

we would have to accept a very long path length of $L = 85$ pc and a low density of $\langle n_{\text{H}} \rangle = 6 \text{ cm}^{-3}$. On the other hand, if we adopt the canonical path length, we must increase the ionization rate to $\zeta = 1.2 \times 10^{-15} \text{ s}^{-1}$. Given the evidence pointing to a short path length, and the fact that ζ is essentially unconstrained in diffuse clouds, we consider the higher ionization rate to be the more likely explanation. A higher value of ζ for diffuse clouds may also find some support from considerations of the abundance of the OH molecule²⁶. A more detailed discussion of the ζ Persei line of sight, as well as other observations of H_3^+ in diffuse clouds, will be presented elsewhere.

The high value of ζ suggested by the CRYRING measurements and the ζ Persei observations can be reconciled with the lower ionization rate in dense clouds by postulating the existence of a large flux of low-energy cosmic rays that can penetrate diffuse clouds but not dense clouds. Such a cosmic-ray flux would bring the models and observations of H_3^+ into agreement, but would also have far-reaching implications for the chemistry and physics of interstellar clouds. From a chemical perspective, a higher value of ζ would proportionately increase the number densities of oxygen compounds such as OH, as well as affecting the relative abundances of deuterium-bearing molecules. The high number density of H_3^+ in diffuse clouds would also increase the rate of proton-transfer reactions, which play the key role in the formation of complex molecules in dense clouds, but which have been considered relatively unimportant in diffuse clouds. From a physical perspective, a higher cosmic-ray ionization rate represents an additional heating source for interstellar gas, and could have a significant impact on the thermal balance of the warm neutral medium²⁷. Further observations of H_3^+ , H_2 and C^+ in lines of sight to other diffuse clouds are needed to determine if the ζ Persei line of sight is unusual, or whether a large, low-energy cosmic ray flux indeed pervades our galaxy. □

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Structure and thermal history of the H-chondrite parent asteroid revealed by thermochronometry

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Our Solar System formed ~4.6 billion years ago from the collapse of a dense core inside an interstellar molecular cloud. The subsequent formation of solid bodies took place rapidly. The period of <10 million years over which planetesimals were assembled can be investigated through the study of meteorites^{1–3}. Although some planetesimals differentiated and formed metallic cores like the larger terrestrial planets, the parent bodies of undifferentiated chondritic meteorites experienced comparatively mild thermal metamorphism that was insufficient to separate metal from silicate^{4,5}. There is debate about the nature of the heat source^{6–9} as well as the structure and cooling

history of the parent bodies^{10–12}. Here we report a study of ²⁴⁴Pu fission-track and ⁴⁰Ar–³⁹Ar thermochronologies of unshocked H chondrites, which are presumed to have a common, single, parent body. We show that, after fast accretion, an internal heating source (most probably ²⁶Al decay^{8–10,13}) resulted in a layered parent body⁶ that cooled relatively undisturbed: rocks in the outer shells reached lower maximum metamorphic temperatures and cooled faster than the more recrystallized and chemically equilibrated rocks from the centre, which needed ~160 Myr to reach 390K.

The first condensation of refractory Ca–Al-rich inclusions (Allende CAIs) in the solar nebula occurred 4,566 ± 2 Myr ago^{1,2}. Accretion and differentiation into silicate crust and metallic core of some asteroids was completed only a few million years later, as demonstrated by Pb–Pb ages of basaltic achondrites³, whereas cooling of the iron cores extended over tens of millions of years¹⁴. In contrast, the cooling history and structure of the parent bodies of undifferentiated chondrites are not well established. Ordinary chondrites of one class (H, L or LL) share common properties such as oxygen isotopic composition, degree of iron oxidation and major element chemistry, suggesting a single parent body for each class. Moreover, each class can be subdivided into different petrologic types^{4,5} that experienced specific degrees of thermal metamorphism: for example, type 6 chondrites were heated to higher metamorphic peak temperatures (~1,120 K) than those of type 4 (~920 K). A possible model for the early evolution of ordinary chondrite parent asteroids is an onion-shell-layered parent body (refs 6, 10) (Fig. 1). After accretion, the parent body consists of primitive material and is heated internally by decay energy of short-lived nuclides^{8,9,13} such as ²⁶Al ($\tau_{1/2} = 0.72$ Myr). The outer shells lose heat more effectively, whereas the rocks in the centre are heated to higher metamorphic peak temperatures and cool down more slowly. However, as some studies did not show the expected correlation between metamorphic grade and cooling rate or age^{15,16}, other hypotheses were advanced that involve either separate parent bodies for each petrologic type¹¹ or early collisional fragmentation of an onion-shell-layered parent body, with final cooling in a ‘rubble-pile’ structure¹². Moreover, alternative heat sources were considered (see review⁷), such as electric currents induced by an early, intense, solar-wind plasma.

Radiochronometry can elucidate the early parent asteroid evolution: in an onion-shell-layered parent body that cools undis-

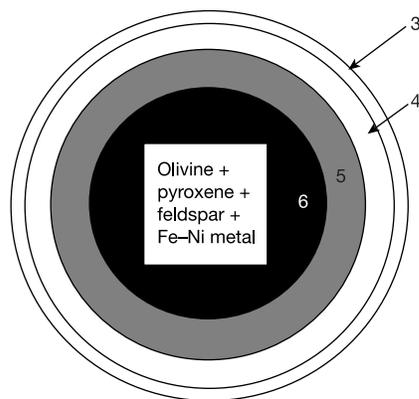


Figure 1 Onion-shell model for undifferentiated ordinary chondrite parent asteroids⁶. A celestial body that is internally heated (probably by the decay energy from short-lived ²⁶Al) reaches higher maximum metamorphic temperatures in its centre, resulting in higher petrologic types (numbers shown) that cool slower than in the outer layers, which in turn results in lower petrologic types with faster cooling. Increasing degrees of thermal metamorphism resulted, for example, in the extinction of primary chondrules, matrix recrystallization, formation of secondary feldspar and phosphates, and chemical equilibration of olivine and pyroxene. However, heating was insufficient for separation of metal and silicate and formation of an iron core.

turbed, type 6 chondrites cooled slower than type 4 chondrites. Slower cooling should result in lower cooling ages, as radiometric ‘ages’ actually represent cooling below a ‘closure temperature’ that is mineral specific, for example when Pb diffusion in phosphates becomes ineffective below ~720 K (refs 17–19), or when ⁴⁰Ar from ⁴⁰K decay is retained quantitatively in oligoclase feldspar below ~550 K (refs 19, 20). Other examples are ²⁴⁴Pu-derived fission tracks stable in orthopyroxene below ~550 K (ref. 19) or in the phosphate merrillite below ~390 K (ref. 19). Most reliable

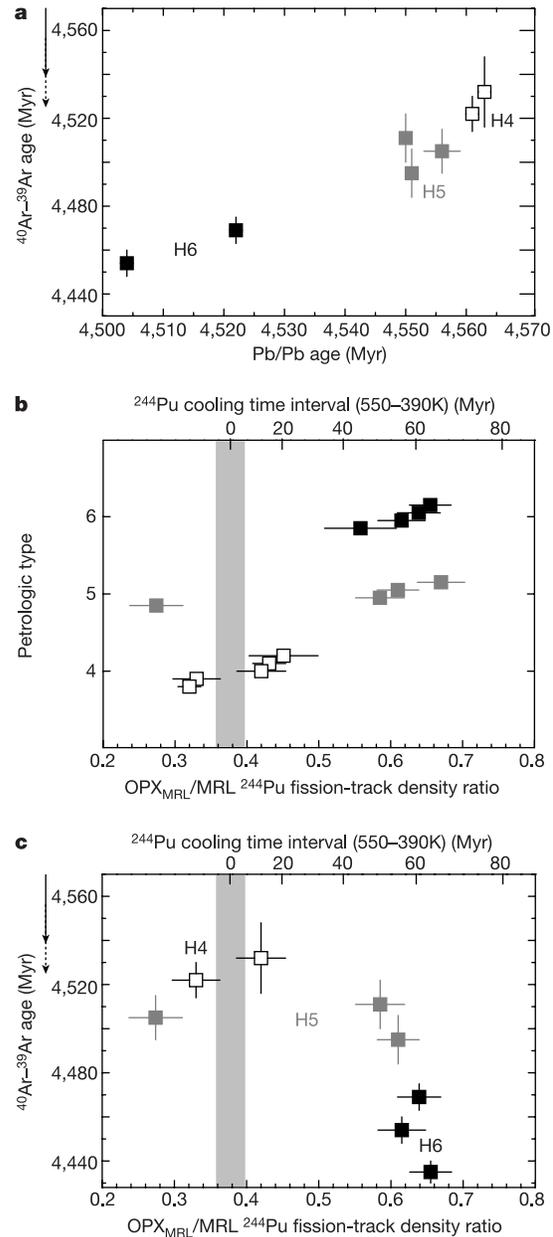


Figure 2 Correlation between cooling ages and metamorphic grade. **a**, Pb/Pb phosphate and ⁴⁰Ar–³⁹Ar feldspar cooling ages demonstrate that low petrographic types cooled faster to Pb closure in phosphates (~720 K) and Ar retention in feldspar (~550 K) than higher petrographic types. The arrow quantitatively indicates a possible shift of the K–Ar timescale caused by systematic error of the K decay constant, but note that age differences are not affected. **b**, Low petrographic types also cooled faster between 550 K and 390 K, as derived from cooling time intervals (upper scale) calculated from the ²⁴⁴Pu fission-track density ratio (lower scale) in merrillite and adjacent orthopyroxene (see Supplementary Table S1). The systematic uncertainty of the ²⁴⁴Pu timescale (induced by the normalization factor) is quantitatively shown by the grey band around zero. **c**, Correlation between ⁴⁰Ar–³⁹Ar feldspar cooling age and ²⁴⁴Pu fission-track cooling time interval.

results are obtained when the different complementary methods (Pb–Pb, ⁴⁰Ar–³⁹Ar, ²⁴⁴Pu fission tracks) are simultaneously applied to the aforementioned minerals that are major carriers of the parent nuclide. However, owing to the fine-grained nature of chondritic material, ⁴⁰Ar–³⁹Ar dating is commonly done on whole rocks^{19,20}. Here we present the first combined feldspar, pyroxene and whole-rock ⁴⁰Ar–³⁹Ar data for ordinary chondrites (see Supplementary Figs S1–S6 and Table S2). We also present the first ²⁴⁴Pu fission-track chronometric results that were evaluated with all-recent methodological improvements^{19,21} (Supplementary Table S1). An indispensable requirement for obtaining information on the early parent-body history is to study exceptionally undisturbed chondrites. Only these preserve the earliest radiometric record from the period shortly after accretion, as they were not affected by secondary-impact-induced shock or reheating during the past ~4,000 Myr. Just a few unshocked H chondrites—like those we studied—satisfy this condition.

Table 1 provides a summary of ²⁴⁴Pu fission-track, ⁴⁰Ar–³⁹Ar, and Pb–Pb chronometries of all H chondrites we studied, for which complete data sets are available now. The highest ages are Pb–Pb phosphate ages of H4 chondrites Forest Vale and Ste Marguerite. Obviously, accretion was complete 3.0 ± 2.6 Myr after Allende CAI formation 4,566 Myr ago (refs 1, 2, 18). H5 and H6 chondrites cooled progressively later below the Pb–Pb closure temperature. Our new results extend this trend to low-temperature chronometers: individual ⁴⁰Ar–³⁹Ar ages are generally lower than the respective Pb–Pb age (Table 1 and Fig. 2a). This can be interpreted as additional cooling time needed to reach ⁴⁰Ar retention in oligoclase feldspar at ~550 K. Moreover, high petrologic types needed a longer cooling time than low petrologic types, and reached isotopic closure later, leading to younger apparent ages. Slower cooling of H chondrites of high petrologic type is also confirmed by the cooling time intervals calculated from ²⁴⁴Pu fission-track densities of orthopyroxene and merrillite, which register tracks at <550 and <390 K (Table 1). This correlation is also valid for other unshocked H chondrites for which, however, there are no complementary ⁴⁰Ar–³⁹Ar and Pb–Pb age data (Fig. 2b and Supplementary Table S1). Figure 2c shows that H5 and H6 chondrites, which needed longer for cooling to the Ar closure temperature of 550 K,

also cooled more slowly afterwards until ²⁴⁴Pu fission-track retention in merrillite at 390 K (except Nadiabondi).

Figure 3a displays integrated cooling curves: following the accretion shortly after 4,566 Myr (refs 1, 2), rapid heating resulted in different metamorphic peak temperatures, between 920 K and 1,120 K (ref. 5), at different depths. H4 Forest Vale and Ste Marguerite cooled down to the Pb closure temperature at 720 K within a few million years (4,561 and 4,563 Myr ago), whereas types H5 needed 10–16 Myr, and H6 Kernouve and Guarena considerably longer¹⁸. Subsequent cooling until ⁴⁰Ar retention in oligoclase at ~550 K needed additional time, and occurred later for H6 than for H5 and for H4. As ²⁴⁴Pu fission tracks in orthopyroxene are also retained at ~550 K, ²⁴⁴Pu cooling-time intervals until track registration in merrillite at ~390 K can thus be attached to the ⁴⁰Ar–³⁹Ar data: consequently H4 chondrites cooled to 390 K faster and earlier than H5 and H6 chondrites. Note that H6 Guarena, H6 Kernouve and H6 Estacado cooled slowly, but with significant differences, whereas the H5 Allegan and H5 Richardton have rather similar cooling histories. H4 Forest Vale and Ste Marguerite are also very similar, whereas H5 Nadiabondi seems to be intermediate between H5 and H4, as indicated by its Pb–Pb age and its steep ²⁴⁴Pu fission-track cooling rate. Apparently, this H5 and the two H4 chondrites share a rather peculiar cooling history: fast cooling above 720 K and below 550 K seems to be interrupted by a slower cooling episode between 720 K and 550 K. However, this is most probably not significant, taking into account the recently suggested revision of the relative Pb–Pb and K–Ar age scales^{22–25}, resulting from the uncertainty in the K decay constant. A shift of the ⁴⁰Ar–³⁹Ar ages (and also ²⁴⁴Pu ages) by 30 Myr (ref. 25) obviously provides a more concise explanation (Fig. 3b): then Ste Marguerite, Forest Vale and Nadiabondi cooled fast through the high- and low-temperature regimes, instead of having rather exotic ‘fast–slow–fast’ cooling histories. It is important to note that the K–Ar and ²⁴⁴Pu age scales are shifted to the same degree, because the fission-track retention in orthopyroxene is linked to ⁴⁰Ar retention in feldspar. Although our data support the need for a revision of the K–Ar age scale, its exact magnitude^{23–25} remains an issue.

We also present in Fig. 3b the modelled cooling curves at different depths of a chondritic asteroid 100 km in diameter that was heated

Table 1 Summary of thermochronological data

Meteorite	²⁴⁴ Pu fission track density ratio of orthopyroxene (merrillite contacts) and merrillite*	²⁴⁴ Pu cooling time interval† (Myr)	⁴⁰ Ar– ³⁹ Ar age‡ relative to NL25 homblende standard§ (Myr)	Pb–Pb age (Myr)
Retention/closure temperature		550K (Opx), 390K (Mrl)	550 ± 20K (Oligoclase feldspar)	720 ± 50K (Phosphates)
H4				
Ste Marguerite	0.420 ± 0.034	12 ± 11	4,532 ± 16 WR	4,563 ± 1
Forest Vale	0.330 ± 0.033	<8 ¶	4,522 ± 8 WR	4,561 ± 1
H5				
Nadiabondi	0.261 ± 0.017	<–8 #	4,505 ± 10 WR, Px	4,556 ± 3
Richardton	0.610 ± 0.029	56 ± 9	4,495 ± 11 WR	4,551 ± 1
Allegan	0.585 ± 0.034	51 ± 9	4,511 ± 11 WR	4,550 ± 1
Sena	0.670 ± 0.033	66 ± 9		4,556 ± 1
H6				
Kernouve	0.639 ± 0.030	61 ± 8	4,469 ± 6 WR, Fs, Px	4,522 ± 1
Guarena	0.615 ± 0.033	56 ± 9	4,454 ± 6 WR, Fs, Px	4,504 ± 1
Estacado	0.655 ± 0.029	64 ± 8	4,435 ± 5 WR, Fs, Px	

*²⁴⁴Pu fission-track densities in orthopyroxene (Opx) crystal surfaces that had been located adjacent to merrillite (Mrl) phosphate crystals; merrillite crystals were pre-annealed at 290 °C to erase cosmic-ray-induced spallation recoil tracks¹⁹.

† The cooling time interval is obtained after correcting the fission-track densities for irradiation geometry and mineral registration efficiency. This correction factor induces an additional systematic uncertainty of the ²⁴⁴Pu timescale, which need not be taken into account for comparison of relative cooling interval differences (see Methods).

‡ ⁴⁰Ar–³⁹Ar ages are error-weighted means of plateau ages of whole rock (WR), feldspar (Fs) and/or pyroxene (Px) separates for H6 chondrites. Plateaux were also obtained for Nadiabondi WR and Forest Vale WR. For Richardton, Allegan and Ste Marguerite we calculated total ages (see Supplementary Figs S2 and S3). Note that in all chondrites feldspar is the dominant K-bearing and, hence, actually dated phase (see Methods and Supplementary Figs S1–S4). There is a very good agreement of ⁴⁰Ar–³⁹Ar ages obtained²⁰ on four of these H chondrites by using a different age monitor (see Supplementary Table S2).

§ Individual K–Ar ages were calculated by using the Steiger and Jäger²² convention, and are calibrated against the age-standard NL25 homblende²⁰ with a K–Ar age of 2,655 ± 9 Myr (see Supplementary Table S2). Uncertainties do not contain the systematic error due to the NL25-standard age error (a possible ± 12 Myr shift of the ⁴⁰Ar–³⁹Ar age scale) and the K-decay constant uncertainty (an upward shift of ages of the order of 30–45 Myr)^{23–25}.

|| Reference 18.

¶ Upper limit for cooling time interval at 2σ level.

Negative cooling time interval within 2σ uncertainties indicates fast cooling.

by ^{26}Al decay (with $^{26}\text{Al}/^{27}\text{Al} = 4 \times 10^{-6}$) 2.5 Myr after Allende CAI formation ($^{26}\text{Al}/^{27}\text{Al} = 5 \times 10^{-5}$) (ref. 8). We used the analytical model of Miyamoto *et al.*¹⁰ (see Methods). Typical cooling curves provide good approximations to the measured cooling histories, with the H6 Estacado, H6 Guarena and H6 Kernouve being deepest and H4 Forest Vale and H4 Ste Marguerite (and possibly Nadiabondi) lying shallowest. It is apparent that this rather simple model not only provides general features like slower cooling in the centre and faster cooling near the surface, but also reproduces the non-exponential cooling paths of the H5 chondrites. Nevertheless, more refined models (for example, those that take into account effects of the slow development of insulating regolith layers that allow faster cooling in the low-temperature regime between 550 K and 390 K for the H4 chondrites) could probably provide even better fits to the data.

Our new results define the thermal history of the H-chondrite parent body to a much greater precision than previous studies not using rigorously unshocked or undisturbed samples¹⁵ or mineral separates¹⁶. It agrees with the thermal history from I–Xe studies of chondritic mineral separates (ref. 26). It supports an internal heating mechanism, and favours decay energy of short-lived nuclides (for example ^{26}Al) as the planetesimal heat source in the early solar system^{7,9,13}. Obviously, the interior regions cooled undisturbed down to 390 K, indicating that this parent body was

not destroyed by early impacts. Fragmentation and re-assembly processes causing a rubble-pile structure of asteroids as currently observed²⁷ probably occurred much later. The early histories of other ordinary chondrite parent bodies remain to be assessed, but complementary radiometric data on mineral separates of unshocked L and LL chondrites with comparable precision are not yet available^{11,15,18,20,26}. □

Methods

Sample selection

Investigating the earliest parent-body history 4,600 Myr ago requires samples that were unaffected by impact-induced shock or heating during the past 4,000 Myr. Thus we applied three criteria to select our samples: (1) absence of shock features (see Supplementary Table S1); (2) presence of ^{244}Pu fission tracks—short-lived ^{244}Pu produces detectable tracks only >4,000 Myr ago, and subsequent reheating to >390 K is excluded because annealing temperatures (in merrillite) are low; (3) absence of major disturbances of the Pb–Pb system in phosphates. Additional studies of even only moderately shocked H4 chondrites (Ochansk, Menow; Supplementary Fig. S3c) revealed irregularities and inconclusive chronological results that simulate complex parent-body histories.

^{244}Pu fission-track thermochronometry

Short-lived ^{244}Pu ($\tau_{1/2} = 80$ Myr) is concentrated in the phosphates apatite and merrillite. Spontaneous ^{244}Pu fission leaves radiation damage visible by etching as fission tracks. These are also registered by accidentally adjacent silicate minerals²⁸. Upon cooling below a certain temperature, radiation damage is no longer annealed and fission tracks are retained, for example in orthopyroxene below ~550 K and in merrillite below ~390 K (ref. 19). If—appropriately corrected¹⁹—the fission-track densities in both minerals are the same, ‘instantaneous’ fast cooling is indicated, whereas a fission-track density ratio of 2 corresponds to a cooling time interval of 80 Myr at an average rate of 2 K Myr^{-1} . Important major corrections to fission-track dating introduced in recent years are (1) erasure of cosmic-ray-induced spallation recoil tracks in phosphates by crystal tempering at 290 °C (refs 19, 21), and (2) correction for different mineral-specific registration efficiencies. The more effective track registration in merrillite compared with that in orthopyroxene results in an effective correction factor of 1.325 ± 0.074 (average of previously used values^{19,21}) for the orthopyroxene/merrillite fission-track density ratio. To account for the irradiation geometry an additional factor of 2 has to be included. To check for relative cooling histories of meteorites, that is, cooling time interval differences, it is, however, appropriate to compare the uncorrected ratios (Table 1 and Fig. 2b, c). This is because the systematic uncertainties of the registration efficiency factor need not be included, which is the case when calculating absolute ^{244}Pu cooling-time intervals (Table 1 and Fig. 2b, c).

^{40}Ar – ^{39}Ar cooling ages

In ^{40}Ar – ^{39}Ar dating we studied whole rock samples, but also feldspar and pyroxene mineral separates of H6 chondrites, where thermal metamorphism had led to growth of large (>50 μm) grains of secondary feldspar^{4,5}. All 15 samples were analysed with high resolution (up to 42 heating steps), crucial for obtaining the spectral fine structure. The spectra (Table 1, and Supplementary Table S2 and Figs S1–S3) exclude significant secondary ^{40}Ar losses. However, those of the low petrologic-type chondrites are somewhat disturbed by ^{39}Ar recoil as expected for fine-grained mineral assemblages. The fine structures of such age spectra that are disturbed by ^{39}Ar recoil, but which still exhibit intermediate age plateaux, have previously been modelled quantitatively²⁹. It was demonstrated that the plateau segments yield reliable age information whereas the ages from initial and final extractions are to be discarded. As is evident from the K/Ca ratio spectra and the release patterns of K-derived ^{39}Ar and Ca-derived ^{37}Ar (Supplementary Figs S1–S4), the chronological information of whole rock samples is controlled by the main K carrier, oligoclase feldspar. Even in pyroxene mineral separates analysed by us, most K was located in fine-grained feldspar impurities that were not successfully separated (Supplementary Figs S1, S2 and S4). This is consistent with our observation of no significant age difference between whole rock, feldspar and pyroxene separates (Table 1 and Supplementary Figs S1 and S2 and Table S2). Accordingly, the average ^{40}Ar – ^{39}Ar age calculated from these different plateau ages from a single H chondrite can be directly interpreted as the feldspar cooling age. To minimize relative uncertainties, all samples were calibrated against the same NL25 age standard³⁰. Ages were calculated by using the convention of Steiger and Jäger²², but a recalibration of the relative K–Ar and Pb–Pb age scales should be considered^{23–25} (see main text). For irradiation details, see Supplementary Table S2 and Fig. S6.

Parent body heating model

In the calculation of the cooling curves of material in a chondritic parent body that is heated by the decay of ^{26}Al (Fig. 2b), we applied the analytical model of Miyamoto *et al.*¹⁰. As in ref. 10 our parameters are thermal conductivity (1.0 W mK^{-1}), density (3.2 g cm^{-3}), heat generation ($11.67 \times ^{26}\text{Al}/^{27}\text{Al} \text{ W m}^{-3}$) and emissivity. We slightly adapted the radius (100 instead of 85 km), accretion temperature T_0 (300 instead of 200 K), and initial $^{26}\text{Al}/^{27}\text{Al}$ ratio (4×10^{-6} instead of 5×10^{-6}). This $^{26}\text{Al}/^{27}\text{Al}$ ratio is a factor of 12.5 lower than in CAIs and corresponds to H chondrite accretion 2.5 Myr after the formation of Allende CAIs. It is in agreement with the Pb–Pb age difference of CAIs of 4,566 Myr and Ste Marguerite of 4,563 Myr (refs 1, 2, 18).

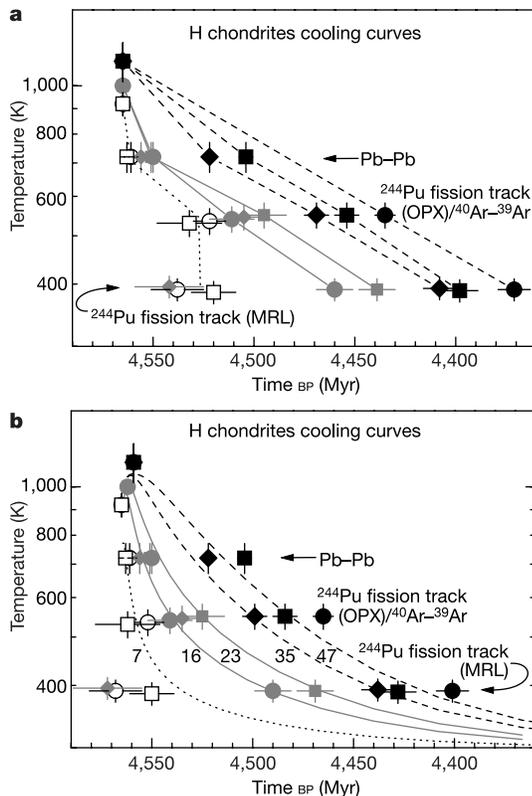


Figure 3 Integrated cooling curves for all H chondrites where complete chronological information is available. The Pb–Pb (at 720 K) and ^{40}Ar – ^{39}Ar (at 550 K) cooling ages and ^{244}Pu fission track retention ages in orthopyroxene (OPX, at 550 K) and merrillite (MRL, at 390 K) are given. Low petrographic types cooled significantly faster than higher ones. **a**, ^{40}Ar – ^{39}Ar ages as calculated after Steiger and Jäger²². Dashed lines: H6 Estacado (filled circles), Guarena (filled square), Kernouve (filled diamond). Solid lines: H5 Richardton (grey square), Allegan (grey circle), Nadiabondi (grey diamond). Dotted lines: H4 Forest Vale (open circle), Ste Marguerite (open square). **b**, Alternative hypothesis resulting from shifting ^{40}Ar – ^{39}Ar and ^{244}Pu ages up by 30 Myr to account for recent suggestions to recalibrate the Pb/Pb and Ar–Ar age scales^{23–25}. The cooling curves are calculated for a chondritic 100-km diameter asteroid that is internally heated by ^{26}Al decay for depths of 47, 35 (dashed), 23, 16 (solid) and 7 km (dotted). Symbols as in **a**.

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Critical thickness for ferroelectricity in perovskite ultrathin films

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The integration of ferroelectric oxide films into microelectronic devices^{1,2}, combined with the size reduction constraints imposed by the semiconductor industry, have revived interest in the old question concerning the possible existence of a critical thickness for ferroelectricity. Current experimental techniques have allowed the detection of ferroelectricity in perovskite films down to a thickness of 40 Å (ten unit cells), ref. 3. Recent atomistic simulations^{4,5} have confirmed the possibility of retaining the ferroelectric ground state at ultralow thicknesses, and suggest the absence of a critical size. Here we report first-principles calculations on a realistic ferroelectric–electrode interface. We show that, contrary to current thought, BaTiO₃ thin films between two metallic SrRuO₃ electrodes in short circuit lose their ferroelectric properties below a critical thickness of about six unit cells (~24 Å). A depolarizing electrostatic field, caused by dipoles at the ferroelectric–metal interfaces, is the reason for the disappearance of the ferroelectric instability. Our results suggest the existence of a lower limit for the thickness of useful ferroelectric layers in electronic devices.

Epitaxial growth of high-quality thin films of ABO₃ perovskite oxides on semiconductors—Si (ref. 6) and Ge (ref. 1)—and metallic⁷ substrates has opened the door to the use of alternative materials in metal-oxide-semiconductor field-effect transistors (MOSFETs)^{1,8} and non-volatile ferroelectric random access memories (FERAMs)^{9,10}. Recently, 30 Gbit cm⁻² data storage densities have been demonstrated for Pb(Zr_{0.2}Ti_{0.8})O₃ films on a metallic oxide electrode². As the size of high-quality perovskite layers of interest for technological applications decreases, the fundamental questions of the thickness dependence of the ferroelectric properties, and of their possible disappearance at a finite critical thickness, become crucial.

It was thought that ferroelectricity was suppressed in small particles and thin films¹¹, but this situation changed after experiments that identified ferroelectric ground states in 40-Å-thick perovskite oxide films³ and in 10-Å-thick crystalline copolymer films¹². In support of these experimental observations, theoretical investigations using a phenomenological approach¹³, first-principles effective hamiltonian calculations⁴ and full first-principles simulations⁵ predicted ferroelectric ground states for various ABO₃ slabs under the condition of vanishing internal electric field. However, in all these approaches, the influence of a real metal–perovskite interface (including the finite screening length of the electrode, the interface chemistry and the strain conditions imposed by the substrate) on both the atomic relaxation and polarization was missing—or was only empirically included through the choice of specific electromechanical boundary conditions. The only more-fundamental study of metal–BaTiO₃ interfaces is due to Rao *et al.*¹⁴, but does not address the question of the ferroelectric instability.

Here we simulate from first principles the behaviour of a typical ferroelectric capacitor structure epitaxially grown on a thick SrTiO₃ substrate, and made of an ultrathin film of BaTiO₃ (a prototypical ferroelectric oxide) between two metallic SrRuO₃ electrodes¹⁵ (Fig. 1). The electrical boundary conditions are fixed by putting the electrodes in short-circuit. Calculations were done within density functional theory and the local density approximation.