model age of the earth based on Pb isotopes can be calculated from Eq. (2) and would represent the age of the earth if the rock experienced no U–Pb fractionation after instantaneous earth formation.

**MORB** Mid-ocean ridge basalt.

**Nuclides** A nuclide is a neutral atomic species characterized by both the atomic number and the neutron number. The definition of nuclides is more general than that of isotopes. For example,  $^{238}\text{U}$  and  $^{235}\text{U}$  are two isotopes.  $^{238}\text{U}$ ,  $^{235}\text{U}$ ,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$  are all nuclides.

**OIB** Ocean island basalt.

$\mu$  The present equivalent of  $^{238}\text{U}/^{204}\text{Pb}$  ratio.

$\varepsilon$  In general,  $\varepsilon = [R_{\text{sample}}/R_{\text{standard}} - 1]10^4$  where  $R$  is an isotopic ratio. There are slightly different definitions of  $R_{\text{standard}}$ . Some authors use time-dependent ratio in chondrite uniform reservoir (CHUR) as  $R_{\text{standard}}$  (e.g.,  $\varepsilon_{143\text{Nd}/144\text{Nd}}$ , DePaolo and Wasserburg, 1976). Others use a constant ratio as  $R_{\text{standard}}$  (e.g.,  $\varepsilon_{182\text{W}/184\text{W}}$  and  $\varepsilon_{92\text{Zr}/91\text{Zr}}$ , Lee and Halliday, 1995, 1996; Munker et al., 2000). Specifically, for  $\varepsilon_{182\text{W}/184\text{W}}$ ,  $R_{\text{standard}} = (^{182}\text{W}/^{184}\text{W})_{\text{NIST-3163}} = 0.865000$  (Lee and Halliday, 1996). For  $\varepsilon_{92\text{Zr}/91\text{Zr}}$ ,  $R_{\text{standard}} = (^{92}\text{Zr}/^{91}\text{Zr})_{\text{AMES}} = 1.53120$  (Munker et al., 2000).

*Subscripts*

- 0 Initial state (usually at 4.56 Ga).  
 B Bjurbole (a meteorite).

*Superscripts*

- \* Radiogenic component.

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