

FIG. 3 Spectral analysis (using CORPAC²⁵) of the bSiO₂ record from site 340, using the initial linear (5.1 cm kyr⁻¹) timescale (dotted line) and the SPECMAP-correlation timescale (solid line). Multi-taper methods³² produced essentially identical results. Power units are arbitrary. Inset, spectral data for the SPECMAP-correlation timescale on a logarithmic scale; the horizontal part of the cross represents the bandpass filter and the vertical part represents error bars. Portions of the curve peaks that exceed the 95% confidence interval are indicated by shading.

loess^{9,10} records and is somewhat unexpected, because summer insolation at high northern latitudes (typically 65° N; refs 2–5) is thought to be critical in initiating ice-sheet growth. Also, because the effect of obliquity on insolation increases with latitude, obliquity dominates total high-latitude insolation. Precession dominates low-latitude insolation, as well as high-latitude seasonal extremes^{8,24,30}. The relative weakness of the 41-kyr obliquity peak in the Baikal record suggests that the influence of climate processes driven by low-latitude insolation may be felt at higher latitudes. Also, because northern maritime land masses are thought to be necessary lead factors in the initiation of glaciation during obliquity cycles^{6,24}, our data suggest that northern interiors such as Baikal may be less important than maritime ones in this initiation.

It appears that the palaeoclimate response in relatively high-latitude, continental Asia, as reflected in the bSiO₂ record of Baikal, is dominated by a 100-kyr cycle, in a manner similar to the nonlinear response to orbital forcing exhibited by global ice volume and various ocean parameters. Despite the sensitivity of Baikal's setting to direct insolation forcing and evidence for the influence of precession and obliquity cycles, the many feedbacks and nonlinearities of the global climate system appear to strongly influence the record of such continental interiors, amplifying the 100-kyr cycle there as well as in the oceans and ice sheets. Our results suggest an integrated, unified response of the global climate system to orbital forcing. □

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Hafnium–tungsten chronometry and the timing of terrestrial core formation

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THE accretion of the Earth and Moon within the solar nebula is thought^{1–3} to have taken 50 to 100 million years. But the timing of formation of the Earth's core has been controversial, with some^{4,5} proposing that it took place within the first 15 Myr of Earth's accretion history and others^{6,7} proposing that it occurred after 50 Myr of accretion. Meteorite chronometry based on the ¹⁸²Hf–¹⁸²W system has the potential to resolve this debate, as segregation of a metal core from silicates should induce strong fractionation of hafnium from tungsten. Here we report tungsten isotope compositions for two iron meteorites, two carbonaceous chondrites, and a lunar mare basalt. We see clear ¹⁸²W deficits in both iron meteorites, in agreement with previous results^{4,5}. But the data for chondrites are inconsistent with the hypothesis of early core formation, suggesting that both this event and the formation of the Moon must have occurred at least 62 ± 10 Myr after the iron meteorites formed.

Hafnium and tungsten are both highly refractory elements that are assumed to be present in chondritic relative proportions in the Earth. Hafnium is a lithophile element whereas tungsten

is a moderately siderophile element that should strongly partition into metal phases during metal/silicate segregation, resulting in a large fractionation of Hf/W between stony and iron meteorites or between the silicate mantle and metallic core of a terrestrial planet. Consequently, if core formation took place when there was still ^{182}Hf (half-life, 9 Myr) on Earth, the W remaining in the silicate mantle would develop an excess abundance of ^{182}W relative to that of chondrites^{4,5}. Conversely, if core formation were late, after all ^{182}Hf had decayed, the W isotope composition of the silicate Earth would be identical to that found in chondrites.

The relationship between W and Hf isotope compositions in the present-day bulk Solar System or in chondrites (CHOND) can be expressed as follows:

$$\left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{CHOND}} = \left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{BSSI}} + \left[\left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{BSSI}} \times \left(\frac{^{180}\text{Hf}}{^{184}\text{W}}\right)_{\text{CHOND}} \right] \quad (1)$$

where BSSI is the initial value for the bulk Solar system and $^{180}\text{Hf}/^{184}\text{W}$ (atomic ratio) = $1.18 \times \text{Hf/W}$ (weight ratio). If the small contribution of s-process ^{182}Hf (ref. 8) is disregarded, $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ is primarily a function of the amount of freshly synthesized r-process Hf introduced to the solar nebula before its collapse, and the time that elapsed between production and collapse. Equation (1) defines a linear relationship between $^{182}\text{W}/^{184}\text{W}$ and $^{180}\text{Hf}/^{184}\text{W}$ that may be obtained by measurements on undisturbed minerals of early Solar System materials such as chondrites. The $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ would then correspond to the slope of such an internal isochron. However, useful limits on this parameter can be obtained from bulk meteoritic material, as in this study.

In the simplest model, the $^{182}\text{Hf}/^{180}\text{Hf}$ at the time of core formation (CF) of a planet such as the Earth that may have started with chondritic Hf/W and at some point segregated and maintained two systems, core and bulk silicate Earth (BSE), is given by the differences in W isotope composition and Hf/W ratio between the BSE and chondrites:

$$\left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{CF}} = \left\{ \left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{BSE}} - \left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{CHOND}} \right\} \left\{ \left(\frac{^{180}\text{Hf}}{^{184}\text{W}}\right)_{\text{BSE}} - \left(\frac{^{180}\text{Hf}}{^{184}\text{W}}\right)_{\text{CHOND}} \right\}^{-1} \quad (2)$$

Terrestrial	Lunar	Chondrite	Fe-meteorite
■ NIST-3163 ¹²	■ 14053-234	▲ Allende	● Arispe
■ NIST-3163 (this study)		▲ Murchison	○ Coya Norte
□ AGV-1		◇ Mean	◆ Mean (this study)
			● Toluca ⁵

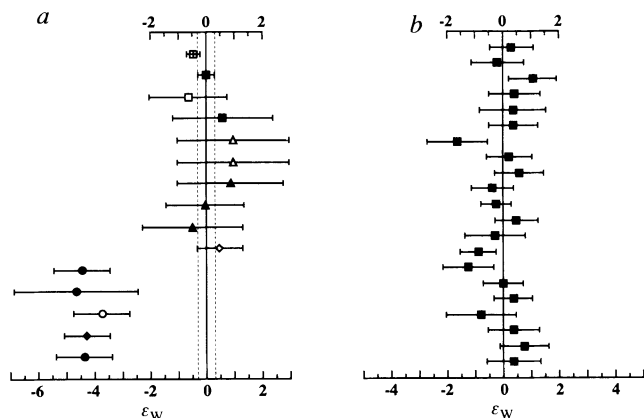


FIG. 1 a, ϵ_W values of terrestrial and lunar samples, chondrites and iron meteorites for this study (Table 1), calculated relative to the mean of 21 independent measurements of NIST-3163 W standard, shown in b. The average value of Toluca⁵ is also included, converted to $^{182}\text{W}/^{184}\text{W}$ assuming $^{183}\text{W}/^{184}\text{W} = 0.467126$ (ref. 12) and, subsequently, to ϵ_W relative to the mean of NIST-3163 of this study.

Obviously the W isotope composition of the core $(^{182}\text{W}/^{184}\text{W})_{\text{CF}}$ cannot be measured directly, but it can be predicted from mass balance if the entire Earth has a chondritic Hf/W ratio. The W isotope composition of the core $(^{182}\text{W}/^{184}\text{W})_{\text{CF}}$ should then balance the W isotope composition of the BSE and produce an average weighted total-Earth W isotope composition that equals $(^{182}\text{W}/^{184}\text{W})_{\text{CHOND}}$.

The Hf isotope composition at the time of core formation $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{CF}}$ can also be expressed as a function of $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$, the decay constant λ , and the amount of time that had elapsed since collapse of the solar nebula ΔT , as follows:

$$\left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{CF}} = \left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{BSSI}} \times e^{-\lambda\Delta T} \quad (3)$$

This yields the time between collapse of the solar nebula and core formation as:

$$\Delta T = -\lambda^{-1} \times \ln \left[\left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{BSSI}} \times \left\{ \left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{BSE}} - \left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{CHOND}} \right\} \left\{ \left(\frac{^{180}\text{Hf}}{^{184}\text{W}}\right)_{\text{BSE}} - \left(\frac{^{180}\text{Hf}}{^{184}\text{W}}\right)_{\text{CHOND}} \right\} \right]^{-1} \quad (4)$$

Because of its very high first ionization potential, negative-ion thermal ionization mass spectrometry (NTIMS) has been the principal analytical technique for W (ref. 9). A recent study using NTIMS reported the first evidence of a deficiency in ^{182}W relative to terrestrial W in the iron meteorite Toluca⁴. An alternative method for determining the isotope composition of elements with high first ionization potential is multiple-collector inductively-coupled plasma mass spectrometry (MC-ICPMS)¹⁰⁻¹³. All the W isotope measurements reported here were performed with this new technique.

The W isotope compositions determined in five independent measurements (full chemistry included) of two carbonaceous chondrites, Allende (CV) and Murchison (CM), agree within analytical uncertainty (Table 1, Fig. 1). This W isotope composition is identical to that of the bulk silicate Earth (BSE) as represented by the W solution standard NIST-3163 and the USGS international rock standard AGV-1. Similarly, the $^{182}\text{W}/^{184}\text{W}$ ratio of an Apollo 14 low-Ti mare basalt, 14053-234, agrees within uncertainty with that of both the BSE and the carbonaceous chondrites (Table 1). In contrast, the two iron meteorites yield low $^{182}\text{W}/^{184}\text{W}$, corresponding to -4.5 ± 1.0 and $-3.7 \pm 1.0 \epsilon_W$ units for Arispe (IA) and Coya Norte (IIA) respectively, expressed as deviations in parts per 10^4 relative to the NIST-3163 W standard (Table 1, Fig. 1). These results confirm, and are in excellent agreement with, the NTIMS data for the Toluca meteorite⁵ ($\epsilon_W = -4.3 \pm 1.0$), suggesting that the observed ^{182}W deficit relative to BSE W is a common feature of iron meteorites. As the modification of W isotopes by neutron capture during space exposure is negligible¹⁴, the observed ^{182}W deficit is most likely the consequence of segregation of metal to form the iron meteorite protolith within the lifespan of ^{182}Hf .

Jacobsen and Harper⁵ argued for a short (<15-Myr) interval of core formation based on the W isotope composition of the iron meteorite Toluca. However, this conclusion was based on the assumption of a low $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ of $\sim 10^{-5}$ (ref. 15), such that the W isotope composition of chondritic material would not change greatly with time. Thus the data for Toluca would provide a close estimate of the W isotope composition of chondrites. Clearly, the W isotope compositions of carbonaceous chondrites and iron meteorites are very different (Fig. 1), and the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ must be high. Its minimum value can be calculated from equation (1) using the measured $^{182}\text{W}/^{184}\text{W}$ of iron meteorites, as this must represent an upper limit for the bulk Solar System initial $(^{182}\text{W}/^{184}\text{W})_{\text{BSSI}}$. The Hf/W ratio of CM type chondrites is 1.33 (ref. 16), corresponding to a $(^{180}\text{Hf}/^{184}\text{W})_{\text{CHOND}}$ of 1.57. Assuming this is precise to at least

TABLE 1 Tungsten isotope data

Sample	$^{182}\text{W}/^{184}\text{W}$	ϵ_{W}
Terrestrial		
NIST-3163*	0.86494 ± 2	-0.46 ± 0.2
NIST-3163†	0.86498 ± 3	0.00 ± 0.3
AGV-1	0.86492 ± 12	-0.64 ± 1.4
Lunar		
14053-234	0.86503 ± 16	0.58 ± 1.8
Chondrite		
Allende-1	0.86506 ± 18	+0.98 ± 2.0
Allende-2	0.86506 ± 18	+0.98 ± 2.0
Murchison-1	0.86505 ± 17	+0.86 ± 1.9
Murchison-2	0.86498 ± 12	-0.05 ± 1.4
Murchison-2	0.86494 ± 16	-0.50 ± 1.8
Mean	0.86502 ± 7	+0.47 ± 0.8
Iron meteorite		
Arispe-1	0.86459 ± 9	-4.45 ± 1.0
Arispe-2	0.86457 ± 19	-4.67 ± 2.2
Coya Norte	0.86466 ± 9	-3.73 ± 1.0
Mean	0.86461 ± 7	-4.27 ± 0.8

All samples processed using chemical techniques to be described elsewhere. Chondrite powders (1–5 g) were made from fresh 25 g pieces provided by the Smithsonian Institution. The iron meteorites were sawed as clean centre cubes from slabs in the University of Michigan meteorite collection, and leached with 6 ml of hot aqua regia three times before total dissolution. All the measurements were performed in static mode and utilized 1 µg to 150 ng of W. All the ratios were normalized to $^{186}\text{W}/^{184}\text{W} = 0.927633$ (ref. 12), and corrected for Os interferences at masses 184 and 186 by monitoring mass 188. The only currently unidentifiable spectral interference is a small baseline effect found in separated natural materials at mass 183. Total process blanks were $\leq 3\%$ of the measured W. An exponential law was used to correct for mass discrimination¹². All the quoted uncertainties are 2σ standard errors, and refer to the least significant digits in the case of $^{182}\text{W}/^{184}\text{W}$. The ϵ_{W} values were calculated relative to the NIST-3163† standard. ϵ_{W} is given by

$$\left\{ \left(\frac{^{182}\text{W}}{^{184}\text{W}} \right)_{\text{meas}} - \left(\frac{^{182}\text{W}}{^{184}\text{W}} \right)_{\text{std}} \right\} / \left(\frac{^{182}\text{W}}{^{184}\text{W}} \right)_{\text{std}} \times 10^4.$$

* From Lee and Halliday¹².

† Mean of 21 measurements conducted during this study.

$\pm 5\%$, from equation (1), the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSE}}$ is therefore $\geq (2.61 \pm 0.13) \times 10^{-4}$.

The Hf/W ratio of BSE is ~ 22 (ref. 17), entirely in keeping with W being moderately siderophile and estimates of $D^{\text{met/sil}}$ during core formation (where D is the distribution coefficient, or ratio of the concentrations, for metal and silicate liquids). The effect of a high Hf/W ratio, like that of the BSE, on W isotope compositions is shown in Fig. 2. If core formation on the Earth and the formation of the iron meteorites were contemporaneous, a residual Hf/W ratio of 22 would generate an easily resolvable $\epsilon_{\text{W}} \approx +90$ relative to carbonaceous chondrites. The later the formation of the core, the more closely the $^{182}\text{W}/^{184}\text{W}$ of the BSE would approach that of carbonaceous chondrites if the Earth accreted with chondritic Hf/W (Fig. 2). The earliest that core formation could have occurred, given all analytical errors and uncertainties in $(^{180}\text{Hf}/^{184}\text{W})_{\text{BSE}}$, is 62 ± 10 Myr after the formation of iron meteorites, or else the W isotope composition of the BSE would not be chondritic (Fig. 2). The data presented here are consistent with the model of Galer and Goldstein⁶, who suggested an accretion and core formation interval of 80 ± 40 Myr for the Earth using U–Th–Pb systematics. A similar result has been obtained by Allègre *et al.* (ref. 18). However, the Pb data are interpreted very differently by others⁵.

The W data present a highly robust constraint that holds true regardless of whether the W inventory of the BSE is affected by a late veneer. Heterogeneous accretion^{19–21} is generally considered to be a multi-stage process with the BSE inventory of W entirely dominated ($>99.9\%$) by late chondritic additions²². But even if this is the case, the effects of early core formation on W would still be resolvable in the BSE, exactly as in Fig. 2.

Qualitatively speaking this is because the greater the proportion of BSE W that comes from late additions, the greater the Hf/W of the mantle must have been before these additions, therefore, the greater the isotopic effect from this stage would be and the harder it would be to overprint the W isotope composition. If the entire Earth is chondritic with respect to Hf/W and is separated into two phases, BSE and core, with higher and lower Hf/W ratios respectively, the W isotope compositions and Hf/W ratios of core, BSE and total Earth (chondrites) must all define an isochron slope that is a function of the $^{182}\text{Hf}/^{180}\text{Hf}$ at the time of core formation, which in turn is a function of the age of the core (equation (2)). Additions of further chondritic material do nothing to alter the slope, that is, the W isotope composition and Hf/W ratio of BSE would be diluted proportionally. The predicted present-day W isotope composition of BSE would be resolvably higher than chondritic until ~ 60 Myr after the formation of iron meteorites, regardless of the fraction of W in BSE that is late, given a BSE Hf/W of 22.

The data presented here also place important constraints on the origin of the Moon. The Hf/W ratio of the lunar mantle is probably similar to that of the BSE given the similarity in W/U ratio²³. Therefore, radiogenic W would be expected for lunar mantle if the Moon formed within ~ 60 Myr of iron meteorites. Not surprisingly, the W isotope composition of the silicate Moon is also chondritic and identical to the Earth (Fig. 1). The Moon may have formed from mixed debris created by a giant impactor that hit the Earth with a glancing blow, after terrestrial core formation^{23–26}. Ringwood²⁶ even proposed that formation of the Moon post-dated the addition of the chondritic veneer to the Earth's mantle on the basis of the presence of enriched magmas preserved as rare glasses, that contrast with mare basalts. Therefore, even without the W isotope data, the age of the Moon has to post-date the iron meteorites by at least 62 ± 10 Myr. This is consistent with the oldest reliable ages for lunar rocks^{3,27}, but is more difficult to reconcile with the recent Sm–Nd age of 4.56 ± 0.07 Gyr (ref. 28), obtained from a clast of a lunar breccia. If this age and uncertainty are correct, the Moon has to have formed 4.50 ± 0.01 Gyr ago.

The W data provide clear support for the long-held assumption that the Earth must have chondritic relative proportions of refractory elements, or else the W isotope composition in BSE would differ from chondritic, regardless of when core formation

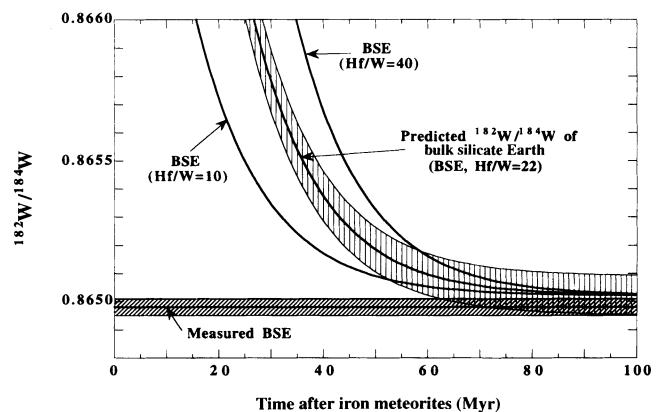


FIG. 2 Predicted $^{182}\text{W}/^{184}\text{W}$ of bulk silicate Earth (BSE) versus the putative time (in Myr after the formation of iron meteorites) of core formation, given that the BSE Hf/W is 22 (ref. 17). The uncertainties are shown by the width of the shaded band. Two separate calculations assuming Hf/W ratios of BSE of 10 and 40 are also shown, representing extremes for the W depletion factors suggested for BSE (ref. 17). The measured BSE $^{182}\text{W}/^{184}\text{W}$ is shown for comparison. The minimum time of core formation, when the uncertainties of the predicted and the measured BSE $^{182}\text{W}/^{184}\text{W}$ start to overlap, is 62 Myr after the formation of meteorites, with an uncertainty of ~ 10 Myr, given that the BSE Hf/W ratio is between 10 and 40.

occurred. Recent studies²⁹ of the ⁵³Mn-⁵³Cr system (half-life, 3.7 Myr) indicate that the Cr isotope composition of the Earth and Moon are similar but distinct from (less radiogenic than) chondritic compositions. Manganese is more volatile than Cr (ref. 22), so the unradiogenic Cr isotope composition of the Earth can be explained if the Earth accreted from volatile depleted material with low Mn/Cr. However, core formation, being late, had no effect on Cr or W isotope compositions. □

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A nesting dinosaur

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A SPECTACULAR fossil specimen that suggests the presence of an avian type of nesting behaviour in oviraptorids, a clade of non-avian maniraptoran theropods, is reported here. The substantial evidence indicating that birds are a type of theropod dinosaur has led to copious discussion concerning the origin and possible presence of advanced avian reproductive behaviour in non-avian dinosaurs. Although the inference of behaviour from fossils is problematic, some remarkable discoveries, such as the incontrovertible evidence of dinosaur nests¹, and more controversial claims made on the basis of dinosaur nesting grounds² and juvenile morphology³, hint at the occurrence of advanced reproductive behaviour in a variety of non-avian dinosaurs. But there is no direct fossil evidence implying advanced parental systems such as those found in modern birds. The closest associations between presumed parents and nests occur in oviraptorid dinosaurs from Late Cretaceous deposits of the Gobi Desert^{4,5}. The specimen described here is the first preserved well enough to determine its precise relationship with the nest. It is a large oviraptorid positioned over a nest of oviraptorid eggs in the same posture taken by many living birds when brooding. This provides the strongest evidence yet for the presence of avian brooding behaviour in non-avian dinosaurs.

Other *Oviraptor* discoveries have been found associated with nests^{4,5}, including the first discovery of *Oviraptor* at the Flaming Cliffs in 1923⁴, and it has been suggested previously that perhaps these individuals were defending or incubating their nests⁵. At the time of the original discovery in 1923, the eggs were thought to belong to *Protoceratops andrewsi*, the most common dinosaur in those deposits. This led to the eponymous suggestion that *Oviraptor* died while scavenging the eggs. The recent discovery of an oviraptorid embryo⁶ within the type of egg associated with

the *Oviraptor philoceratops* holotype suggests instead that this individual's proximity to the nest was related to parental care rather than to predation.

The specimen (IGM 100/979) (Fig. 1) was collected at Ukhaa Tolgod, a Late Cretaceous fossil locality in South Central Mongolia^{7,8}, during the 1993 segment of the Mongolian Academy of Sciences/American Museum of Natural History of Paleontological Project. To preserve spatial relationships definitively the entire specimen was collected in a single large block. No eggs were exposed on the surface, indicating that the entire nest as preserved was collected.

At Ukhaa Tolgod, remains of oviraptorids are the most common theropod elements encountered, rivalling ankylosaurs as the most common dinosaur discovered at this locality⁷. Like most specimens from Ukhaa Tolgod, the specimen shows no evidence of transportation after death, and is preserved in a facies hypothesized to be deposited by large sandstorms⁷. The specimen is of a large individual, although it is not outside the range of Ukhaa Tolgod oviraptorids. The skull, vertebrae, tail and dorsal pelvic bones, and proximal parts of both hindlimbs are missing, yet the majority of the remaining elements including the gastralia and ribs are preserved (Fig. 1).

The maniraptoran affinity of this specimen is shown by the presence of a semilunate carpal that is firmly secured to metacarpals I and II⁹. The clavicles are fused forming a stout furcula, a feature typical of oviraptorids¹⁰. IGM 100/979 has a forward-pointing pubis and metatarsal III is not pinched proximally by II and IV; digit three in the hand is gracile as is typical of many maniraptorans. Differences in manual proportions have been used to differentiate oviraptorid taxa^{10,11}. In *Oviraptor* and *Conchoraptor*, digits II and III are subequal in length and longer than digit I, whereas all three digits are nearly equal in length in *Ingenia*. Furthermore, the digits of *Oviraptor* are longer and thinner than in other oviraptorids and the taxon uniquely displays large, laterally compressed, recurved claws, with extremely large flexor tubercles as expressed in IGM 100/979. The specimen displays several pathologies, including a right ulna that was broken and healed during life.

IGM 100/979 is the best preserved and most complete oviraptorid specimen of any yet found on a nest, and offers the first evidence of the precise position of the skeleton to the nest (Fig. 2). Both hindlimbs are tightly folded (Fig. 1c), with the feet and the lower legs nearly parallel to one another. The feet lay atop and adjacent to eggs on the inner perimeter of the circle defined