# A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites

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**Determining the chronology for the assembly of planetary bodies in the early Solar System is essential for a complete understanding of star- and planet-formation processes. Various radionuclide chronometers (applied to meteorites) have been used to determine that basaltic lava flows on the surface of the asteroid Vesta formed within 3 million years (3 Myr) of the origin of the Solar System[1–3]. Such rapid formation is broadly consistent with astronomical observations of young stellar objects, which suggest that formation of planetary systems occurs within a few million years after star formation[4,5]. Some hafnium–tungsten isotope data, however, require that Vesta formed later[6] (~16 Myr after the formation of the Solar System) and that the formation of the terrestrial planets took a much longer time[7–10] ($62^{+4504}_{-14}$ Myr). Here we report measurements of tungsten isotope compositions and hafnium–tungsten ratios of several meteorites. Our measurements indicate that, contrary to previous results[7–10], the bulk of metal–silicate separation in the Solar System was completed within <30 Myr. These results are completely consistent with other evidence for rapid planetary formation[1–5], and are also in agreement with dynamic accretion models[11–13] that predict a relatively short time (~10 Myr) for the main growth stage of terrestrial planet formation.**

It has been argued that the rate of terrestrial core formation was limited by accretion, that it started very early, and that it was largely completed within the first 10–20 Myr or less of Earth history[14,15]. The decay of now extinct $^{182}$Hf (half-life, 9 Myr) to $^{182}$W is an ideal chronometer for tracing this process, because Hf is retained in the silicate mantle while W is largely partitioned into the core during core segregation[6–10,14–20]. However, it is now widely accepted that the reports of almost identical $^{182}$W/$^{183}$W ratios of chondritic meteorites and the bulk silicate Earth (BSE) imply that core segregation in the Earth took place about 60 Myr after the beginning of the Solar System[7,8,10]—that is, when $^{182}$Hf was essentially extinct. As core segregation probably occurred in an early terrestrial magma ocean, the observed solar He and Ne components of the Earth's mantle also require that most of the planetary accretion occurred before the gas of the solar nebula had dissipated[21,22]. The timescale for this dissipation is <3 Myr after the beginning of the Solar System[4,23], and highlights the problem of inconsistent chronologies for the early Earth.

Our new data (Table 1 and ref. 24) for ordinary chondrites Dalgety Downs and Dhurmsala yield a well defined 'fossil isochron' array (Fig. 1). Four separate whole-rock samples of carbonaceous chondrites (three from Allende and one from Murchison) and a calcium-aluminium-rich inclusion (CAI) from the Allende meteorite plot on this isochron. Although the absolute ages of the two ordinary chondrites are not well known independently, the fact that a CAI from the Allende meteorite plots within error of this isochron requires the Hf–W age of these ordinary chondrites to be within ~1 to 2 Myr of the age of Allende CAIs (the oldest solid objects of the Solar System). The chondrite isochron gives an initial $^{182}$Hf/$^{180}$Hf ratio of $(1.00 \pm 0.08) \times 10^{-4}$ and an initial $^{182}$W/$^{183}$W ratio corresponding to $\varepsilon_w = -3.45 \pm 0.25$ ($\varepsilon_w$ is defined in Table 1). The lowest initial $\varepsilon_w$ we have obtained based on metals from chondrites and iron meteorites is about $-3.5 \pm 0.5$ (Table 1 and unpublished data). Thus, the $^{182}$Hf/$^{180}$Hf ratio of $1 \times 10^{-4}$ and the initial $\varepsilon_w$ of $-3.5$ must be very close to their respective initial solar values. This initial $^{182}$Hf/$^{180}$Hf value is significantly lower than, and clearly inconsistent with, the commonly cited value of $2.75 \times 10^{-4}$ (ref. 18). In addition to obtaining a lower initial solar $^{182}$Hf abundance compared to the earlier work, one of the features of Fig. 1 is that three repeat measurements of Allende whole rock and the Dalgety Downs whole rock all plot consistently ~2 $\varepsilon$ units below the terrestrial standard and have a chondritic Hf/W ratio ($f^{Hf/W} = 0$; $f^{Hf/W}$ is defined in Table 1). This is inconsistent with previously measured whole-rock samples of Allende and Murchison[7,8] that yielded $\varepsilon_w \approx 0$ (discrepancies with published chondrite data are further discussed in Fig. 1 legend). Both ordinary chondrite isochrons are consistent with a chondritic uniform reservoir (CHUR) value of $\varepsilon_w = -1.9 \pm 0.2$ and $f^{Hf/W} = 0$. This means that the BSE with its high Hf/W ratio has a radiogenic $^{182}$W/$^{183}$W signature about 2 $\varepsilon$ units higher than the chondritic value. A comparison of results based on the old and the new data are given in Table 2.

Our Juvinas (eucrite) measurement plots on the eucrite isochron of ref. 6 with $^{182}$Hf/$^{180}$Hf $= 7.96 \times 10^{-5}$. The eucrites post-date our ordinary chondrites by only ~3 Myr. In contrast, the Hf–W data for eucrites[6], when compared to the currently accepted high initial solar $^{182}$Hf/$^{180}$Hf value[7,8,18,19], indicate a late parent body (Vesta) differentiation at ~16 Myr after the formation of the Solar System. This is

Table 1 **Hf–W isotope data for meteorites**

| Sample | Hf (p.p.b.) | Hf/W | $f^{Hf/W}$ | $\varepsilon_W$ | $\pm 2\sigma$ |
|---|---|---|---|---|---|
| Allende, WR no. 1 | 187.5 | 1.096 | −0.0236 | −1.93 | 0.28 |
| Allende, WR no. 2 | 187.7 | 1.098 | −0.0226 | −2.03 | 0.82 |
| Allende, WR no. 3 | 210.2 | 1.229 | 0.0946 | −2.02 | 0.36 |
| Allende, CAI (A44A) | 5,639 | 3.477 | 2.095 | 1.16 | 0.55 |
| Murchison, WR | 157.1 | 0.878 | −0.218 | −2.62 | 0.33 |
| Dhurmsala, silicate | 185.2 | 6.717 | 4.982 | +5.81 | 0.67 |
| Dhurmsala, metal | 8.25 | 0.0382 | −0.966 | −3.07 | 0.35 |
| Dhurmsala, WR | 181.1 | 1.395 | 0.242 | −1.27 | 0.51 |
| Dalgety Downs, silicate | 177.0 | 2.494 | 1.221 | +0.18 | 0.69 |
| Dalgety Downs, metal | 6.09 | 0.00946 | −0.992 | −3.50 | 0.23 |
| Dalgety Downs, WR | 159.7 | 1.125 | 0.001 | −1.85 | 0.46 |
| Juvinas, WR | 1,268 | 10.48 | 8.332 | +9.84 | 0.56 |
| Toluca, MC-ICPMS (Lyon), $N = 1$ | | | | −3.31 | 0.31 |
| Toluca, MC-ICPMS (Harvard), $N = 8$ | | | | −3.16 | 0.15 |
| Toluca, N-TIMS (Harvard), $N = 7$ | | | | −3.07 | 0.39 |

Data representation and analytical procedures. Here $f^{Hf/W} = (^{180}Hf/^{183}W)_{sample}/(^{180}Hf/^{183}W)_{CHUR} - 1$, where $(^{180}Hf/^{183}W)_{CHUR} = 2.836$ and the weight ratio $(Hf/W)_{CHUR} = 1.123$ (refs 14, 15). Also $\varepsilon_w = [(^{182}W/^{183}W)_{sample}/(^{182}W/^{183}W)_{standard} - 1] \times 10^4$, using $(^{182}W/^{183}W)_{standard} = 1.85130 \pm 4$ (ref. 16) obtained for our terrestrial W standard (Harvard-W1). WR, 'whole rock' sample. The samples were all ~1–2 g, except for the CAI (~0.2 g). In selecting samples, we specifically avoided using un-equilibrated chondrites to construct internal isochrons, especially petrologic types between 3.0 and 3.9. This is because there is good evidence that metamorphism resulted in a net transfer of W from oxidized phases to metal before the complete consumption of reductants (carbides, organics, and so on), which may complicate the interpretation of the resulting Hf–W systematics. This process is considered complete for type 4 and higher[29]. Therefore, an L4 chondrite, and an LL6 chondrite were selected for our work. The LL6 meteorite Dhurmsala was chosen for this study because its silicate fraction yielded a very high Hf/W ratio, which helps to define a precise isochron. Hf and W were separated at Harvard by anion exchange separation chemistry and their concentrations were determined precisely and accurately (to within ±0.5%) using calibrated $^{180}$Hf and $^{184}$W isotopic tracers. Total procedural blanks for Hf and W are negligible (13–15 pg and <0.19 ng, respectively). For the BCR-1 standard we obtained Hf = 4,995 ± 24 p.p.b. and W = 412 ± 3 p.p.b., identical within error to accepted values for this standard, demonstrating the accuracy of our Hf–W ratios (analysed by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) and N-TIMS at Harvard and MC-ICP-MS in Lyon). The W isotope data were corrected for instrumental mass fractionation using an exponential law with $^{184}W/^{183}W = 2.14078$ and/or $^{186}W/^{183}W = 1.98613 \pm 4$. The $\varepsilon_w$ values in this table were obtained by MC-ICP-MS in Lyon, except for most of the Toluca measurements. The accuracy of our measurements of the $^{182}W/^{183}W$ ratio in meteorite samples relative to our terrestrial W standard (the $\varepsilon_w$ value) was verified by comparing data for this meteorite ($N$ = number of repeat measurements) obtained using three different mass spectrometers and two different techniques (MC-ICP-MS vs N-TIMS): (1) MC-ICP-MS using both the Micromass IsoProbe at Harvard as well as the VG Plasma 54 in Lyon, (2) N-TIMS using the Finnigan MAT262 at Harvard.

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inconsistent with the 3-Myr timescale implied by our present Hf–W data, as well as with evidence for now extinct $^{53}$Mn (half-life $t_{1/2}$ = 3.7 Myr, ref. 1) and $^{26}$Al ($t_{1/2}$ = 0.7 Myr, refs 2, 3) in eucrites. From our present Hf–W data and the available $^{53}$Mn and $^{26}$Al chronologies, we conclude that the eucrites formed ~3 Myr after Allende's CAIs. The eucrite isochron in Fig. 1 exhibits a high initial $\varepsilon_W$ of about −1 compared to the solar initial $\varepsilon_W$ of about −3.5. The mantle of the eucrite parent body (EPB; probably the asteroid Vesta) must have evolved as a high Hf/W reservoir in order to develop radiogenic $^{182}$W signatures. Core formation in the EPB resulted in a $f^{La/W} \approx f^{Hf/W} \approx 15$ for the EPB mantle[25]. Thus, using the eucrite isochron[6], the EPB mantle should have a present-day $\varepsilon_W$ of +17. As 90–95% of W in the EPB is in its core, it follows by mass balance that the W isotope composition of the core is in the range 0.9 to 1.7 $\varepsilon$ units below the present CHUR value of −2. This is (within error) the same as the difference between present and initial CHUR of 1.5 $\varepsilon$ units as obtained in our work, and also consistent with W isotope data for most iron meteorites and metals in chondrites[8,15–19]. This requires that the time of eruption of these basalts on the surface of the EPB post-dates core formation in the EPB. Thus, the difficulties encountered in interpreting Hf–W systematics between eucrites and iron meteorites[6] is resolved by using the chondrite data determined in the present study.

Using our present estimate of the CHUR values for the $^{182}$Hf–$^{182}$W system, we can explore the implications for the timing of accretion and core formation of the Earth. The difference between $\varepsilon_W$ in the BSE and CHUR ($\Delta\varepsilon_W = \varepsilon_W(BSE) - \varepsilon_W(CHUR)$) together with the $f^{Hf/W}$ of ~12 for the BSE[15] provide the basis for such a calculation. The $\Delta\varepsilon_W$ value of the BSE is +2, and a plot of $\Delta\varepsilon_W$ versus the mean time of core formation is shown in Fig. 2. A two-stage model age for the BSE of 29 Myr since the formation of the

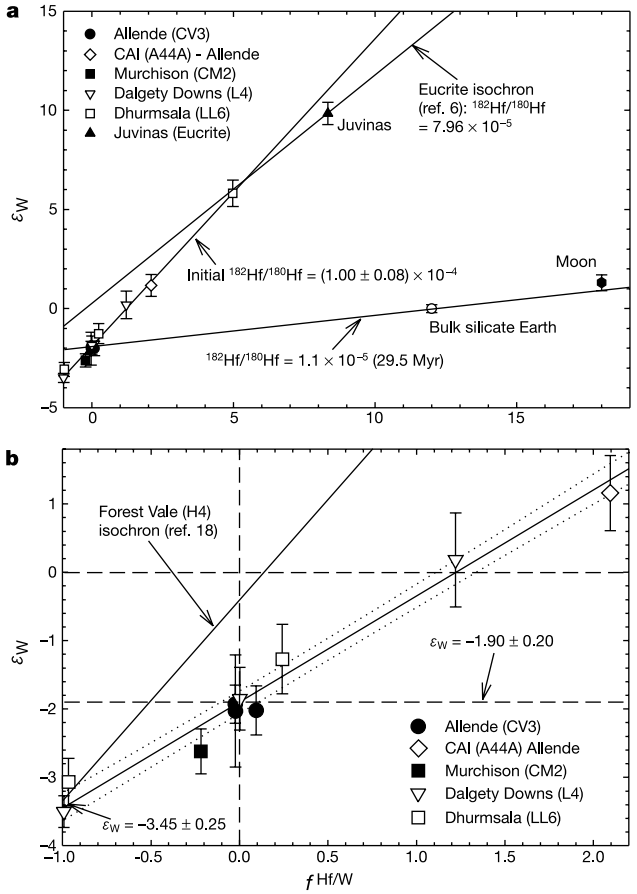


**Figure 1** Hf–W systematics for the early Solar System. Shown is a plot of $\varepsilon_W$ versus $^{180}$Hf/$^{183}$W represented as $f^{Hf/W}$ (see Table 1 for definitions of $\varepsilon_W$ and $f^{Hf/W}$). **a**, Data for metal and silicate fractions from ordinary chondrites Dalgety Downs (L4) and Dhurmsala (LL6), and from carbonaceous chondrites Allende and Murchison, define a good fossil isochron, identical within error of the individual isochrons for the two ordinary chondrites. Least-squares fitting of the data include the Allende and Murchison whole-rock data, but exclude the Allende CAI. Including or excluding the Murchison and Allende whole-rock data or the CAI data does not significantly change the slope or the intercept. Our Juvinas eucrite datum plots on the eucrite isochron[6]. The Moon, with a residual $\varepsilon_W = 1.3 \pm 0.4$ from $^{182}$Hf decay[27] and $f^{Hf/W} = 18$ defined by the lunar La/W ratio[28], falls within error on the extension of the tie-line between the bulk chondrite (CHUR) and bulk silicate Earth (BSE) points. **b**, Magnified area for bulk chondrite data. Dotted curves show the 2$\sigma$ error band. Our results are consistent with E-chondrite data[19], the zircon data for the Simmern (H5) chondrite[30], Ste Marguerite (H4) and Richardton (H5) ordinary chondrites[18], and inconsistent with published Allende and Murchison data[7,8] and the published initial $^{182}$Hf/$^{180}$Hf value of Forest Vale (H4)[18]. The position of our isochron relative to the Forest Vale isochron cannot be explained by late metamorphism. In that case the two isochrons would intersect at the bulk chondrite point ($f^{Hf/W} = 0$), which is not observed. Plausible reasons for discrepancy are: (1) uncorrected or improperly corrected interference; (2) contamination of the meteorite with terrestrial W either during or before chemical separation; and (3) incomplete dissolution, yielding a non-representative isotopic composition.

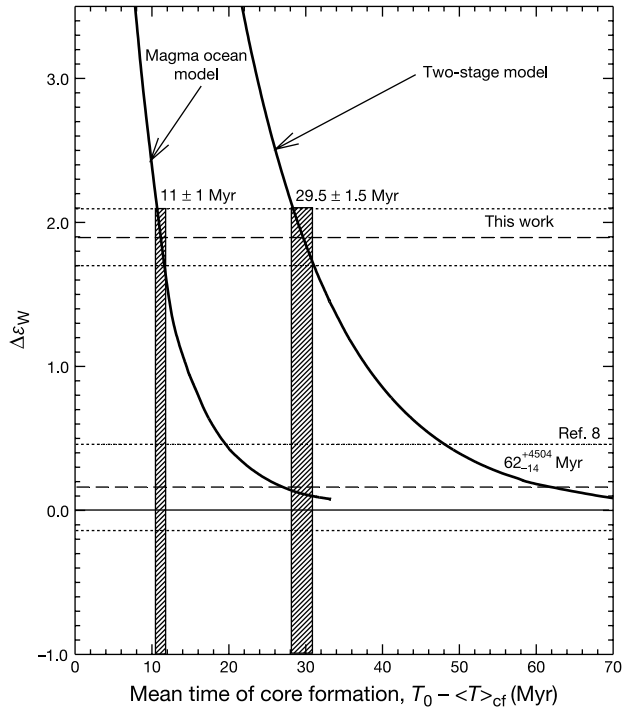


**Figure 2** Models for timing of core formation in the Earth. Shown is the expected radiogenic $^{182}$W/$^{183}$W value in the Earth relative to chondrites ($\Delta\varepsilon_W = [\varepsilon_W(BSE) - \varepsilon_W(CHUR)]$ for a range of mean times of core formation (given by $T_0 - \langle T\rangle_{cf}$, where $T_0$ is the age of the Solar System and $\langle T\rangle_{cf}$ is the mean age of core formation; see ref. 14) in the Earth for two different models of core segregation: a two-stage model, and a magma ocean model. For the $\Delta\varepsilon_W$ value of +1.9 ± 0.20 reported in this work, we obtain as shown a two-stage model age of 29.5 ± 1.5 Myr and a mean time of core formation of 11 ± 1.0 Myr (63% of core formed) for the continuous model (calculated as described in ref. 15). The vertical hatched bars represent the age uncertainties. We believe that the magma-ocean segregation model yields the most realistic estimate (11 ± 1.0 Myr) for the mean time of core formation. For comparison, we show the previous results[8] with a $\Delta\varepsilon_W$ value of +0.17 ± 0.29. The timescale with the previous data[8] is about a factor of $2^{+153}_{-0.3}$ longer (two-stage model age = $62^{+4504}_{-14}$ Myr) than the one obtained in this work. With the old data of ref. 8 the time of core formation is highly uncertain ($62^{+4504}_{-14}$ Myr), as the upper error limit corresponds to no radiogenic $^{182}$W compared to chondrites in the silicate Earth.

Table 2 **Comparison of new and old chronology**

| | New (this work) | Old (refs 7, 8, 18) |
|---|---|---|
| Initial $^{182}Hf/^{180}Hf$ | $(1.00 \pm 0.08) \times 10^{-4}$ | $(2.75 \pm 0.24) \times 10^{-4}$ |
| Present bulk Solar System $^{182}W/^{183}W$ ratio | $\varepsilon_w = -1.90 \pm 0.20$ | $\varepsilon_w = -0.17 \pm 0.29$ |
| Earth core formation* | 10–29 Myr | $62^{+4504}_{-14}$ Myr |
| Moon* | 29 Myr, and consistent with radiogenic $^{182}W$ on the Moon | >60 Myr, but inconsistent with radiogenic $^{182}W$ on the Moon |
| Vesta* | ~3 Myr | 16 Myr |
| Solar nebula gas dissipation | During planetary accretion | Before the main stage of planetary accretion |
| Mantle He and Ne isotope evidence | Consistent | Inconsistent |

*Time given as Myr after the formation of the Solar System.

Solar System is shown as the intersection of the two-stage model line in Fig. 2 with $\Delta\varepsilon_w = +2$. Note that this corresponds to the 29-Myr fossil isochron for BSE in Fig. 1. This two-stage age has strict time significance only in the case where there is complete equilibration between the core and the silicate mantle at a single point in time, with no subsequent additions of material to the Earth. Thus, if Earth's accretion was terminated by a giant impact (giving rise to the Moon) and accompanied by complete metal–silicate equilibration, then the Hf/W system constrains this event to occur at 29 Myr after the beginning of the Solar System. However, as we have discussed earlier[14–16,24], continuous models of core formation should, in general, yield a more realistic time constraint. Here we consider a magma-ocean differentiation model[15] with exponentially decreasing rates of accretion and with the rate of core formation limited by (and equal to) the accretion rate. In this model, all the metal segregated into the core is first equilibrated with the entire silicate mantle, as there is abundant evidence for an early magma ocean[21,22,26]. This results in a mean time of core formation of 11 ± 1 Myr (63%) (and 24 Myr for 90%), substantially shorter than the two-stage model age. These results strongly suggest that the Earth's core formation took place earlier than stated in many recent publications[7,8,20].

Earlier reports[9] required the Moon to have a substantially higher value of $\varepsilon_w$ than the Earth. This made it extremely difficult to explain the Moon as being derived by a late (>50 Myr after the formation of the Solar System) giant impact at the end of Earth's accretion[20]. It is now apparent that a significant portion of the observed $^{182}W$ excess in lunar samples was not the result of $^{182}Hf$ decay, but was instead the consequence of the $^{181}Ta(n,\gamma)^{182}Ta(\beta^-)^{182}W$ reaction induced by the bombardment of cosmic rays while these rocks were exposed on the surface of the Moon[27]. The residual radiogenic $^{182}W$ signature from $^{182}Hf$ decay for the Moon is now 1.3 ± 0.4 $\varepsilon$ units higher than for the Earth[27]. Therefore, W isotope data are consistent with formation of the Moon at ~25–30 Myr after the formation of the Solar System, as it plots within error of the BSE fossil isochron (see Fig. 1; here $f^{Hf/W}$ for the silicate Moon is estimated using the La/W ratio of the Moon[28]). In fact, the absence of any differentiated silicate data below the chondrite–Earth–Moon line suggest that essentially the bulk of metal–silicate separation in the Solar System was completed in <30 Myr.

Astronomical observations place a severe constraint on the formation time of a gas-giant planet (possibly with a solid core of ten Earth masses) to within a few million years after central star formation and before complete dissipation of nebula gas[4,5]. It is now well accepted from dynamical models that Mars-sized bodies will form within 0.1 Myr of the origin of the Solar System[13]. Dynamic accretion models favour the main growth stage (~60%) of the terrestrial planets (from Mars-sized to Earth-sized bodies) taking about 10–20 Myr, but the 'tail' of accretion may arguably continue for another 80–90 Myr (refs 11, 12). As shown here, our present W isotope data imply that the main growth stage is largely completed in about 10 Myr. Our data also resolve the inconsistency between Hf–W chronology and Mn–Cr and Al–Mg chronologies for meteorites derived from the Vesta asteroid, and support a very short timescale (<3 Myr) for formation and melting of asteroid-sized bodies. We conclude that the Hf–W data reported here produce a consistent model for early Solar System chronology (see Table 2). □

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**Competing interests statement**

The authors declare that they have no competing financial interests.

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# Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf–W chronometry

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**The timescales and mechanisms for the formation and chemical differentiation of the planets can be quantified using the radioactive decay of short-lived isotopes[1–10]. Of these, the $^{182}$Hf-to-$^{182}$W decay is ideally suited for dating core formation in planetary bodies[1–5]. In an earlier study, the W isotope composition[1] of the Earth's mantle was used to infer that core formation was late[1] (≥60 million years after the beginning of the Solar System) and that accretion was a protracted process[11,12]. The correct interpretation of Hf–W data depends, however, on accurate knowledge of the initial abundance of $^{182}$Hf in the Solar System and the W isotope composition of chondritic meteorites. Here we report Hf–W data for carbonaceous and H chondrite meteorites that lead to timescales of accretion and core formation significantly different from those calculated previously[1,3,5,11,12]. The revised ages for Vesta, Mars and Earth indicate rapid accretion, and show that the timescale for core formation decreases with decreasing size of the planet. We conclude that core formation in the terrestrial planets and the formation of the Moon must have occurred during the first ~30 million years of the life of the Solar System.**

Chemically and mineralogically, carbonaceous chondrites represent some of the most primitive material in the Solar System. The chemical composition of type 1 (CI) carbonaceous chondrites is, except for extremely volatile elements (H, C, N, O, rare gases), identical to that of the bulk Solar System. Other types of carbonaceous chondrites are fractionated relative to CI chondrites, but refractory elements occur in chondritic (solar) proportions in all types. Hence, all carbonaceous chondrites should have the same ratio of the two refractory elements Hf and W, and therefore a uniform W isotope composition. Variations in the Hf/W ratio among different groups of carbonaceous chondrites of up to ~30% would result in W isotope variations indistinguishable at the currently obtained analytical resolution. We analysed the W isotope compositions of seven carbonaceous chondrites—Orgueil (CI), Allende (CV), Murray (CM), Murchison (CM), Cold Bokkeveld (CM), Nogoya (CM) and Karoonda (CK)—using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), and found them to be identical within analytical error. The weighted average of the $^{182}$W/$^{184}$W ratios for these samples differs by $-1.9 \pm 0.2\,\varepsilon$ units from the terrestrial standard (Table 1, Fig. 1), but agrees with Hf–W data for enstatite chondrites[13].

The most reliable method for determining the initial abundance of $^{182}$Hf is by measuring internal Hf–W isochrons of samples with independently known age. The H chondrites Ste Marguerite and Forest Vale were selected because their phosphates have been dated previously by the high-precision Pb–Pb method. The preservation of U–Pb phosphate ages of 4.5627 ± 0.0006 Gyr for Ste Marguerite[14] and 4.5609 ± 0.0007 Gyr for Forest Vale[14] precludes late disturbance or alteration of these meteorites. A four-point metal-silicate isochron for Ste Marguerite (Fig. 2a) defines an initial $^{182}$Hf/$^{180}$Hf ratio of $(0.85 \pm 0.05) \times 10^{-4}$ at the time of closure of the Hf–W system. Likewise, a four-point isochron for Forest Vale gives an initial $^{182}$Hf/$^{180}$Hf ratio of $(1.0 \pm 0.5) \times 10^{-4}$ (Fig. 2b). These two isochrons pass through the newly defined chondritic $\varepsilon_w$ at the chondritic Hf/W ratio of ~1.1.

Back calculation of these initial values to the Pb–Pb age of Ca-Al-rich inclusions (CAI; 4.566 ± 0.002 Gyr, ref. 15), which is commonly used as reference for condensation of the first solid matter in the Solar System, yields a $^{182}$Hf/$^{180}$Hf ratio of $(1.09 \pm 0.09) \times 10^{-4}$ for Ste Marguerite and $(1.5 \pm 0.7) \times 10^{-4}$ for Forest Vale. These values define the initial abundance of $^{182}$Hf in the Solar System, provided that the $^{182}$Hf–$^{182}$W system in metal and silicate closed at approximately the same time as the U–Pb system in phosphates. This is likely, as these H chondrites do not show evidence for later thermal overprint. The more precise value of $(1.09 \pm 0.09) \times 10^{-4}$ for Ste Marguerite is our preferred approximation for the initial $^{182}$Hf/$^{180}$Hf ratio of the Solar System. This precisely defined value is in agreement with previous estimates obtained from internal chondrite isochrons[16], the comparison of W isotopes in iron meteorites and chondrites[16,30], and the W isotope compositions of

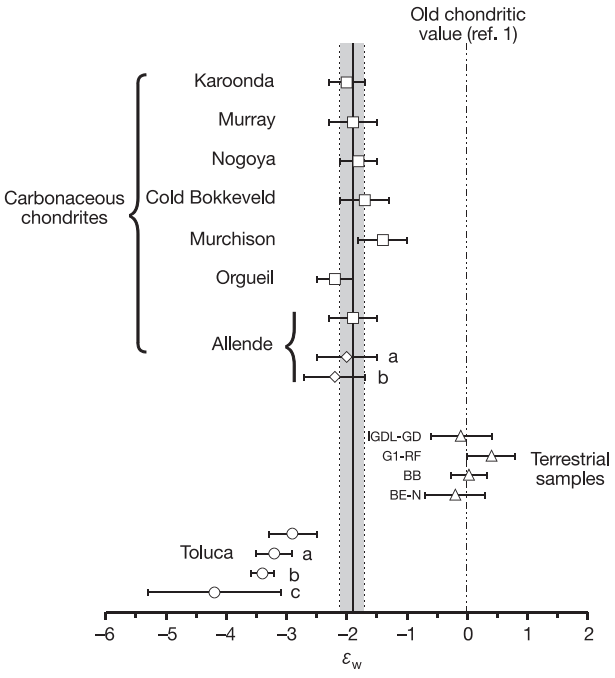


**Figure 1** $\varepsilon_w$ values of carbonaceous chondrites compared with those of the Toluca iron meteorite and terrestrial samples analysed in this study. The values for Toluca, Allende, G1-RF and IGDL-GD are the weighted averages of four or more independent analyses. Also included are data from ref. 16 (indicated by a), ref. 30 (b), and ref. 2 (c). For the definition of $\varepsilon_w$ see Table 1. The vertical shaded bar refers to the uncertainty in the W isotope composition of chondrites. Terrestrial samples include IGDL-GD (greywacke), G1-RF (granite) and BB and BE-N (basalts).

  

meteoritic zircons[17]. This newly determined value is significantly lower than the previous estimate[18] of $(2.75 \pm 0.24) \times 10^{-4}$.

The revision of both the chondritic W isotope composition and the initial $^{182}Hf/^{180}Hf$ has fundamental implications for the Hf–W chronometry of planetary core formation. Assuming that core formation occurred as a single-stage event, the time of metal–silicate separation can be calculated using the differences in the W isotope composition and Hf/W between a silicate or metal reservoir and chondrites[1].

All known classes of iron meteorites exhibit $\varepsilon_W$ anomalies ranging from $-5$ to $-3$ relative to the terrestrial value[4], indicating that core formation in iron meteorite parent bodies took place within 10 Myr of the beginning of the Solar System (defined here as the condensation of the oldest dated phases in the Solar System). This constraint is consistent with the timescale deduced from $^{107}Pd$–$^{107}Ag$ systematics in iron meteorites[9,10]. Owing to the low Solar System initial $^{182}Hf/^{180}Hf$ of $(1.09 \pm 0.09) \times 10^{-4}$ and the low Hf/W in metals, variations in the W isotope composition of iron meteorites and thus time differences for metal differentiation cannot be resolved with current analytical techniques. However, precise timescales for core formation can be obtained from the silicate portions of planetary bodies (Vesta[5], Mars[3], Earth and Moon[19]), which have high Hf/W. Published Hf–W data for eucrites, which are widely considered to be from the asteroid Vesta[20], define a whole-rock isochron corresponding to an initial $^{182}Hf/^{180}Hf$ of $(7.96 \pm 0.34) \times 10^{-5}$ (ref. 5). Using our new parameters, this yields a Hf–W age for silicate differentiation on Vesta of $4.2 \pm 1.3$ Myr after the beginning of the Solar System. With the old Hf–W parameters, a value of $16.1 \pm 1.3$ Myr was reported[5]: this young age was difficult to reconcile with the general view that decay of $^{26}Al$, which was only present in significant amounts during the first ~5 Myr of the Solar System, was the main heat source for internal differentiation of planetesimals. In fact, the former presence of $^{26}Al$ has been detected in the Piplia Kalan eucrite[8]. Our revised age of $4.2 \pm 1.3$ Myr after the beginning of the Solar System is in notable agreement with timescales deduced from the $^{53}Mn$–$^{53}Cr$ (ref. 6), $^{60}Fe$–$^{60}Ni$ (ref. 7) and $^{26}Al$–$^{26}Mg$ chronometers[8], which all suggest mantle–crust differentiation on Vesta within the first ~4 Myr of the Solar System.

To obtain direct age constraints for core formation on Vesta, the W isotope composition and the Hf/W of the bulk mantle of Vesta need to be known. Using a Hf/W of 34.9 (calculated from W/La and La/Hf; refs 21, 22) for the bulk mantle of Vesta, we deduce a W isotope composition of $+35.8\ \varepsilon_W$ from the eucrite Hf–W whole-rock isochron, yielding a W model age for core formation of $3.8 \pm 1.3$ Myr since the beginning of the Solar System. This age is

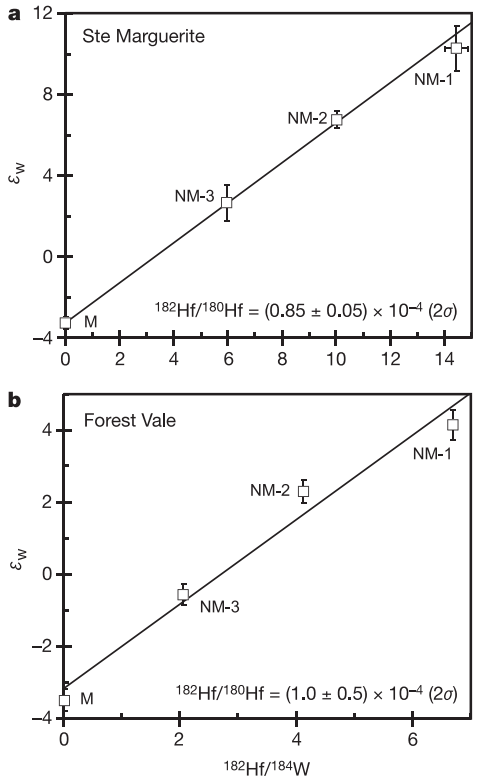


**Figure 2** $\varepsilon_W$ versus $^{180}Hf/^{184}W$ for different fractions of the H chondrites Ste Marguerite (**a**) and Forest Vale (**b**). NM-1, NM-2 and NM-3 refer to different nonmagnetic fractions, M is the magnetic fraction. We interpret the positive correlation of $\varepsilon_W$ with $^{180}Hf/^{184}W$ as an internal Hf–W isochron whose slope corresponds to the initial $^{182}Hf/^{180}Hf$ ratio at the time of closure of the Hf–W system.

Table 1 **W isotope data for carbonaceous and H chondrites**

| Sample | Hf (p.p.b.) | W (p.p.b.) | $^{180}Hf/^{184}W$ ±2σ | $^{182}W/^{184}W$ ±2σ | $^{183}W/^{184}W$ ±2σ | $\varepsilon_W$ ± 2σ |
|---|---|---|---|---|---|---|
| Carbonaceous chondrites | | | | | | |
| Allende | | | | 0.864532 ± 35 | 0.467052 ± 23 | −1.9 ± 0.4 |
| Orgueil | | | | 0.864506 ± 26 | 0.467122 ± 14 | −2.2 ± 0.3 |
| Murchison | | | | 0.864575 ± 35 | 0.467052 ± 19 | −1.4 ± 0.4 |
| Cold Bokkeveld | | | | 0.864549 ± 35 | 0.467066 ± 19 | −1.7 ± 0.4 |
| Nogoya | | | | 0.864540 ± 26 | 0.467052 ± 14 | −1.8 ± 0.3 |
| Murray | | | | 0.864532 ± 35 | 0.467047 ± 19 | −1.9 ± 0.4 |
| Karoonda | | | | 0.864523 ± 26 | 0.467038 ± 14 | −2.0 ± 0.3 |
| Weighted average | | | | 0.864533 ± 20 | 0.467050 ± 10 | −1.9 ± 0.2 |
| H chondrites | | | | | | |
| Ste Marguerite | | | | | | |
| M | 11.6 | 856.2 | 0.0155 ± 2 | 0.864412 ± 26 | 0.467067 ± 14 | −3.3 ± 0.3 |
| NM-1 | 204.9 | 16.2 | 14.4 ± 4 | 0.865583 ± 95 | 0.467068 ± 50 | 10.3 ± 1.1 |
| NM-2 | 148.8 | 17.0 | 10.0 ± 1 | 0.865279 ± 35 | 0.467049 ± 14 | 6.7 ± 0.4 |
| NM-3 | 183.3 | 35.3 | 5.9 ± 2 | 0.864925 ± 78 | 0.467010 ± 34 | 2.7 ± 0.9 |
| Forest Vale | | | | | | |
| M | 8.22 | 664.5 | 0.0142 ± 1 | 0.864394 ± 26 | 0.467060 ± 12 | −3.5 ± 0.3 |
| NM-1 | 179.0 | 30.7 | 6.68 ± 6 | 0.865054 ± 36 | 0.467088 ± 16 | 4.1 ± 0.4 |
| NM-2 | 148.6 | 41.2 | 4.13 ± 3 | 0.864896 ± 28 | 0.467060 ± 14 | 2.3 ± 0.3 |
| NM-3 | 170.0 | 95.0 | 2.05 ± 1 | 0.864648 ± 26 | 0.467080 ± 13 | −0.6 ± 0.3 |

The W isotope composition of a sample is generally reported in $\varepsilon_W$ units relative to a terrestrial standard, given by $\varepsilon_W = \{[(^{182}W/^{184}W)_{sample}/(^{182}W/^{184}W)_{standard}] - 1\} \times 10^4$. Uncertainties refer to the last significant digits. The accuracy of the measured W isotope ratios is monitored by the analysis of $^{183}W/^{184}W$. For all samples except Orgueil, the $^{183}W/^{184}W$ ratios agree with the terrestrial standard. The higher $^{183}W/^{184}W$ for Orgueil is caused by an organic peak on mass 183 that for all other samples was successfully removed by treatment with $HNO_3$-$H_2O_2$. For the H chondrites, M and NM denote magnetic and nonmagnetic fractions, respectively.

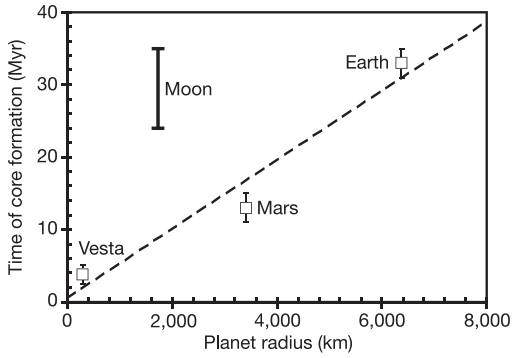


**Figure 3** Time of core formation in Myr after CAI condensation for Vesta, Mars, Earth and Moon versus planet radius as deduced from Hf–W systematics. For the Moon, the two data points refer to the endmember model ages. The Moon plots distinctly to the left of the correlation line defined by Vesta, Mars and Earth, suggesting a different formation process.

indistinguishable from the silicate differentiation age obtained from the eucrite whole-rock isochron. $^{182}$Hf–$^{182}$W systematics therefore show that both core formation and silicate differentiation on Vesta occurred within the first ~5 Myr of the Solar System.

Martian meteorites display W isotope compositions ranging from +0.3 $\varepsilon_w$ to +2.9 $\varepsilon_w$ (ref. 3). Correlated $^{182}$W and $^{142}$Nd anomalies on Mars indicate that the observed spread in $\varepsilon_w$ is caused by internal silicate differentiation in the martian mantle[3] because Sm and Nd are both lithophile elements that do not fractionate during core formation. As martian meteorites with no excess $^{142}$Nd have $^{182}$W/$^{184}$W ratios that are identical to the earlier chondritic value, core formation and silicate differentiation on Mars were interpreted as contemporaneous processes that occurred within the first 30 Myr of the Solar System (ref. 3). However, with the revised chondritic W isotope composition, even the least radiogenic martian meteorites display a $^{182}$W excess of ~2.2 $\varepsilon$ units relative to the new chondritic value. As the $^{142}$Nd/$^{144}$Nd ratio in these meteorites is chondritic, the increased $^{182}$W/$^{184}$W can be uniquely attributed to Hf–W fractionation that is caused by core formation, suggesting a decoupling of core formation and silicate differentiation on Mars. Assuming a Hf/W of 5.1 for the primitive martian mantle[22,23], the new W model age for core formation on Mars is 13 ± 2 Myr after the beginning of the Solar System.

Revision of the $^{182}$Hf–$^{182}$W parameters has far-reaching implications for the timing of terrestrial core formation and the origin of the Earth–Moon system. Most importantly, the bulk silicate Earth (BSE) has a clearly resolvable $^{182}$W excess of 1.9 $\varepsilon$ units relative to chondrites, and does not have a chondritic W isotope composition as previously suggested[1]. Using a Hf/W ratio of 17.7 for the BSE[24,25], core formation on Earth occurred 33 ± 2 Myr after the beginning of the Solar System. The W isotope composition of the lunar mantle ranges from +1.3 ± 0.4 to the terrestrial value of 0 $\varepsilon_w$ (ref. 19). Assuming that the Hf/W ratios of the lunar mantle and BSE are identical[1], W model ages for the Moon are between 26 ± 2 and 33 ± 2 Myr after the beginning of the Solar System, and thus substantially older than previously suggested[19].

The revised Hf–W model ages for core formation indicate rapid accretion and early core formation on planetary bodies, and an early origin of the Moon. These timescales are consistent with the rates suggested by Wetherill-type accretion models[26–28]. The fact that the time of core formation increases with planet size suggests a more protracted growth history for the larger planets (Fig. 3). The Moon does not fit this simple relationship, indicating that it formed by a different process—such as a giant impact during Earth's early accretion. □

## Methods

### Sample preparation

Samples were cleaned in an ultrasonic bath, washed in 0.05 M $HNO_3$ for a few minutes, and powdered in an agate mortar. Metal–silicate separation for the H chondrites was performed using a hand magnet. Silicate dust adhering to the metal grains was removed by repeated crushing of the magnetic fractions in ethanol. Some non-magnetic fractions were further purified by alternately grinding the powder in an agate mortar and removing the remaining metal grains with a magnet. Carbonaceous chondrites and the non-magnetic fractions from H chondrites were dissolved in Savillex vials at 180 °C on a hotplate using HF-$HNO_3$-$HClO_4$ (5:3:2). Metal separates from H chondrites were dissolved in 5:1 $HNO_3$-HF at 120 °C on a hotplate. After digestion, the samples were dried and redissolved in $HNO_3$-$H_2O_2$ to remove organic compounds. After drying down, the samples were completely dissolved in 6 M HCl-0.06 M HF. A 10–20% aliquot of the sample was spiked with a mixed $^{180}$Hf–$^{183}$W tracer that was calibrated against pure Hf and W metals. The use of high-pressure bombs for sample digestion was specifically avoided because Savillex vials contain significant W (up to several nanograms) that is released at high pressure. Furthermore, W is adsorbed by Savillex Teflon, thus requiring thorough cleaning of the beakers. For this reason, the W blank of every vial was checked in a blank digestion procedure before each sample digestion. This procedure was found to be absolutely necessary to achieve low and reproducible blanks. Separation of Hf and W from the matrix was performed by anion exchange (AG-1X8 resin) in HCl-HF following procedures modified from refs 4 and 29. Hafnium was eluted using 9 M HCl-0.01 M HF, and W was collected in 7 M HCl-1 M HF. Total procedural blanks were ~250 pg for W isotope composition measurements, and ~50 pg W and ~10 pg Hf for the concentration measurements.

### Isotope measurements

All measurements were made using the IsoProbe MC-ICP-MS at Münster. Tungsten isotope measurements were normalized to $^{186}$W/$^{184}$W = 0.92767 using the exponential law. Repeated measurements of a ALFA AESAR standard metal during the course of this study yielded $^{182}$W/$^{184}$W = 0.864696 ± 0.000009 (2$\sigma$ of the mean) and $^{183}$W/$^{184}$W = 0.467052 ± 0.000006 (2$\sigma$ of the mean). The accuracy and external reproducibility of the W isotope measurements (±0.5 $\varepsilon$, 2$\sigma$) were determined by repeated measurements of the Toluca iron meteorite and the Allende carbonaceous chondrite (Fig. 1). The robustness of our method is furthermore documented by several independent measurements (separate digestions) of different terrestrial samples (Fig. 1). Small isobaric Os interferences on masses 186 and 184 were corrected by monitoring $^{188}$Os. To assess possible interferences on $^{186}$W and $^{184}$W, measured $^{182}$W/$^{184}$W values were also normalized to $^{186}$W/$^{183}$W and $^{183}$W/$^{184}$W using the exponential law. For the chondrites identical results of −1.9 ± 0.2 and −1.8 ± 0.4 $\varepsilon$ units are obtained when using $^{186}$W/$^{183}$W and $^{183}$W/$^{184}$W, respectively, for mass bias correction.

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**Competing interests statement**

The authors declare that they have no competing financial interests.

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# Metal–insulator transition in chains with correlated disorder

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**According to Bloch's theorem, electronic wavefunctions in perfectly ordered crystals are extended, which implies that the probability of finding an electron is the same over the entire crystal[1]. Such extended states can lead to metallic behaviour. But when disorder is introduced in the crystal, electron states can become localized, and the system can undergo a metal–insulator transition (also known as an Anderson transition)[2–4]. Here we theoretically investigate the effect on the physical properties of the electron wavefunctions of introducing long-range correlations in the disorder in one-dimensional binary solids, and find a correlation-induced metal–insulator transition. We perform numerical simulations using a one-dimensional tight-binding model, and find a threshold value for the exponent characterizing the long-range correlations of the system. Above this threshold, and in the thermodynamic limit, the system behaves as a conductor within a broad energy band; below threshold, the system behaves as an insulator. We discuss the possible relevance of this result for electronic transport in DNA, which displays long-range correlations[5,6] and has recently been reported to be a one-dimensional disordered conductor[7–10].**

The tight-binding model of a solid is characterized by a hamiltonian in which one orbital (single electron) and a single energy $\varepsilon_i$ are assigned to each lattice site $i$

$$H = \sum_i \varepsilon_i |i\rangle\langle i| + \sum_{\langle i,j\rangle} t|i\rangle\langle j| \qquad (1)$$

where $t$ is the electronic overlap (hopping term) between the wavefunctions of electrons centred at two neighbouring sites $i$, $j$. For a perfectly ordered crystal, all site energies $\varepsilon_i$ have the same value or follow a periodic pattern. For disordered solids, $\varepsilon_i$ can be randomly chosen from a certain probability distribution—for example, a uniform distribution or a gaussian. The probability distribution generating $\varepsilon_i$ is characterized by a parameter $W$ which quantifies the spread of the distribution, and thus the degree of disorder. In the case of a uniform distribution $W$ is the distribution width, whereas in the case of a gaussian distribution $W$ is the standard deviation. Models for one-dimensional (1D) disordered solids traditionally consider only two parameters of interest, namely the interaction term between nearest neighbours, $t$, and the disorder of the system, $W$. Thus the controlling parameter is the ratio $W/t$. Typically, $t$ is fixed (for example, $t = 1$), thus fixing the energy scale in the system, and $W$ is changed to study the effects produced by different levels of disorder.

In the limit $W \to 0$, where the coupling energy $t$ between neighbours dominates, a perfect lattice is recovered, and Bloch's theorem applies: there are extended electron states, and the system can conduct[1]. This is valid for finite system size only, because localization theory asserts that in the limit of large systems all electron states are localized in the 1D case[3]. For sufficiently large $W$, where the disorder dominates, the wavefunctions are strongly localized. This localization phenomenon depends on the system dimension. For three-dimensional (3D) systems at zero temperature, $T = 0$, there is a critical value $W_c$ for which a metal–insulator transition occurs[11,12]. For a uniform distribution, $W_c = 16.5$. For $W < W_c$, despite some degree of disorder, the electron wavefunctions are extended, and the system behaves as a metal, whereas for $W > W_c$, the wavefunctions become localized, and the system behaves as an insulator. For two-dimensional (2D) and 1D disordered systems even infinitesimal disorder produces localized states[3], so at $T = 0$ the system behaves as an insulator in the thermodynamic limit, although for some particular cases in two dimensions it is possible to find a metal–insulator transition[13–15].

We consider the case of a 1D system, and show that randomly chosen but long-range correlated $\{\varepsilon_i\}$ can lead to extended wavefunctions and thus to conductivity, in contrast to the expectation—based on the assumption of uncorrelated disorder—that no extended states can be found in 1D disordered systems at $T = 0$ (ref. 1). Traditionally, localization of the electron wavefunction in one dimension is considered to be unaffected by the form and width of the distribution from which the $\{\varepsilon_i\}$ are chosen. Although all proofs establishing localization in one dimension are model-dependent, exponential localization of all eigenstates in one dimension is believed to occur at $T = 0$ (refs 16–18). In this case, electron wavefunctions are of the form $\Psi(x) = f(x)\exp(-|x - x_0|/\lambda)$, where $f(x)$ is a random function which depends on the particular realization of the disordered chain, and $\lambda$ is the localization length, which is a measure of the size of the wavefunction.

The simplest 1D model exhibiting Anderson localization is the random binary alloy[19], where there are two types of atoms, A and B, and two different diagonal energies, $\varepsilon_A$ and $\varepsilon_B$. To build the series of diagonal energies of the hamiltonian (equation (1)), $\varepsilon_A$ and $\varepsilon_B$ are assigned at random to each lattice site with probabilities $p$ and $1 - p$, respectively. For the random binary alloy, the corresponding wavefunctions are localized and the system behaves as an insulator (Fig. 1a).

We now show that introducing correlations in the disorder can markedly change the physics. The first attempt to introduce correlations into the random binary alloy model was the random dimer model[20,21]. In this model, short-range correlations are introduced by