

GEOCHEMISTRY

Does U–Pb date Earth's core formation?

Arising from: B. J. Wood & A. N. Halliday *Nature* **437**, 1345–1348 (2005)

Constraining the timing of the formation of Earth's core, which defines the birth of our planet, is essential for understanding the early evolution of Earth-like planets. Wood and Halliday¹ and Halliday² discuss the apparent discrepancy between the U–Pb (60–80 Myr) and Hf–W clocks (30 Myr) in determining the timescale of Earth's accretion and core formation. We find that the information the authors present is at times contradictory (for example, compare Fig. 1 in ref. 1 with Fig. 1 in ref. 2) and confusing and could suggest that the U–Pb clock constrains core formation better than the Hf–W system. Here we point out the limitations of the U–Pb system and show that the U–Pb age cannot be used to argue for protracted accretion and/or core formation (>50 Myr) because this clock only records the processes that occurred during the last 1% of Earth's accretion and core formation in the Wood and Halliday mechanism¹.

For both the U–Pb and Hf–W systems to be able to date Earth's accretion and core formation, we need accurate estimates of the following parameters: the initial Solar System tungsten and lead isotope ratios; the bulk Earth elemental ratios of Hf/W and U/Pb; the present tungsten and lead isotope composition of the silicate Earth; and the present U/Pb and Hf/W ratios of the silicate portion of Earth. Whereas we know all the required parameters for the Hf/W system, several of the parameters for the U/Pb system are highly uncertain and are unlikely ever to be determined accurately enough to infer age resolution of a few tens of millions of years at 4.5 Gyr ago.

First, the U/Pb ratio of the bulk Earth (that is, μ_{TOPE} in ref. 1) is not well known, as it is a ratio of a refractory and a volatile element. Rocky planetary objects are depleted in volatile elements, including Pb to various degrees. We therefore have no way of knowing *a priori*

what the building-blocks of Earth are made of in terms of the U/Pb ratio. The same is not true for the Hf–W system, as both elements are refractory. The bulk Earth Hf/W ratio has been estimated from that of primitive chondritic values with a high degree of confidence^{3,4}. Using refractory elements for estimating the bulk composition of planets is one of the cornerstones of modern geochemistry.

Second, because of the long half-lives of ²³⁸U (~4.5 Gyr) and ²³⁵U (~0.7 Gyr), the lead isotope composition of terrestrial rocks varies widely and is continuously evolving. As a result, there is no easy way of deriving a single value for the present lead isotope composition of the bulk silicate Earth that can be used to date early Earth events precisely within the first 30 Myr. The same is not true for the Hf–W system. The now-extinct radionuclide ¹⁸²Hf only has a 9-Myr half-life and decayed to ¹⁸²W. Every rock on the surface of Earth records a single value of ¹⁸²W, which is 2 parts per 10,000 higher than the bulk Earth value (obtained from chondrites). The difference is a consequence of metal extraction during core formation, which also produces a high Hf/W ratio in the silicate portion of Earth. Thus, we have a well-determined tungsten isotope composition for the bulk silicate Earth, but a highly uncertain one for lead isotopes.

The accretion process is not a well-defined point in time and, in fact, is technically still continuing today. The best designation of the 'end' of our planet's formation (>99% mass accreted) is probably the final major event in Earth's accretion process, the formation of the Moon by a Mars-sized impactor. This time is constrained by the tungsten isotope data to be about 30 million years after the formation of the Solar System^{4–8}. New tungsten isotope data from lunar samples reinforce this conclusion (see Fig. 3b of ref. 9).

Wood and Halliday¹ invoke the late-stage sulphide phase segregation into the core to explain the inconsistency between U–Pb and Hf–W. However, to account for the increased U/Pb ratio in the silicate Earth by lead partitioning into the core, note that additional mass added to the core after the last Moon-forming giant impact is trivial (<1%)¹. The U–Pb clock therefore sees one of the 'trees but not the forest' of core formation, as the U–Pb record necessarily misses >99% of the core-formation processes. The U–Pb system is strongly influenced by Earth's surface processes, and the so-called 'Pb paradox' still has many alternative interpretations to core formation¹⁰. Late sulphide segregation may explain the putative age difference between U–Pb and Hf–W, but it is misleading to portray the U–Pb ages as the time of Earth's core formation¹.

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How well can Pb isotopes date core formation?

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Timescale and the physics of planetary core formation are essential constraints for models of Earth's accretion and early differentiation. Wood and Halliday¹ use the apparent mismatch in core-formation dates determined from tungsten (W) and lead (Pb) chrono-

lograms to argue for a two-stage core formation, involving an early phase of metal segregation followed by a protracted episode of sulphide melt addition. However, we show here that crust–mantle Pb isotope systematics do not require diachronous core formation. Our

observations indicate that very early (≤ 35 Myr) core formation and planet accretion remain the most plausible scenario.

Core formation could have entailed a severe fractionation of the U/Pb ratio in the mantle, ultimately causing the average lead (radiogenic

daughter) isotope composition of the silicate Earth to be displaced from the array defined by undifferentiated meteorites. The extent of this displacement would depend on the time of fractionation. Therefore, the lead isotope composition of the bulk silicate Earth (BSE), if it were precisely known, could serve to estimate the timing of core formation²; however, it is not well known. This is because homogenization as a result of mantle stirring has not been sufficiently fast to eradicate the isotopic heterogeneities that reflect differences in time-integrated U/Pb ratios between parts of the silicate Earth. Attempts to obtain a precise mass balance of the heterogeneous mantle and crustal reservoirs are bedevilled by the unknown masses of reservoirs with characteristic lead isotope compositions.

Specifically, terrestrial lead isotope evolution models have been presented for the crust–mantle system³. In the preferred solution for these, a timescale for core segregation of 60 Myr after Solar System formation, based on the then (1997) prevailing interpretation of chondritic tungsten isotope data⁴ (later shown to be erroneous^{5,6}), was used as an imposed constraint³. This yielded the BSE lead isotope composition estimate shown as KT 97 in Fig. 3 of Wood and Halliday¹. Using this value to derive a core-formation age is therefore circular. The core-formation timescale is not a

critical parameter for terrestrial Pb modelling (Fig. 9 of ref. 3). The much faster core formation now implied by tungsten-isotope models^{5–7} is equally consistent with the lead data.

The BSE lead-isotope estimate MKC 03 (in Fig. 3 of Wood and Halliday¹) was a by-product of finding a refined solution to the first lead-isotope paradox⁸. It depends on the core-formation age preferred by Murphy *et al.*⁸, who maintain that the slope of the calculated 'geochron' corresponds to an age of 4,503 Myr and that this implies catastrophic core formation within about 65 Myr. Wood and Halliday's model¹ returns exactly that age for their proposed stage of lead loss with a late sulphide melt. Again, the argument is circular.

These examples show that it is not possible to determine the lead isotope composition of BSE directly with sufficient precision to constrain a relatively short time interval at the beginning of Earth's history. Early work on the 'U–Pb age' of Earth⁹, which required implausibly protracted core formation (200 Myr), historically influenced all estimates for the lead isotope composition of BSE. Six of the 11 estimates used by Wood and Halliday¹ were published before 1990 and yield an average time of core formation of 91 Myr. The five more recent estimates return a faster average core-formation date of 61 Myr. This demonstrates that, as we learn to appreciate the complexity of terres-

trial differentiation¹⁰, our estimates of the BSE lead isotope composition are moving closer to the meteorite isochron than was previously thought possible⁹. It may be that the true BSE lead composition is compatible with tungsten isotope constraints for very rapid (that is, ≤ 30 Myr) accretion and core formation. We therefore find no solid observational evidence for the complex core-formation process proposed by Wood and Halliday¹.

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Wood & Halliday reply

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Yin and Jacobsen¹ and Kamber and Kramers² highlight several issues to do with the tungsten (W) and lead (Pb) isotopic chronometry of terrestrial accretion and core segregation, although none of these affect our model or conclusions³. Yin and Jacobsen¹ suggest that it is not clear from our analysis³ that ^{182}Hf – ^{182}W provides a reliable system of chronometry for the bulk of core formation, whereas $^{235/238}\text{U}$ – $^{207/206}\text{Pb}$ relates to the very last stage of sulphide segregation — which was exactly our point³ and is clarified here.

The concern of Yin and Jacobsen¹ that we used different versions of Fig. 1^{3,4} to illustrate scenarios for the accretion of the Earth is addressed in the respective figure captions and texts^{3,4}, which demonstrate the wide range of different kinds of accretion model that underlie the W and Pb isotope modelling. There is no inconsistency. None of the accretion curves shown is likely to represent the actual growth of the Earth, which is underconstrained. ^{182}Hf – ^{182}W chronometry does not provide a unique mass accretion and core-formation history of the Earth^{4,5}.

The difficulties both sets of authors raise^{1,2}

about the determination of the average Pb isotopic composition of the bulk silicate Earth (BSE) are correct, but these are well known and illustrated by the range of existing estimates^{4–6}. They have not prevented Pb isotope estimates being made and inferences drawn about their significance^{6,7}. Explanations for certain facets of the Pb paradox that are based on melting and recycling of material within the BSE are irrelevant; they cannot change the average composition. Either all 11 of these estimates, and the Pb isotope space between them, are incorrect, or the timing and mechanism of U/Pb and Hf/W fractionation are different, with $^{235/238}\text{U}$ – $^{207/206}\text{Pb}$ always yielding longer timescales^{3–7}. This is not a random scatter that reflects a poorer ability to determine the average Pb isotopic composition of the BSE. Rather, there is a systematic offset that provides evidence for a different fractionating process, or a systematic error, as we state^{3,4}. Yin and Jacobsen¹ agree with this¹; Kamber and Kramers² do not, but do not explain how this discrepancy can be eliminated.

The weak constraints on the μ_{TOPE} of the Earth are well known^{4–7}. We used³ an esti-

mate⁷ based on chondrite volatile depletion trends⁴. Estimates based on half-mass condensation temperature (see ref. 6, for example) are slightly higher⁸, but these increase the discrepancy between the timing deduced from $^{235/238}\text{U}$ – $^{207/206}\text{Pb}$ and ^{182}Hf – ^{182}W (ref. 4). Our arguments are, if anything, conservative.

Kamber and Kramers² point out that ^{182}Hf – ^{182}W constraints have been used to determine the average Pb isotopic composition of the BSE^{9,10}. It would have been better not to use their estimates because of the circularity involved. Based on partitioning, the approach of using ^{182}Hf – ^{182}W to predict the Pb isotopic composition of the BSE is flawed³. Our concern was mainly to demonstrate that all estimates were consistent with our model. The three most recent estimates attributable to Kamber and Kramers are similar to the average of the eight earlier, more varied, estimates (see ref. 4). The means of the two-stage model ages are 67 and 81 Myr, respectively, whereas the equivalent calculation for ^{182}Hf – ^{182}W yields about 30 Myr (ref. 11).

Although Kamber and Kramers² clarify how they made their estimates and Yin and Jacobsen¹