Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life

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Sources of organic molecules on the early Earth divide into three categories: delivery by extraterrestrial objects; organic synthesis driven by impact shocks; and organic synthesis by other energy sources (such as ultraviolet light or electrical discharges). Estimates of these sources for plausible end-member oxidation states of the early terrestrial atmosphere suggest that the heavy bombardment before 3.5 Gyr ago either produced or delivered quantities of organics comparable to those produced by other energy sources.

MICROSCOPIC fossils[1] and fossil stromatolites[2] indicate life originated on Earth more than 3.5 Gyr ago. Evidence for biologically mediated carbon isotope fractionation[3] suggests that life may already have existed by 3.8 Gyr ago. The terrestrial origins of life must therefore have coincided with the final stages of the heavy bombardment of the inner Solar System, during which those planetesimals 'left over' from planetary formation were largely swept up or scattered. This bombardment[4,5], known from radioactive dating of cratered surfaces on the Moon, and by comparisons of the lunar, martian and mercurian cratering records, declined in intensity through orders of magnitude, reaching its present comparatively low level by ~3.5 Gyr ago.

The heavy bombardment seems to have had important consequences for the origins of life, some deleterious and some favourable. Sufficiently large and fast impacts can erode planetary atmospheres. This effect, although possibly critical for Mars[6], was probably of little importance for the Earth[7]. The largest impactors could have led to an 'impact frustration' of life's origins[8-10], through the creation of a globe-encircling rock vapour atmosphere and evaporation of the euphotic zone, or even the entire terrestrial ocean[10].

During the heavy bombardment, volatile-rich impactors would have been delivering essential 'biogenic' elements to the terrestrial surface[7,11-13]. Moreover, comets, carbonaceous asteroids, and interplanetary dust particles (IDPs) are rich in organic molecules[14-16], so may have contributed directly to terrestrial prebiotic inventories. Impacts would also have shock-synthesized organics in the atmosphere[17,18]. Here we focus on these last two effects, comparing them quantitatively with the principal non-heavy-bombardment sources of prebiotic organics.

Delivery of intact exogenous organic matter

Exogenous sources deliver organic molecules more or less intact to Earth today. These include[14] those interplanetary dust particles small enough to be gently decelerated by the atmosphere, and meteorites large enough to avoid complete ablation, but small enough to be substantially decelerated during their fall. Some impactors catastrophically fragment during atmospheric passage, as seems to have happened[19,20] to a comet or comet fragment over Tunguska, Siberia, in 1908. Fragmentation of a CI carbonaceous chondrite took place over Revelstoke, Canada, in 1965; photomicrographs of recovered millimetre-sized fragments reveal unheated interiors[21], within which organics should have survived. (An investigation, probably requiring the examination of carbon isotope ratios, of whether exogenous organics are in fact present in the Revelstoke fragments needs to be done.) Finally, the discovery of apparently extraterrestrial amino acids in Cretaceous/Tertiary (K/T) boundary sediments at Stevns Klint, Denmark, has been taken to suggest that a large fraction of cometary organics might in fact survive giant impacts[22], although both xenon measurements at the K/T boundary[14] and hydrodynamic simulations of organic pyrolysis in impacts[15] argue strongly otherwise. Zahnle and Grinspoon[23] have invoked the accretion of cometary dust as an explanation; other explanations may also be possible[24].

Each of these exogenous sources of organics should have been present on early Earth. Here we estimate their quantitative importance, scaling by the lunar impact record. We give our results as an exogenous organic mass flux through time, to allow the influx to be readily determined for whatever epoch a particular model for the origin of life suggests is appropriate. Such an approach involves several uncertainties, about which we are explicit; we also argue, however, that these are no worse than many encountered in typical estimates of endogenous sources of prebiotic organics.

Attempts to estimate the impact environment of early Earth often begin with analytical fits to the lunar cratering record[6-8], intended to minimize the model-dependence of the conclusions. In practice, however, this procedure faces numerous difficulties, which have often been disregarded. The oldest lunar province for which a radiometric date actually exists (the Apollo 16 and 17 uplands) is only 3.85–4.25 Gyr old; the ages of more heavily cratered provinces can at present only be estimated[4]. The entire interpretation of the heavy bombardment as representing exponentially decaying remnants of planetary formation is occasionally questioned by those favouring a lunar cataclysm[25]. We have previously shown[7] that different choices[6,8] for the decay rates fitted to lunar cratering data[4,5] can lead to substantially different conclusions about terrestrial mass influx during the heavy bombardment. More recently, we have argued that the more extreme of these choices can be excluded, as in contradiction with lunar and terrestrial geochemical data on meteoritic input[26]. Here we employ a model lunar bombardment history that we have demonstrated is in good agreement with the geochemical constraints[26]. Both the model and the constraints are summarized in Box 1.

Asteroid and comet impacts. The model developed in Box 1 for terrestrial mass accretion during the heavy bombardment is based on counts for lunar craters larger than 4 km in diameter. By equation (2), these correspond to impactors of masses greater than $\sim 10^{10}$ kg, or radii above ~100 m. What is the fate of organics in such objects incident on Earth? Some might catastrophically fragment ('airburst') while traversing the atmosphere; this case is treated below. We have demonstrated that such objects that do not airburst are insufficiently decelerated ('aerobraked') by a 1-bar terrestrial atmosphere for their organics to survive the heat of impact[15]. But some models suggest that Earth may have had a dense, ~10-bar CO_2 atmosphere some time before 3.8 Gyr ago[29,30]. Under these conditions, comets with radii as large as ~100 m would have been sufficiently aerobraked (after substantial ablation during atmospheric passage) for most remaining organics to have survived impact with the terrestrial ocean[15]. Carbonaceous asteroids of similar size would not have been sufficiently aerobraked. Our earlier work on this topic[15] considered a broad range of possible early terrestrial impact environments, because of uncertainties in lunar cratering data[7]. Since then (see Box 1), we claim to have reduced these uncertainties by appealing to geochemical constraints[26].

Following Delsemme's analysis of comet Halley data[16], we take comets to be ~14% organic carbon by mass. The mass flux of cometary organic carbon surviving impact at time t is given by

$$\dot{m}(t) = \dot{m}(0)[\dot{n}(t)/\dot{n}(0)] = \dot{m}(0)f(t) \quad (8)$$

where $\dot{n}(t)$ is given by equation (7), and, if we use the results of Chyba *et al.*[15] for cometary ablation, deceleration and resulting organic pyrolysis, $\dot{m}(0) = 6.6\times10^2(\psi/0.1)$ kg yr^{-1}. Here ψ is the mass fraction of the ancient impacting flux in the relevant size range (here, radii $\leqslant$ 100 m) that was cometary. We review the data pertaining to the value of ψ elsewhere[13] and find it inconclusive. Certain models[31,32] of outer planet formation imply comet fluxes through the inner Solar System that require the bulk of the heavy bombardment to have been cometary. But disparities between the cratering records of the terrestrial planets (the planets nearest the Sun) and those of some outer planet satellites suggest that comets could not have been the main component of the heavy bombardment population[33]. Admittedly, as long as only the lunar cratering record can be assigned absolute ages, such an objection remains unconfirmed. For now, it is best to treat ψ as a free parameter. Our results, labelled 'comet impacts' in Fig. 1, take $\psi = 0.1$, and scale linearly, so the effect of a different choice for ψ is evident. More recent numerical modelling, extending earlier two-dimensional hydrodynamic impact models[15] to a full three dimensions, suggests[34] the two-dimensional results used here may underestimate organic delivery from cometary impacts by a factor of ~3.

Catastrophic airbursts. Photometric observations of Earth-crossing asteroids imply that $\sim\frac{1}{3}$ of the current asteroid flux at Earth is C-type[35]. Of 17 terrestrial craters for which impactor type may be identified, only two seem to have had a carbonaceous chondritic composition[36]. Similarly, carbonaceous chondrites constitute only ~5-6% of stony meteorite falls[14], although they seem to represent over a third of 10^2-10^6 g Prairie Network fireballs (with another third seemingly having cometary origins)[37]. It therefore appears that carbonaceous chondrites have material strengths so low that they are typically unable to survive atmospheric passage without breakup[38]. Evidence from meteorite falls[20,38] seems consistent with a compressive strength for carbonaceous chondrites of $\sigma_c \approx 10^6$ Pa (10 bars), orders of magnitude below typical rock strengths. In this case, the catastrophic fragmentation of the Revelstoke object[21] may be a typical fate for carbonaceous impactors. Because of the increased surface-area-to-volume ratio of the resulting fragments, such airbursts might then provide an efficient mechanism for exogenous organics to reach Earth[15,24].

We estimate the magnitude of this source as follows. Melosh[39] has calculated the critical radius R_c of a meteoroid, greater than which—even should the object fragment—the fragments will have insufficient time to accelerate away from one another and follow independent trajectories before striking the ground. Only objects smaller than R_c are therefore able to deposit the bulk of their kinetic energy explosively in the atmosphere (that is, to

BOX 1 Impact statistics on the early Earth

Data[4] for the cumulative surface density of lunar craters with diameter $>D$, as a function of surface age t in billions of years (Gyr), are well modelled by an equation of the form[6,8]

$$N(t, D) = \alpha[t + \beta(e^{t/\tau} - 1)](D/4{,}000\text{ m})^{-1.8}\text{ km}^{-2} \quad (1)$$

We take $\tau = 144$ Myr, corresponding to a 100-Myr decay half-life for the impactor population, $\alpha = 3.5\times10^{-5}$, and $\beta = 2.3\times10^{-11}$ (refs 7, 26). Relying on the recent modelling of post-excavation crater collapse by McKinnon *et al.*[27], we have related[26] crater diameter D (in m) observed on the Moon to the mass m (in kg) and collision velocity v (in m s^{-1}) of an impactor by

$$m = 0.54\gamma v^{-1.67}D_c^{0.44}D^{3.36} \quad (2)$$

where $D_c \approx 1.1\times10^4$ m is a transition diameter at which lunar craters change morphology from simple to complex forms[27], and $v = 1.2\times10^4$ m s^{-1} for typical impacts on the Moon. The constant $\gamma = 1.4\times10^3$ kg s$^{-1.67}$ m$^{-2.13}$ depends on target and impactor densities, surface gravity, and impactor incidence angle. Equations (1) and (2) may be combined to give the number of objects of mass $>m$ that have struck the Moon as a function of time t:

$$n(>m, t) = 3.1\times10^8[t + 2.3\times10^{-11}(e^{t/\tau} - 1)]m^{-b}\text{ kg}^b \quad (3)$$

where $b = 0.54$. The total mass, $M(t)$, incident on the Moon after some time t in impactors with masses in the range m_{min} to m_{max} is given by the integral:

$$M(t) = \int_{m_{max}}^{m_{min}} m[\partial n(>m, t)/\partial m]\text{d}m \quad (4)$$

which yields

$$M(t) = 3.7\times10^8[t + 2.3\times10^{-11}(e^{t/\tau} - 1)](m_{max}^{1-b} - m_{min}^{1-b})\text{ kg}^b \quad (5)$$

To scale to the Earth, $M(t)$ must be multiplied by $\xi \approx 24$, the ratio of the terrestrial to the lunar gravitational cross sections at typical asteroid approach velocities[26].

Taking m_{max} to equal the mass of the lunar impactor that excavated the South Pole-Aitken basin ($D \approx 2{,}200$ km), or $\sim1.4\times10^{19}$ kg by equation (2), and m_{min} to be negligible, equation (5) yields a total mass of 1.0×10^{20} kg incident on the Moon subsequent to the solidification of the lunar crust ~4.4 Gyr ago. About half this mass would actually have been retained by the Moon. This result is in good agreement with the geochemical estimates of Sleep *et al.*[10] of the meteoritic component mixed into the lunar crust, which yield $(0.4$–$1.5)\times10^{20}$ kg. Similarly, scaling equation (5) to Earth, and taking proper account of the statistical probability that the largest impactors incident on Earth were more massive than the largest incident on the Moon, gives an estimate of 1.5×10^{22} kg of material accumulated by Earth after 4.4 Gyr ago. This result is in good accord with geochemical estimates of post-core-formation meteoritic input. These estimates, based on chondritic abundances of highly siderophile elements in the terrestrial mantle, lie in the range $(1$–$4)\times10^{22}$ kg (refs 4, 26, 28). Certain proposed fits[8] to other lunar cratering data sets[5] seem to predict siderophile abundances two orders of magnitude in excess of those observed; such fits can probably be excluded as models for the early terrestrial impact environment. On the other hand, the close agreement of equation (5) with both the lunar cratering record and the available lunar and terrestrial geochemical constraints suggests that it provides a reasonable, albeit procrustean, model for post-core formation terrestrial mass accretion during the heavy bombardment.

Equation (5), multiplied by ξ, gives the total mass incident on Earth in impactors within a certain size range, after some time t. A more useful quantity is the mass flux (kg yr^{-1}) at a particular time in the Earth's past. Combined with estimates of the organic mass fraction surviving delivery, this allows a quantitative comparison of these sources with photochemical or other *in situ* production rates of prebiotic organics as a function of time. To this end, we define $\dot{M}(t) \equiv \xi[\partial M(t)/\partial t]$, the terrestrial mass flux from objects within a given mass range (m_{min} to m_{max}) being accreted by Earth at a time t. From equation (5),

$$\dot{M}(t) = 8.9f(t)(m_{max}^{1-b} - m_{min}^{1-b})\text{ kg}^b\text{ yr}^{-1} \quad (6)$$

where $f(t) \equiv (1 + 1.6\times10^{-10}e^{t/\tau})$. Our discussion will also require $\dot{n}(t) \equiv \xi[\partial n(>m, t)/\partial t]$, the number flux of objects within a given mass range being accreted by Earth as a function of time. From equation (3),

$$\dot{n}(t) = 7.4f(t)(m_{max}^{-b} - m_{min}^{-b})\text{ kg}^b\text{ yr}^{-1} \quad (7)$$

airburst). For an incidence angle of 45°, the critical radii for icy and stony meteoroids in a 1-bar terrestrial atmosphere are 407 m and 235 m, respectively.

These results are consistent with the few relevant observations that are available. The Tunguska object is typically estimated[19,20] to have had a mass of several billion (10^9) kilograms, corresponding to a comet ~100 m in radius. It seems to have exploded at an altitude of 6-9 km (ref. 19). The Lappajärvi crater, apparently the result of an impactor with a carbonaceous chondritic composition[36], required an object with a diameter of ~1 km; this impactor evidently did not airburst.

An approximate upper limit to organic delivery from airbursting asteroids and comets may therefore be obtained by taking m_{max} in equation (6) to be that appropriate to 235-m chondrites and 407-m comets. We take 10% of the impact object mass (for objects below ~0.5 km in radius) to be cometary, with the remainder split evenly between carbonaceous and non-carbonaceous objects (which average together to give a 1.3% organic carbon content[14]). Results are readily scaled to other assumptions about impactor compositions. Equation (6) then takes the form of equation (8), with $\dot{m}(0) = 3.6 \times 10^4$ kg yr^{-1}, and is shown in Fig. 1. Clearly this value is an upper limit, as it ignores organic destruction in the airburst event itself (the Tunguska object exploded with an energy of ~10^{16} J, or several megatons of high explosive[20]) or in subsequent ablation of the resulting fragments. Moreover, not all objects with radii $< R_c$ will airburst. If the early terrestrial atmosphere were as thick as ~10 bar, larger objects could airburst[39], and the upper limit derived here would increase by a factor of about 30.

Interplanetary dust particles (IDPs). Anders[14] has estimated the flux of intact organic matter reaching the contemporary Earth in IDPs and meteorites. The bulk of the mass in IDPs is in the ~100-μm radius range, or, for a typical initial density[40] ~1 g cm^{-3}, in particles with masses ~10^{-5} g. The mass scaling in equation (6) leads one to expect most incident mass to lie in the largest particles, but in fact this scaling breaks down for particles with masses $\leq 10^2$ g, probably because of dust production from larger bodies[41]. The global mass flux in particles below 10^2 g is observed[42,43] to increase with decreasing size until it peaks at ~10^{-5} g. This peak reaches a flux ~$10^5 - 10^6$ times higher than would be the case if the IDP mass spectrum did not deviate from power-law scaling.

Anders takes IDPs to be ~10% organic carbon by mass, a mean carbon content determined from 30 IDPs by X-ray analysis[44]. He takes IDPs in the $10^{-12} - 10^{-6}$ g (~0.6-60 μm radius) range to be sufficiently gently decelerated during atmospheric entry to deliver their organics intact; his 60-μm upper limit is in good agreement with results of both theoretical modelling[40] and direct examination of IDPs[45]. His lower limit is based on an estimate of the size below which IDP organics would be destroyed by ultraviolet photolysis; this choice could vary considerably without significant quantitative effects on the final result. It remains unclear whether the more fragile organic species would survive IDP atmospheric passage[24], especially at the high velocities appropriate to cometary-derived particles[40]; there is probably a kind of deceleration-heating natural selection of the thermally most stable species.

Earth is currently accreting[41] ~3.2×10^6 kg yr^{-1} of 10^{-12}–10^{-6} g IDPs, or $\dot{m}(0) \approx 3.2 \times 10^5$ kg yr^{-1} of intact organics[14]. It is unclear how we should scale this back in time through the heavy bombardment: would the mass influx peak at ~10^{-5} g have persisted? There are some suggestive, although less than compelling, data relevant to this question.

The current terrestrial mass influx from IDPs found by Hughes[42] from meteor observations agrees well with accretion rates inferred from terrestrial and lunar data. As Table 1 shows, these data rely on a number of different sampling methods, and show a remarkably constant net IDP mass flux over the past ~3.6 Gyr, suggesting that the current IDP mass flux is at least not a recent anomaly. Most of these data, however, take the form of an integral over the IDP size distribution, so cannot prove that the shape of the flux curve has remained unchanged with time. In any case, they do not extend further back than the end of the heavy bombardment.

Most IDPs currently collected in the stratosphere belong to one of three main classes; on the basis of particle heating and compositional data, these have been tentatively identified as corresponding to origins in main-belt asteroids, comets with perihelia outside 1.2 AU, and Earth-crossing asteroids or comets[46]. The first two sources seem to be the most common. Main-belt asteroids seem unlikely to be a source representative of 'typical' heavy bombardment sources for IDPs, but Earth-crossing objects and comets with perihelia beyond 1.2 AU might well be.

Clearly we cannot say with confidence how to scale the IDP flux back beyond 3.6 Gyr ago. If IDPs are the product of cometary evaporation or of asteroid-asteroid collisions, one might expect their number to scale linearly, or as the square, respectively, of the number of such objects in the inner Solar System. Loss mechanisms, however, must also be considered. Whipple[47] has argued that, for dust whose loss rate is collisionally dominated, terrestrial accretion will scale as the square root of the cometary flux. But those IDPs actually able to contribute organics intact to Earth ($m \leq 10^{-6}$ g) have lifetimes dominated by Poynting-Robertson drag, not by collisions[43]. The relative importance of these two loss mechanisms could have changed in an early Solar System in which the IDP flux was greater. Production of $\leq 10^{-6}$ g particles (whose collisional production at present greatly exceeds their collisional destruction) would, however, also have increased as the square of the number of larger colliding particles. Relative production and destruction rates would have to be simultaneously modelled. To our knowledge, no such model currently exists.

Here we scale the IDP flux linearly with the lunar impact record, using equation (8) with $\dot{m}(0) \approx 3.2 \times 10^5$ kg yr^{-1} of organic carbon. A reasonable lower limit for the IDP flux on

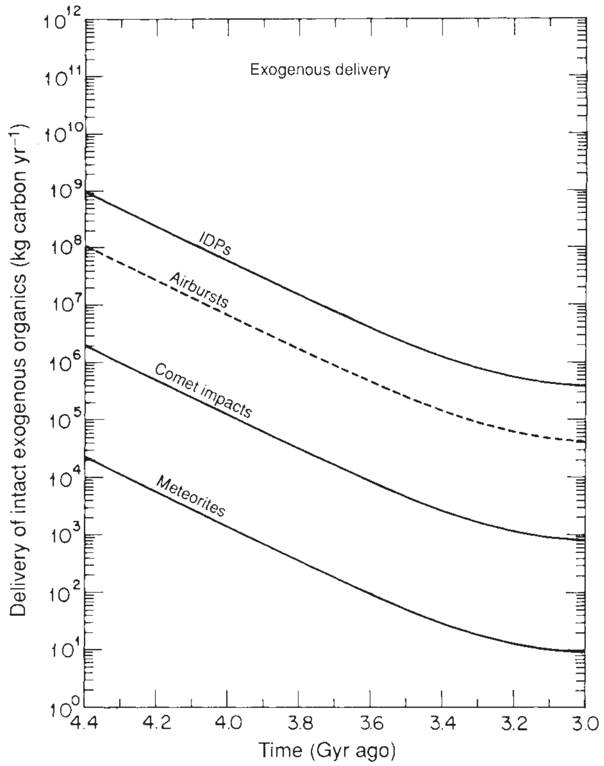

FIG. 1 Exogenous organic carbon delivered to the Earth as a function of time. Labels correspond to the appropriate sections of the text, where uncertainties are discussed. The dashed line indicates an upper bound.

Earth during the heavy bombardment is the current value. At 4 Gyr ago, this leads to an uncertainty of a factor of $\sim 10^2$.

Meteorites. Anders[14] has estimated contemporary terrestrial accretion of intact organic matter from meteorites, finding 7.6 kg carbon yr^{-1}. Taking this value as $\dot{m}(0)$ in equation (8) gives the meteoritic organic carbon input through time, as shown in Fig. 1. Despite uncertainties, this source is clearly negligible compared with IDPs.

Accretion of interstellar dust. An additional source of exogenous organics on early Earth, independent of the heavy bombardment, would have been the terrestrial accretion of dust as the Solar System passed through interstellar clouds. Greenberg[48] has estimated that during its first 7×10^8 years, Earth should have passed through ~4-5 such clouds, accreting organic molecules during each $\sim 6\times10^5$ yr passage at a rate 10^6–10^7 kg yr^{-1}. Even during cloud passage, this source would have been one to two orders of magnitude smaller than that due to IDPs.

Shock synthesis of organic molecules

Gilvarry and Hochstim suggested that shock waves from meteoroids traversing the terrestrial atmosphere may have synthesized organics on early Earth[49]. Bar-Nun *et al.* demonstrated that shock heating of reducing gas mixtures in the laboratory yielded amino acids in high yield[17], although more recent results[50] suggest that the yields first reported[17] for amino acid synthesis in $CH_4/C_2H_6/NH_3/H_2O$ atmospheres were overestimated by a factor of ~30. Nevertheless, atmospheric shock synthesis may have been an important source of terrestrial organics[17,18]. Estimates of both the early terrestrial impact environment and the coupling efficiency of an impactor's energy with the atmosphere may now be updated.

The mass of organics shock-synthesized in the atmosphere by an impactor is proportional to η, the organic synthesis efficiency (kilograms organic carbon produced per joule of shock energy): η is strongly dependent on atmospheric composition. Earlier models for a primordial reducing terrestrial atmosphere rich in CH_4 and NH_3 are now less favoured than that of a neutral atmosphere rich in CO_2 and N_2. (Geochemical and photochemical arguments for this conclusion have been summarized in, for example, refs 15 and 29.) Nevertheless, both because this recent preference is not beyond doubt, and because many atmospheric compositions intermediate between the two extremes have been considered, we will treat two oxidation state end-members of a continuum of possible early-Earth atmospheres, one rich in CH_4, the other rich in CO_2.

A thermochemical model of shock synthesis in reducing $CH_4/N_2/H_2O$ atmospheres[51] gives an HCN production efficiency $\sim 10^{17.5}$ molecules J^{-1}, in excellent agreement with laboratory results[50,52] of $\sim 2\times10^{17}$ molecules J^{-1}. These experiments also show simultaneous formation of simple hydrocarbons, such as C_2H_2 and C_2H_4, as well as carbon soot[52]. Although these results are temperature-dependent, typical organic C yields, ignoring soot, are ~3 times that of HCN alone[52].

Because of the strength of the N_2 bond, we might expect efficiencies to increase in atmospheres where nitrogen is present as NH_3, rather than N_2. In fact, this effect is unimportant at the high shock temperatures appropriate here. Both high-power laser simulation, and theoretical high-temperature-equilibrium modelling, of shocks in NH_3/CH_4 atmospheres give HCN production yields[53] of $\sim 3\times10^{17}$ molecules J^{-1}. Hydrocarbons at least up to pentane (C_5H_{12}) are also produced. Using the experimental yields reported for all C-containing organic species gives a total efficiency for organic C production $\eta \approx 1.2\times10^{-8}$ kg J^{-1} for a reducing atmosphere[53], a result virtually identical with that found for N_2/CH_4 atmospheres[50-52]. Efficiencies for HCN production in $CO_2/N_2/H_2O$ atmospheres, are $\sim 10^{7.5}$ times smaller[51]. In this case, formaldehyde (H_2CO) production is comparable[18] to that of HCN, giving $\eta \approx 2.5\times10^{-16}$ kg J^{-1} for CO_2 atmospheres.

Shocks from meteors. Roughly 1.6×10^7 kg yr^{-1} strikes the Earth's atmosphere in meteors of mass 10^{-14}–10^2 g (refs 14, 41). These objects lose 100% of their kinetic energy to the atmosphere. Assuming an average velocity of 15 km s^{-1}, about midway between those typical for asteroidal and cometary IDPs[40], meteors deposit 1.8×10^{15} J yr^{-1} into the present atmosphere. Some fraction, e_c, of this energy is converted into atmospheric shock waves. Pollack *et al.*[54,55] have selected a value $e_c \approx 0.3$ for the efficiency of converting impactor kinetic energy into atmospheric shock heating, based on analyses of meteorite ablation in the contemporary atmosphere[56]. With this value, total organic production in the atmosphere by meteors (Fig. 2) is given by $\dot{m}(t) = \eta(6\times10^{14}\ \mathrm{J\ yr^{-1}})f(t)$. Again, this result assumes that scaling with the lunar impact record is appropriate.

Shocks from airbursts. Objects as large as ~200–400 m in radius may airburst (see above), thereby coupling their entire kinetic energy to the atmosphere[57]. Equation (6) can be used to put an upper limit on the importance of this effect. If we assume that all objects with radii ≤ 300 m will airburst, then Equation (6), for this choice of m_{max} and multiplied by $v^2/2$ (we take $v =$ 15 km s^{-1}, the median terrestrial collision velocity of Earth-crossing asteroids[26]), gives $\dot{m}(t) = \eta(1.5\times10^{14}\ \mathrm{J\ yr^{-1}})f(t)$. This upper limit is shown in Fig. 2.

Shocks from post-impact vapour plumes. For large impactors, the total energy imparted to the atmosphere by the rapidly expanding post-impact plume is much greater than that lost by the impactor during atmospheric passage[58,59]. Moreover, for a large impact, much of the atmosphere shocked by the incoming object will be shocked again by ejecta, largely pyrolysing products just synthesized during atmospheric passage[60]. Meteors (see above) deliver about ten times as much net shock energy to the atmosphere than does the atmospheric passage of all impactors

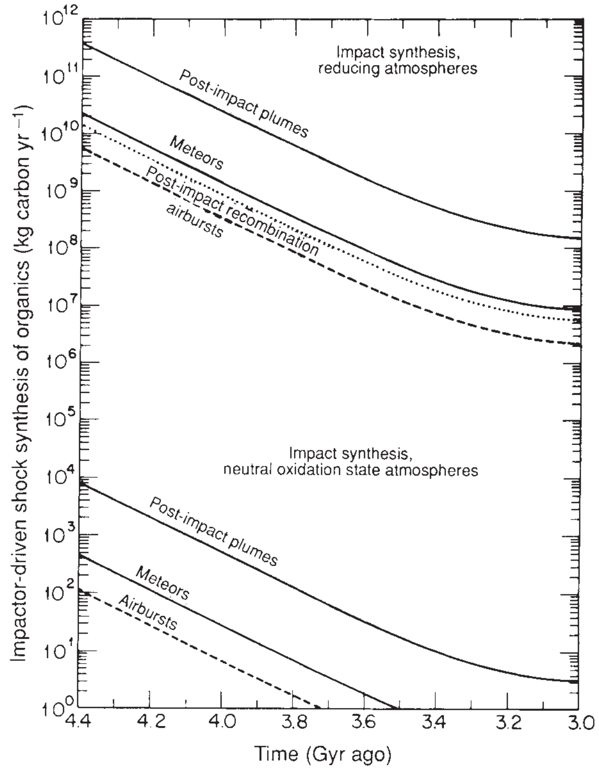

FIG. 2 Impactor-driven shock synthesis of organics in the terrestrial atmosphere as a function of time. Labels correspond to the appropriate sections of the text, where uncertainties are discussed. The upper curves are for CH_4 + (N_2 or NH_3) + H_2O reducing atmospheres, and the lower curves are for CO_2 + N_2 + H_2O neutral oxidation state atmospheres. Dashed lines indicate upper bounds, and the dotted line denotes an estimate that is especially poorly understood, although perhaps largely independent of the oxidation state of the atmosphere.

TABLE 1 Estimates of terrestrial meteoric mass accretion

Sampling method	Effective sampling time	Mass influx (10^7 kg yr^{-1})
Atmospheric[86]	~1 yr	0.6–1.1
Satellite, radio, and visual observations[14,42,43]	past few decades	0.3–8.0*
Pleistocene abyssal clays[87]	past ~10^6 yr	3–9†‡
Cretaceous and Tertiary abyssal clays[41]	33–67 Myr ago	1–5‡
Micrometeorite component in lunar soils[48,49]	past ~3.6 Gyr	1.8–2.8§

* Hughes' preferred value[42] is 1.6×10^7 kg yr^{-1}, with an uncertainty (adopted here) of 'at least half an order of magnitude'.

† As corrected by Kyte and Wasson[41].

‡ After subtracting contribution from larger objects, following Kyte and Wasson[41].

§ Scaled by a factor of 24 from the Moon to the larger gravitational cross section of Earth[26].

with masses $>10^2$ g combined[61]. Therefore we neglect atmospheric passage of large impactors, and concentrate on shock processing due to post-impact (plume) effects.

The simplest treatment of this problem would be first to multiply Equation (6) by $v^2/2$, to calculate the net kinetic energy flux at the terrestrial surface through time. Multiplying this result by η, and by ε, the fraction of an impactor's kinetic energy at surface impact returned to the atmosphere as shock energy, would then give an atmospheric organic production rate. We find $\dot{m}(t)=\eta\varepsilon(6\times10^{17}\,\mathrm{J\,yr^{-1}})f(t)$. Typical published values[59] for ε are ~1/8.

This approach, however, ignores several important effects. Most important, the plumes arising from the largest impacts are poorly matched to the atmosphere; they rise far above the atmosphere and encounter only a small fraction of it[60]. The result is that the shock processing yield per unit of impact energy decreases as the energy of the impact increases. (Failing to take such effects into account leads, following the procedure in the preceding paragraph, to the absurd conclusion that the largest objects (South Pole–Aitken size) striking the Earth would have shock-processed ~50% of an early reducing atmosphere.) Zahnle[60] has modelled these effects in detail for the case of impact production of nitric oxide in the present atmosphere. For an impact energy of 2×10^{25} J, he finds a NO yield ~1/40 that calculated by Prinn and Fegley[59] with the assumption of a constant NO production yield (independent of impact energy). Kasting[62] has integrated Zahnle's results over an impactor mass (hence, kinetic energy) distribution extending from 10^{13} to 10^{27} J, and finds an average NO production yield of 3.3×10^{14} molecule per joule of impact energy. (Kasting's choice of upper limit for impact energy is nearly identical to the one that we take for the South Pole–Aitken impactor; moreover, production efficiency depends only very weakly on the exact choice of exponent for the impactor mass distribution. We may therefore adopt his integration, an approximate treatment in any case, for our purposes here.) Prinn and Fegley[59] use a constant production yield of 2×10^{16} molecule per joule of energy imparted to the atmosphere. (Taking only 1/8 of an impactor's kinetic energy to be so imparted, their production yield is really 2.5×10^{15} molecule per joule of impact energy.) In laboratory shock-tube experiments, η measures production per joule imparted to the atmosphere, so Kasting's result implies that η for shock production of organics should analogously be scaled down by a factor $(3.3\times10^{14})/(2\times10^{16})\approx1/60$ for production by impact plumes. We therefore have $\dot{m}(t)=\eta(1/60)(6\times10^{17}\,\mathrm{J\,yr^{-1}})f(t)$, as shown in Fig. 2.

The resulting timescale at 4.4 Gyr ago for complete shock processing of a 1-bar CH_4 atmosphere is ~10^8 yr. A 1-bar CH_4 atmosphere on early Earth could therefore only have been sustained if terrestrial volcanism or exogenous sources resupplied CH_4 to the atmosphere at a rate ~$2\times10^7 f(t)$ kg yr^{-1}, or 5×10^{10} kg yr^{-1} 4.4 Gyr ago. Terrestrial volcanoes are estimated[63] to release as much as ~4×10^{10} kg yr^{-1} of carbon into the atmosphere, today mostly in the form of CO_2. If carbon were released on a reducing primitive Earth as CH_4, early terrestrial volcanism would need to have been no more intense than today to maintain an early reducing atmosphere against impactor shock-processing.

Finally, we note that the effects of erosion of the atmosphere because of especially energetic impacts are unlikely to have substantially altered the results found here. Only ~10% of asteroid, and ~50% of comet, collisions with the Earth occur at velocities high enough to cause erosion[26], effects small compared with other uncertainties in the problem (unless comets made up the bulk of heavy bombardment impactors).

Post-impact recombination. Several authors have suggested that organic molecules may have formed on early Earth by recombination from reducing mixtures resulting from the shock vaporization of bolides on impact[64-66]. Others have suggested organic molecules might be similarly produced by impact shocks of terrestrial rocks[64,67]. McKay *et al.* have attempted to simulate the former process using a thermochemical model[65]. Their preliminary results show evidence for post-impact organic shock synthesis. But these simulations assumed as initial conditions a reducing mixture equivalent to the elemental composition of comets. In an actual impact, as much target material (oxygen-rich surface rocks) as impactor would be incorporated into the expanding and cooling vapour plume[6], and background atmosphere, possibly CO_2-rich, might also be entrained. The applicability of results for an initially reducing vapour mixture ($[O]<[H_2]$) is therefore unclear. Kasting[62] argues that organic carbon in the hot rock vapour plume resulting from an impact would have been nearly entirely converted to CO.

At the same time, there are some relevant experimental data. Barak and Bar-Nun have demonstrated amino acid shock synthesis even when initial gas mixtures contain large quantities of H_2O and air[68]. Mukhin *et al.* have stimulated shock vaporization and organic recombination using laser-pulse heating of a variety of terrestrial rocks and meteorite samples, and report a wide range of products of varying oxidation states[64]. Unfortunately, their experiments vaporized only a fraction of the target, so organics may have been released from melted and heated target material, as well as synthesized in post-vaporization recombination. Experiments in which the entire target is vaporized would be informative.

In the Mukhin *et al.* experiment, most carbon was incorporated into CO and CO_2, but typically several per cent went into hydrocarbons, and smaller amounts into HCN and aldehydes. The resulting ratio of $(CO+CO_2)$ to hydrocarbons was roughly constant, even as the initial wt% carbon of the sample varied over more than an order of magnitude; this seems to be consistent with post-shock recombination, rather than escape of unshocked organics. Hydrocarbon production (like that of CO and CO_2) scaled with the carbon content of the sample. We will consider the result of directly scaling these experiments up to impacts of comets and asteroids with the early Earth. First, we note that organic production from surface rocks is unimportant (~10%) compared with that for the carbon-rich impactors, so we henceforth ignore the former. Taking 10% of the impactor mass to be cometary (~17% C), of which 50% is blown out into space[26], and the remainder asteroidal (~1.3% C), and taking the Mukhin *et al.* result that ~4% of impactor carbon is incorporated into organics, we find post-impact recombination produced organic carbon at a rate $\dot{m}(t)=(4.6\times10^6\,\mathrm{kg\,yr^{-1}})f(t)$ on the early Earth. To the extent that recombination occurs without significant entrainment of atmosphere, this result is independent of terrestrial atmosphere oxidation state. We emphasize the great uncertainties in the preceding calculation by displaying post-impact recombination results as a dotted line in Fig. 2.

TABLE 2 Inventory of main sources of prebiotic organics on Earth 4 Gyr ago

Source	Energy dissipation ($J\,yr^{-1}$)	Production efficiency, reducing atmosphere ($kg\,J^{-1}$)	Production efficiency, neutral* atmosphere ($kg\,J^{-1}$)	Organic production, reducing atmosphere ($kg\,yr^{-1}$)	Organic production, neutral* atmosphere ($kg\,yr^{-1}$)
Lightning	1(18)†	3(−9)	3(−11)	3(9)	3(7)
Coronal discharge	5(17)	3(−10)	3(−12)	2(8)	2(6)
Ultraviolet light ($\lambda < 2{,}700$ Å)‡	1(22)	2(−11)	—	2(11)	—
Ultraviolet light ($\lambda < 2{,}300$ Å)§	5(21)	—	5(−14)	—	3(8)
Ultraviolet light ($\lambda < 2{,}000$ Å)‖	6(20)	5(−12)	—	3(9)	—
Atmospheric shocks (meteors)	1(17)	1(−8)	3(−16)	1(9)	3(1)
Atmospheric shocks (post-impact plumes)	1(20)	2(−10)¶	4(−18)	2(10)	4(2)
IDPs	—	—	—	6(7)	6(7)
Totals	—	—	—	2(11)	4(8)

* $[H_2]/[CO_2] \approx 0.1$.
† 1(18) should be read 1×10^{18}.
‡ Appropriate to absorption by H_2S (ref. 79).
§ Appropriate to absorption by CO_2 (ref. 74).
‖ Appropriate to absorption by H_2O in H_2O/CH_4 atmospheres (ref. 78).
¶ Following Kasting[62], averaged over Zahnle's[60] results for impactor energies from 10^{13} J to 10^{27} J.

Endogenous sources of prebiotic organics

At the time of the origins of life ~4 Gyr ago, IDPs may have been delivering $\sim 10^8\,kg\,yr^{-1}$ of organic carbon, regardless of the oxidation state of the terrestrial atmosphere. In the case of an early reducing atmosphere, shocks by post-impact plumes would have been producing organic carbon at $\sim 10^{10}\,kg\,yr^{-1}$. How important would these heavy bombardment sources have been? We can put such rates into context by comparing them to the main endogenous sources of organics on the early Earth. Our list of possible terrestrial sources is not meant to be exhaustive. We do, however, explicitly cite those endogenous sources that have traditionally been considered to be the most important (Table 2). In the case of sources producing organics in the terrestrial atmosphere, Table 2 lists estimates of energy dissipation ($J\,yr^{-1}$), and experimentally derived values of production efficiency of organics ($kg\,C\,J^{-1}$) for reducing and neutral atmospheres. Organic production rates ($kg\,yr^{-1}$) are then derived.

As our standard 'neutral' or intermediate oxidation state atmosphere, we take one in which $[H_2]/[CO_2] \approx 0.1$. This choice is by no means the least reducing plausible neutral atmosphere. Kasting has recently considered an atmospheric H_2 mixture ratio of $\sim 10^{-3}$, at the upper end of the range used in many photochemical models for the early Earth, and based on H_2 outgassing rate near the upper limit of the flux likely to have been produced by early volcanoes or by photostimulated reduction of ferrous iron in the surface ocean[62]. (On the other hand, large impacts may have enhanced the atmospheric CO/CO_2 ratio[62].) We list $[H_2]/[CO_2] \approx 0.1$ in Table 1, as it is that neutral atmosphere in which organic delivery by IDPs just begins to match endogenous production. It has been experimentally demonstrated[69,70] that organic production rates drop precipitously by orders of magnitude as the ratio $[H_2]/[CO_2]$ falls below ~1, so that lower $[H_2]/[CO_2]$ ratios will strongly favour IDPs as the dominant early source of organics.

In a review[71] of contemporary data for terrestrial lightning and coronal energy dissipation, we recommended values of $1 \times 10^{18}\,J\,yr^{-1}$ and $5 \times 10^{17}\,J\,yr^{-1}$, respectively. (These values are factors of about 20 and 120 times smaller than those originally suggested by Miller and Urey[72] in their compilation of sources of organics on the prebiotic Earth. The greatest uncertainty in these estimates, which is difficult to quantify, may be the extrapolation from contemporary rates of electrical energy discharge back to the primitive Earth.) We reviewed experimental work on organic production efficiencies for these sources, finding coronal discharge efficiencies to be about an order of magnitude less than those for lightning[71]. Schlesinger and Miller have found[70] that organic yields drop by $\sim 10^2$ for H_2CO, HCN, and amino acids[69] as $[H_2]/[CO_2]$ drops from several (for which values organic production is roughly equal to that in CH_4 atmospheres) to ~0.1. We have therefore scaled production efficiencies for the latter atmosphere in Table 2 down by 10^2 relative to the reducing case.

Apart from electrical energy sources, a principal source of energy for organic production on the early Earth was ultraviolet light from the Sun. In the past decade it has been recognized, from observations of young solar analogue stars, that the early ultraviolet luminosity of the Sun would have been greater than is the case today (despite lower net solar luminosity)[73,74]. In Fig. 3, we use the results of Zahnle and Walker[73] for the evolution of the solar spectrum in 50-Å wavelength intervals (their Fig. 10) to derive the evolution of solar ultraviolet energy at the Earth as a function of time. Their model includes the evolution of important solar spectral lines; we follow it from a 10^8-yr-old Sun (4.5 Gyr ago) until the present. Our values for the current (4.6-Gyr-old) solar ultraviolet fluxes are drawn from Heroux

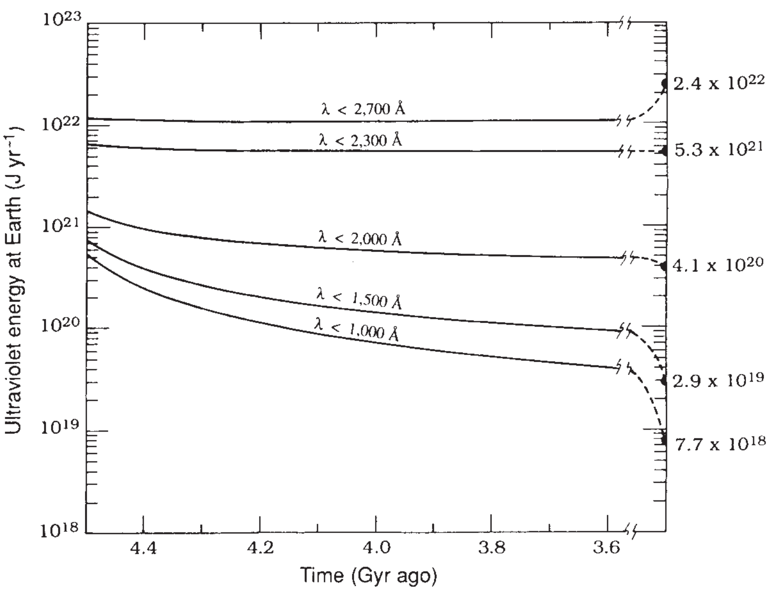

FIG. 3 Evolution of solar ultraviolet luminosity through time, beginning with a $\sim 10^8$-Myr-old Sun at 4.5 Gyr ago, and extending to the present. Dashed lines beyond 3.6 Gyr ago indicate qualitative evolution to current values (labelled numerically).

and Hinteregger[75] for wavelengths below 2,000 Å, and from Arvesen *et al.*[76] from 2,000 Å to 2,700 Å.

Figure 3 shows the evolution of solar energy at the Earth for wavelengths below some selected value. The values shown are chosen as upper limits to the photodissociation continuum of gases that may have been of importance in the early atmosphere. For example, CH_4 is transparent at wavelengths above ~1,500 Å (ref. 77), H_2O above ~2,000 Å (ref. 78), CO_2 above ~2,300 Å (ref. 74), and H_2S above ~2,700 Å (ref. 79). Table 2 lists the net energy available on Earth below the latter three wavelengths at 4 Gyr ago (taking into account cosine incidence and diurnal effects).

In Table 2, the production efficiency for reducing (CH_4/H_2O) atmospheres (at wavelength $\lambda < 2{,}000$ Å) is taken from experimental work by Ferris and Chen[78], and that for atmospheres containing a long-wavelength ultraviolet photon acceptor generating superthermal hydrogen atoms, such as H_2S (or H_2CO), is taken from Sagan and Khare[79] and Hong *et al*[80] (the latter authors demonstrate amino acid production using only CH_4 as a carbon source). These authors cite quantum yields for amino acids only; here we assume total organic carbon produced is ~10 times that incorporated into amino acids, a typical ratio[69,70]. We assume that production efficiencies by ultraviolet acting on neutral atmospheres are ~100 times lower than those appropriate for CH_4 atmospheres, again following ref. 70. (This scaling agrees with photochemical modelling results[81] for ultraviolet production of H_2CO in atmospheres where $[H_2]/[CO_2]$ varies from ~3 to ~0.3.) For all these results it was assumed that production in a given candidate atmosphere was limited by the flux of ultraviolet light, not by the abundance of reactants—an assumption which may or may not have held for a given early Earth atmosphere.

An inventory of organics on early Earth

Our results for exogenous delivery, impact-shock synthesis and endogenous production of organic molecules 4 Gyr ago are summarized in Table 2. As indicated by Miller and Urey[72], more energy is potentially available for organic synthesis from long-wavelength ultraviolet radiation than from any other source; and as indicated by Bar-Nun *et al.*[17], shock synthesis has the highest specific efficiency. The total productivities listed in Table 2 show $\sim 10^{11}$ kg yr^{-1} for reducing atmospheres 4 Gyr ago, and $\sim 10^{8}$ kg yr^{-1} for mainly neutral CO_2 atmospheres with 10% H_2. With lower $[H_2]$, the endogenous productivities will be considerably less. Other atmospheres may have special mechanisms: for example, $[CH_4] \approx 10^{-4}$ in an N_2 atmosphere will give[82] $\sim 10^{10}$ kg yr^{-1} of HCN through short-ultraviolet photolysis. For both oxidation state end-member models, the heavy bombardment either generated or delivered quantities of organics roughly comparable to those from endogenous sources.

If all organic products were fully soluble in oceans of contemporary extent and depth, and had a mean lifetime of $\sim 10^7$ yr against thermal degradation in mid-ocean vents or subducted plates, the steady-state organic abundance in the oceans 4 Gyr ago would have been $\sim 10^{-3}$ g per g for a reducing atmosphere and 10^{-6} g per g for our intermediate oxidation state atmosphere. Although freeze–thaw and other concentration mechanisms doubtless existed, reducing atmospheres seem to be more favourable for the origin of life by three orders of magnitude or more; the entire ocean would then have been, almost literally, a 'dilute soup' of organic matter.

Qualitative as well as quantitative differences are likely. For example, IDPs are radiation-hardened from their stay in interplanetary space and may be rich in amorphous carbon and polycyclic aromatic hydrocarbons, which are less interesting for the origin of life than the amino acids and nucleotide bases produced by endogenous and impact processes. But a pathway from such hydrocarbons to amino acids has been proposed[83] (and disputed[84]), and exogenous organics may be preferentially rich in amphiphilic vesicles, conceivably relevant to the origin of the cell[85].

To summarize, which sources of prebiotic organics were quantitatively dominant depends strongly on the composition of the early terrestrial atmosphere. In the event of an early strongly reducing atmosphere, production by atmospheric shocks seems to have dominated that due to electrical discharges. Organic synthesis by ultraviolet light may, in turn, have dominated shock production, but only if a long-wavelength absorber such as H_2S were supplied to the atmosphere at a rate sufficient for synthesis to have been limited by ultraviolet flux, rather than by reactant abundance. In the apparently more likely case of an early terrestrial atmosphere of intermediate oxidation state, atmospheric shocks were probably of little importance for direct organic production. For $[H_2]/[CO_2]$ ratios of ~0.1, net organic production was some three orders of magnitude lower than for reducing atmospheres, with delivery of intact exogenous organics in IDPs and ultraviolet production being the most important sources. At still lower $[H_2]/[CO_2]$ ratios, IDPs may have been the dominant source of prebiotic organics on the early Earth. Endogenous, exogenous and impact-shock sources of organics could each have made a significant contribution to the origins of life. □

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ARTICLES

Experimental constraints on strong-field relativistic gravity

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Experiments in our Solar System can test relativistic gravity only in the weak-field limit, but systems containing pulsars necessarily involve the effects of strong-field gravity. Timing observations of three binary pulsars yield tight constraints on the nature of gravity in the strong-field regime, allowing the measurement of velocity-dependent and nonlinear phenomena separately from the effects of gravitational radiation. General relativity passes these new experimental tests with complete success.

ALL tests of general relativity within the Solar System[1,2], including perihelion advances of planetary orbits, the bending and delay of light rays passing near the Sun, and limits on the violation of the strong equivalence principle in the Earth–Moon system, have examined the gravitational interaction only in connection with weakly self-gravitating objects (for example, for the Sun, $GM_{\odot}/c^2R_{\odot} \approx 2\times10^{-6}$). The measured relativistic effects are therefore but small perturbations to newtonian expectations, usually very difficult to measure even with modern technologies. More significantly, even when the experimental accuracy is high these tests have an important qualitative weakness: they say nothing about how the 'correct' theory of gravity might behave when gravitational forces are very strong, such as near a neutron star or black hole. Pulsars in gravitationally bound binary orbits provide nearly ideal laboratories for the testing of strong-field gravity: they have surface gravitational potentials $GM/c^2R \approx 0.2$; they move with mildly relativistic velocities ($v/c \approx 10^{-3}$) through a repetitive cycle well suited to experimental averaging techniques; and they emit periodic pulses of radio noise, detectable over interstellar distances, in some cases as stable as the ticks of an atomic clock[3].

Here we make use of 10 years of high-quality timing observations[4] of the binary pulsar PSR1913+16, and 1 year of similar data[5] for the newly discovered system PSR1534+12, to obtain experimental constraints on gravity in the strong-field regime. We use a methodology recently advocated by two of us (T.D. & J.H.T.; ref. 6) and we combine the new results with a published limit[7] based on the binary pulsar PSR1855+09. The results are interpreted in terms of a parametrized family of tensor-biscalar theories containing general relativity as a special case[8]. Our experimental constraints impose significant limits on how far the 'correct' theory of gravity can deviate from general relativity in the strong-field, non-quantum regime.

A related use of binary pulsar data for establishing the existence of gravitational radiation is by now well known[9–13]. This work is based on observations of times of arrival (TOAs) of pulses from PSR1913+16, which have been accumulating over more than 17 years. The TOAs are analysed by comparing them with predictions of a relativistic timing model[14–17], providing in the process accurate measurements of five 'keplerian' parameters of the orbit and three 'post-keplerian' ones: the advance of periastron $\dot{\omega}$, a time-dilation and gravitational redshift parameter γ, and the secular change of the orbital period, $\dot{P}_b$. Gravitational radiation is expected to remove energy and angular momentum from the orbit, causing the period to decrease. A quantitative test for gravitational radiation can therefore be carried out by comparing the observed $\dot{P}_b$ with the value predicted by general relativity (or another theory to be evaluated), given the measured values of $\dot{\omega}$, γ and the keplerian parameters.

General relativity now passes this $\dot{\omega}-\gamma-\dot{P}_b$ test for PSR1913+16 with an accuracy better than 0.5% (see further details below). But Damour and Esposito-Farèse[8] have recently

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