

a true soil fauna². A further contributory factor may be that herbivorous arthropods would be largely unsclerotized, and therefore unlikely to survive the acid-bath extraction that yielded most of the cuticles.

Palaeobotanists have transformed knowledge of early land plants and their evolution in recent decades, yet still they cry "We need more fossils"¹⁰. That is even truer of early land arthropods, but must

METEORITICS

Extraterrestrial amino acids and terrestrial life

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SINCE the Swedish chemist Baron Jöns Jacob Berzelius first analysed the Alais meteorite for organic molecules¹ in 1834, attempts to forge a link between extraterrestrial organic materials and terrestrial life have remained alluring, but often deceptive. Two distinct investigations are demanded in exploring such links: accurately characterizing the organics present in extraterrestrial bodies; and evaluating possible mechanisms for delivering these molecules intact to Earth. New studies reported in this and last week's issues^{2,3} hold the promise of important advances in both endeavours. The results of Engel *et al.*², if upheld, would suggest that the characteristic 'handedness' of biochemistry on Earth may ultimately have been determined by an asymmetry already existing in extraterrestrial amino acids. The paper on page 157 of this issue³ by Zahnle and Grinspoon presents one mechanism, the gentle collection of organic-rich dust evolved from an evaporating comet, whereby amino acids might in fact reach the Earth without being destroyed. A similar suggestion has been made previously in the prebiotic context⁴, but Zahnle and Grinspoon directly confront the most important datum currently available to test such hypotheses: the apparently extraterrestrial amino acids discovered⁵ in abundance in sediments at Stevns Klint, Denmark, marking the Cretaceous-Tertiary (K/T) boundary, the stratum associated with the major extinction 65 million years ago.

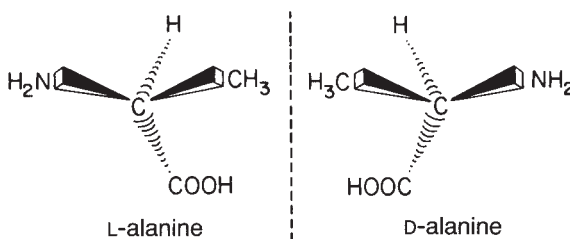
Murchison meteorite

The first identifications of amino acids in meteorites failed to survive doubts concerning terrestrial contamination, and were made in the midst of an acrimonious controversy over claimed observations of microfossils and biogenic organic molecules in meteorites⁶. In 1970, Kvenvolden *et al.*⁷ published the first of a series of studies which unequivocally demonstrated that amino acids in the Murchison meteorite, which had fallen the previous year,

palaeozoologists continue to rely on the rich pickings of palaeobotanists for earlier finds? Several recent research grant proposals from fossil arthropod workers suggest not, and we can look forward to earlier Palaeozoic records as the search intensifies. □

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were extraterrestrial and probably abiogenic. The evidence was threefold: Murchison's amino acids were nearly racemic (equal) mixtures of the D and L enantiomers (see the figure), whereas terrestrial organisms use almost exclusively the L enantiomer; extractable Murchison



The L and D enantiomers (from the Greek *enantios*: opposite) of the amino acid alanine. The two molecules are mirror images; no rotation through three dimensions can superimpose them. The enantiomers rotate the plane of polarization of light in opposite directions; unequal mixtures are therefore optically active. A mixture consisting of equal numbers of each is said to be racemic. Terrestrial life uses almost exclusively the L-amino-acid enantiomers.

organic compounds had $\delta^{13}\text{C}$ values (which measure the carbon isotope ratio $^{13}\text{C}/^{12}\text{C}$) that were greater than those in any naturally occurring terrestrial organics; and Murchison contained non-biological amino acids — those not among the 26 or so commonly found in terrestrial organisms. At least 74 amino acids have now been identified in Murchison extract⁸.

There is no difficulty in the non-destructive delivery of organic molecules to Earth in objects as small as the Murchison fragments. The bulk of the mass in potential terrestrial impactors, however, is concentrated in much larger bodies. For extraterrestrial material to have had a substantial influence on prebiotic chemistry, it would seem that this reservoir must somehow be tapped. Yet even objects as small as 100 metres in radius cannot be sufficiently decelerated by the Earth's present atmosphere for organic inclusions to survive the ensuing violent impact⁹.

This is one reason why the reported⁵ high abundance of the presumably extra-

terrestrial amino acids α -amino-isobutyric acid (AIB) and isovaline at the K/T boundary is so remarkable. (AIB and isovaline are extremely rare in the biosphere, but common in meteorites; moreover, the K/T isovaline is racemic.) A cosmochemical interpretation of the iridium (Ir) abundance at the boundary implies that it was created by an impactor with a diameter of 10 km; such an object would hit the Earth with a kinetic energy equivalent to 10^8 megatons of explosive, enough to incinerate even the hardest organics⁹. Yet the AIB/Ir ratio at Stevns Klint is substantially higher than for Murchison. More puzzling still, the amino acids were found tens of centimetres above and below the K/T boundary, but not in the boundary clay itself.

Assuming that these data are not anomalous, how are they to be explained? Zahnle and Grinspoon take the sedimentary record at face value, and suggest that Earth swept up the amino acids "gently and non-destructively" in cometary dust over a period of around 10^5 years. Organic molecules in interplanetary dust particles (IDPs) reach the Earth today⁴; a sufficiently large comet trapped in the inner Solar System could have provided the high IDP flux needed to deposit the amino acids around the K/T boundary. The boundary clay itself would then record the impact of a fragment of the parent comet, an impact which amino acids did not survive.

Zahnle and Grinspoon cite a report by D. Carlisle of amino acids found within, rather than around, the boundary clay at a Canadian K/T site. These results apparently corroborate the existence of K/T amino acids; it will be important to know if Stevns Klint AIB/Ir ratios are typical or anomalously high. Only the depositional history of the Canadian site, combined with detailed knowledge of the amino acid distribution, will show whether these results are consistent with the comet-dust model.

A difficulty that has received too little attention in all IDP organic-delivery schemes is the question of whether IDP atmospheric deceleration is really gentle enough for amino acids to survive. Models predict cometary IDPs to be typically heated to around 900 K for 5–15 seconds during atmospheric entry¹⁰. A naive application of thermal decomposition rates for amino acids⁹ suggests these molecules would survive around 800 K for 1 s. But the sole data available are for decomposition in solution, and these rates are of dubious relevance to degradation of amino acids in a mineral matrix. Laboratory rate parameters for a variety of matrices are badly needed to resolve this

question. In any case, the harder organics⁹, after some thermal processing, will certainly survive, and one is free to speculate³ that surviving amino acid precursors may then be synthesized into the observed products.

One apparent problem with the comet-dust model may be less severe than has been suggested³. Data collected by R. Rocchia *et al.*, cited by Officer and Drake¹¹, show that Ir values at Stevns Klint are correlated with the clay fraction; expressed on a carbonate-free basis, Ir concentrations stay within a factor of two of the peak clay abundance out to 30–40 cm above and below the boundary, and remain above background levels out to around 50 cm. These distances correspond to 10^4 – 10^5 -year depositional times, and suggest that the putative comet dust was delivering Ir as well as amino acids throughout its accretion. (However, high AIB/Ir levels in the dust still appear to be required.) I emphasize that such long-term cometary depositional histories rebut the argument¹¹ that claimed 10^4 – 10^5 -year timescales for K/T Ir deposition necessarily favours explanations of the K/T catastrophe in terms of extended terrestrial volcanism.

In any case, altogether different explanations for the K/T amino acids are possible. Extensive experimental data show that amino acids can be synthesized by quenched shock heating of reducing gases¹². It is commonly asserted that such recombination could not have occurred for vaporized impactor material in an O₂-rich background atmosphere^{3,5}. In fact, production efficiency remains high even in background air¹², so post-impact shock synthesis is not yet ruled out⁹. A final possibility is organic delivery following catastrophic impactor fragmentation. A 10-km diameter bolide would be too large to be affected by the atmosphere, but if several smaller objects or fragments were responsible for the K/T geochemical signatures, each might have airburst in the atmosphere before hitting the ground. A carbonaceous chondrite did exactly this over Revelstoke, Canada, in 1965; photomicrographs of the millimetre-sized fragments recovered reveal unheated interiors¹³ within which organics should have survived⁹.

Significant sources

Our preliminary quantitative work¹⁴ suggests that IDPs⁴, airbursts and, possibly, quench syntheses, could have been significant sources of prebiotic organics on early Earth. In the first two cases, the report last week by Engel *et al.*² of an excess of L-type alanine in Murchison is potentially of great importance. No convincing explanation yet exists for why terrestrial life uses L, not D, amino acids. Abiotic explanations must either account for L/D ratios which differ from unity by

more than statistical fluctuations, or provide an amplification mechanism that proceeds faster than natural racemization. Neither programme has yet been successful¹⁵, and the possibility that the predominance of L-forms is simply an accident of early biology remains a leading alternative. Finding a meteoritic preference for L-amino acids would 'explain' terrestrial biology's choice by pushing the problem out into the cosmos — or it might imply yet-undiscovered abiotic processes that could also have operated on the early Earth.

If the data of Engel *et al.* are valid, there is a third possibility that must be forthrightly addressed. Non-racemic mixtures of amino acids have long been suggested as indicators of biologically derived molecules¹⁶. Entire papers at 'exobiology' meetings have been devoted to instrumentation designed to detect optical activity. Does not scientific honesty then require us to consider the new results as *prima facie* evidence of extraterrestrial life?

Scientific humility answers no. A simple failure to find an abiotic mechanism cannot in itself require an appeal to biology. (Indeed, A. Salam and J. Strathdee (personal communication) have just proposed a low-temperature quantum amplification of the inequal ground-state energies — around 10^{-19} electron volts, due to parity-violating weak nuclear interactions — of L and D amino acid enantiomers, which they argue could create non-racemic mixtures.) Results from the Viking biology packages on Mars are powerful reminders that prejudices about supposedly unambiguous attributes of terrestrial biology may crumble in the face of unanticipated extraterrestrial chemistry. In any case, the complete structural diversity of the Murchison amino acids argues for non-catalytic, thermodynamically-controlled (that is, abiotic) synthesis⁸.

Any detection of non-racemic amino acid mixtures must exclude the possibility of contamination due to L-rich terrestrial microorganisms. This concern was raised over an earlier report of non-racemic Murchison amino acids; it is especially worrying that only protein amino acids have been claimed to be non-racemic, and that it is the L enantiomer of alanine that is found in excess¹⁷. Both these results are, of course, consistent with contamination. The key result of Engel *et al.*² is that the L and D enantiomers of alanine in Murchison have extraterrestrial $\delta^{13}\text{C}$ values of +27 and +30 parts per thousand (‰), respectively. A putative terrestrial alanine contaminant, they show, would need an isotopic composition of +10 ‰ to arrive at the observed L-alanine bulk value, and the authors argue that no such terrestrial sources are apparent. (Terrestrial inorganic carbon has $\delta^{13}\text{C}$ 0‰; microorganisms typically fractionate carbon

isotopes to lighter values, producing organics with $\delta^{13}\text{C}$ as low as –40‰.)

Unfortunately, at least one plausible such contaminant does exist. It has recently been shown¹⁸ that a wide variety of common bacteria are able to obtain their carbon and energy needs from abiotically produced 'tholins', laboratory materials that provide good analogues to meteoritic and cometary organics⁹. This raises the possibility of contamination of Murchison by terrestrial bacteria that consume ¹³C-rich organics, then produce $\delta^{13}\text{C}$ -rich amino acids. Methane from Murchison, for example, has $\delta^{13}\text{C}$ = +9.2‰, and certain other organics have higher values⁸. Moreover, at least one bacterium, *Methanobacterium thermoautotrophicum*, fractionates (admittedly under special circumstances) carbon to heavier isotopes¹⁹, by as much as +13 ‰. A bacterium capable of such fractionation while metabolizing, say, the Murchison benzene-methanol extract (which includes⁸ nonvolatile aromatics and the higher alkanes, and has $\delta^{13}\text{C}$ = +5 ‰), could produce the required effect.

Unanticipated chemistry and uncertain contamination have been the bane of 'exobiology'. Occam's razor, the nineteenth century name given to various versions of William of Ockham's fourteenth century maxim, remains a useful warning. The actual formulation was "*pluralitas non est ponenda sine necessitate*": plurality is not to be posited without necessity. This was meant as a methodological, not an ontological, admonition²⁰. Understood in this way, it puts the pursuit of familiar explanations before that of more encompassing ones: the former must be excluded before we may embrace the latter. □

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