limit of $>10^8$ K rules out galactic disks and star formation as the source of the radio emission from VLA J065349.4 + 791619.

Next we consider the possibility that the radio emission from VLA J065349.4 + 791619 originates from the central 'engine' of an AGN. The radio power of the source at a rest frequency of 17 GHz (for an assumed redshift of 1) is 10^{24} W Hz⁻¹. This is comparable to the radio powers of nearby low-luminosity AGNs⁴. These radio sources, however, are generally dominated by emission from extended radio lobes. In the few cases where the cores are sufficiently strong, VLBI observations have revealed considerable structure⁵. In most cases this structure has a surface brightness a factor of 20-80 below that of the peak, so it is difficult to make a direct comparison to VLA J065349.4 + 791619 as (at best) the r.m.s. noise level is a factor of 20 below the peak brightness. The radio spectrum of VLA J065349.4 + 791619 (ref. 1), on average, resembles that of the socalled "GHz-peaked" radio sources. However, these sources show little variability and have complicated structure on the parsec scale^{6,7}. Gravitationally lensed sources at similar redshifts may have a comparable intrinsic radio power, but these also show much less radio variability than GRB970508, from 0 to 10%. The morphologies of the gravitationally lensed sources are predominantly core plus jet8,9. The extreme variability of VLA J065349.4 + 791619 (ref. 1) is characteristic of a class of radio sources known as intraday variables, but these originate in flatspectrum radio sources such as BL Lacs and quasars 10.

Optical observations of the galaxy in which this radio source is located are also relevant. The optical source continues to fade and as yet there are no indications of any host galaxy to a limit of R-band magnitude $R \approx 24.5$ mag (ref. 11). This rules out typical radio galaxies as the host galaxy of these objects would be bright.

We conclude that GRB970508 is unlikely to be either radio emission from a normal galaxy or radio emission from the nucleus of an active galaxy. This conclusion is quite interesting as there are some models which posit that GRBs are beamed nuclear sources. The evidence presented above does not offer firm proof that this is not the case, but renders such a hypothesis less likely. Thus we now arrive at the preferred interpretation: GRB970508 is the radio counterpart or afterglow of the γ -ray burst of 8 May 1997 located in a faint galaxy.

Proceeding with the hypothesis that VLA J065349.4 + 791619 is the radio afterglow from GRB970508 we note that our observations rule out significant gravitational lensing on scales of 10 mas—300 arcsec. This covers the range of lenses discussed in the literature and rules out any substantial flux magnification of the γ -ray burst by gravitational lensing.

According to theoretical estimates of the angular diameter of the fireball¹², a future burst with the same radio luminosity as GRB970508 but at a redshift of 0.2 could be resolvable by VLBI observations. This would open the way for using VLBI to study the detailed evolution of a resolved GRB in much the same way as has recently been done for extragalactic supernovae¹³.

Received 8 August; accepted 28 August 1997.

- Frail, D. A., Kulkarni, S. R., Nicastro, L., Feroci, M. & Taylor, G. B. The radio afterglow from the γ-ray burst of 8 May 1997. Nature 389 261–263 (1997).
- Johnston, K. J. et al. A radio reference frame. Astron. J. 110, 880–915 (1995).
- Windhorst, R. A., Fomalont, E. B., Partridge, R. B. & Lowenthal, J. D. Microjansky source counts and spectral indices at 8.44 GHz. Astrophys. J. 405, 498–517 (1993).
- Giovannini, G., Feretti, L. & Comoretto, C. VLBI observations of a complete sample of radio galaxies. I. Snapshot data. Astrophys. J. 358, 159–163 (1990).
- Lara, L. et al. VLBI observations of a complete sample of radio galaxies. VII. Study of the FR I Sources 3C 31, 4C 35.03 and 3C 264. Astrophys. J. 474, 179–187 (1997).
- Taylor, G. B., Readhead, A. C. S. & Pearson, T. J. Pinpointing the center of activity in compact symmetric objects. I. Sources from the Pearson-Readhead survey. *Astrophys. J.* 463, 95–104 (1996).
 O'Dea, C. P., Stanghellini, C., Baum, S. A. & Charlot, S. On the host galaxies of the gigahertz peaked-
- spectrum radio sources. Astrophys. J. 470, 806–813 (1996).

 8. Campbell, R. M., Lehar, J., Corey, B. E., Shapiro, I. I. & Falco, E. E. VLBI observations of the
- gravitational lens system 0957 + 561. Astron. J. 110, 2566–2569 (1995).

 9. Porcas, R. W. in Radio Emission from Galactic and Extragalactic Compact Sources (eds Zensus, J. A.,
- 9. Porcas, R. W. In Radio Emission from Galactic and Extragalactic Compact Sources (eds Zensus, J. A., Wrobel, J. M. & Taylor, G. B.) (IAU Colloq. 164, Astron. Soc. Pacific, San Francisco, in the press).
- Wagner, S. J. & Witzel, A. Intraday variability in quasars and BL Lacs objects. Annu. Rev. Astron. Astrophys. 33, 163–197 (1995).

- Pian, E. et al. Hubble space telescope imaging of the optical transient associated with GRB970508 Astrophys. J. (submitted).
- 12. Sari, R. Hydrodynamics of GRB afterglow. Preprint astro-ph/9706078 (1997).
- 13. Marcaide, M. et al. Expansion of SN 1993J. Science 270, 1475-1478 (1995).
- Beasley, A. J. & Conway, J. E. in Very Long Baseline interferometry and the VLBA (eds Zensus, J. A., Diamond, P. J. & Napier, P. J.) 327–341 (ASP Conf. Ser. Vol. 82, Astron. Soc. Pacific, San Francisco, 1995).

Acknowledgements. The VLA and VLBA are facilities of the NSF operated under cooperative agreement by Associated Universities, Inc. We thank the VLBA, VLA and Effelsberg operational staff, and the VLBA correlator staff, for their extraordinary efforts on behalf of this project. S.R.K. is supported by the NSF and NASA.

Correspondence should be addressed to G.B.T. (e-mail: gtaylor@nrao.edu).

Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite

M. H. Engel* & S. A. Macko†

- * School of Geology and Geophysics, The University of Oklahoma, Norman, Oklahoma 73019, USA
- † Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia 22903, USA

Many amino acids contain an asymmetric centre, occurring as laevorotatory, L, or dextrorotatory, D, compounds. It is generally assumed that abiotic synthesis of amino acids on the early Earth resulted in racemic mixtures (L- and D-enantiomers in equal abundance). But the origin of life required, owing to conformational constraints, the almost exclusive selection of either L- or Denantiomers^{1,2}, and the question of why living systems on the Earth consist of L-enantiomers rather than D-enantiomers is unresolved3. A substantial fraction of the organic compounds on the early Earth may have been derived from comet and meteorite impacts⁴⁻⁶. It has been reported previously that amino acids in the Murchison meteorite exhibit an excess of Lenantiomers⁷, raising the possibility that a similar excess was present in the initial inventory of organic compounds on the Earth. The stable carbon isotope compositions of individual amino acids in Murchison support an extraterrestrial origin⁸ rather than a terrestrial overprint of biological amino acids although reservations have persisted (see, for example, ref. 9). Here we show that individual amino-acid enantiomers from Murchison are enriched in 15N relative to their terrestrial counterparts, so confirming an extraterrestrial source for an L-enantiomer excess in the Solar System that may predate the origin of life on the Earth.

The Murchison meteorite is the most recently observed fall of an organic-rich, Type CM meteorite. Engel and Nagy⁷ reported an L-enantiomer excess for several amino acids in Murchison. The exotic amino-acid distribution, notably the absence or trace level of many common protein amino acids (for example, serine, threonine, methionine, tyrosine, phenylalanine, histidine, lysine, arginine), indicated that the L-excess for amino acids detected (for example, alanine, glutamic acid, aspartic acid) was not likely to be the result of contamination after impact. These results were incongruous with the initial report of approximately racemic amino acids in another Murchison stone¹⁰. Consequently, criteria independent of amino-acid distribution and stereochemistry have been sought to determine the source of the L-excess.

Stable isotopes have been used to assess the origins of organic matter in extraterrestrial materials (see, for example, refs 11–13). For instance, stable-isotope values (δ^{13} C, δ^{15} N, δ D) of organic extracts of the Murchison meteorite are moderately-to-highly

letters to nature

enriched in the heavy stable isotopes (13 C < 15 N < D) 11,14,15 . Similar isotope enrichments for interstellar clouds indicate that this is a likely source for the precursors of the Murchison amino acids (see, for example, ref. 9). In contrast, terrestrial organic matter of biogenic origin on Earth is usually moderately-to-substantially depleted in 13 C, 15 N and D relative to interstellar values, a consequence of isotope fractionations associated with biosynthetic processes such as photosynthesis 16 .

To date, most stable-isotope analyses of Murchison's organic matter have been determined on bulk extracts by conventional methods (see, for example, ref. 11). However, bulk organic extracts are comprised of mixtures of compounds, each having a potentially distinct isotopic composition. Thus, the stable-isotope values for bulk samples are weighted average values for the mixtures. In the few instances where δ^{13} C values have been determined for individual compounds (for example, carboxylic acids, amino acids, hydrocarbons)^{8,14,17,18}, differences in isotope compositions suggest distinct fractionations resulting from the apparent synthesis of higher-molecular-weight compounds from lower-molecular-weight homologues.

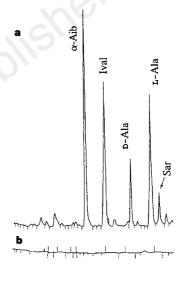
We previously attempted to determine whether the L-enantiomer excess in Murchison was extraterrestrial by using gas chromatography/combustion/isotope-ratio mass spectrometry (GC/C/IRMS) to obtain δ^{13} C values of individual amino-acid enantiomers. The results, although encouraging, were not definitive, because the δ^{13} C values for some components were only slightly-to-moderately enriched in 13 C relative to terrestrial organic matter. The δ^{15} N value for a bulk amino-acid extract of Murchison was substantially enriched (+90‰) 11 relative to biological material (-10 to +20‰). Thus, establishing the δ^{15} N values of individual amino acids should provide a better test of the hypothesis that the L-enantiomer excess in Murchison is extraterrestrial in origin.

A 7.3-g interior sample of a 103-g Murchison meteorite stone from the R. A. Langheinrich collection was ground to fine powder and extracted in distilled water for 8 h at 100 °C. This water extract was evaporated to dryness and then hydrolysed in 6M HCl for 24 h at 100 °C. The amino-acid fraction was isolated by cation-exchange chromatography as previously reported⁷. A portion of the aminoacid extract was analysed by high performance liquid chromatography (HPLC) to determine amino-acid abundances¹⁹. A second aliquot was derivatized to trifluoroacetyl isopropyl esters to determine stereochemistry and compound purity by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) as well as stable nitrogen isotope compositions of the individual stereoisomers by GC/C/IRMS. Specific details of the modifications to the GC/C/IRMS carbon-isotope methodology, as well as assessments of precision on standard materials are reported elsewhere^{20,21}. Briefly, derivatization of amino acids for stable nitrogen isotope analysis by GC/C/IRMS results in minimal isotopic fractionation and no additional nitrogen is added to the amino acid during the acylation and esterification steps²². Thus, unlike stable carbon isotope analysis of amino acids by GC/C/IRMS^{23,24}, no corrections are required to obtain the $\delta^{15}N$ values of the underivatized amino acids. Bulk δ^{15} N, δ^{13} C analyses of acidified portions of the meteorite were accomplished using an off-line preparation procedure involving high-temperature combustion in quartz, cryogenic gas purification and isotope analysis on a PRISM IRMS. Carbonate isotope abundances (δ^{13} C, δ^{18} O) on a non-acidified portion of the stone were determined on a PRISM Micromass automated carbonate system.

The δ^{13} C and δ^{15} N values for the acidified bulk sample of this Murchison stone are -11.3% (with respect to the PDB standard) and +30.1% (with respect to atmospheric N_2), respectively, and are in agreement with previous findings⁸. Stable carbon and oxygen isotope values for the carbonate component of this stone are +38.6% (PDB) and +29.9% (SMOW standard), respectively, within the range of values reported for other Murchison stones²⁵.

Amino-acid distributions and abundances (Table 1) are also in good agreement with previous findings (for example, refs 8 and 26).

Owing to the need for adequate separation between individual amino acids eluting from the gas chromatographic column, not all amino acids or both stereoisomers were able to be isotopically assessed. For amino acids that could be analysed (Table 1), the $\delta^{15}N$ values are enriched in ^{15}N and fall well out of the average range of values reported for terrestrial organic matter (~ -10 to +20%). With the notable exceptions of α -aminoisobutyric acid, sarcosine and glycine, the remaining amino acids have similar $\delta^{15}N$ values, implying a single, possibly interstellar ^{15}N , homogeneous source for this nitrogen. The extreme ^{15}N enrichment observed for α -aminoisobutyric acid and sarcosine indicates either a unique precursor source or perhaps isotope fractionation during its formation or subsequent decomposition. The more depleted value for glycine may be associated with processes of formation or destruction of this or other amino acids, as glycine is known to form by the decom-



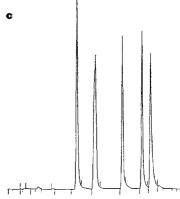


Figure 1 a, Gas chromatogram showing the resolution of p-alanine and L-alanine in the Murchison meteorite. **b**, Procedural blank chromatogram that preceded the meteorite analysis. **c**, Chromatogram of a standard mixture of the amino acids. Abbreviations are as follows: α -Aib, α -aminoisobutyric acid; Ival, isovaline; p-Ala, p-alanine; L-Ala, L-alanine; Sar, sarcosine. For GC, GC/MS and GC/C/IRMS, the separation of the trifluoroacetyl isopropyl esters of the amino acid stereoisomers was accomplished using a Chirasil-Val 50 m × 0.25 mm (internal diameter) fused-silica capillary column (Alltech, Deerfield, IL). The GC/C/IRMS consists of a Hewlett Packard 5890 GC coupled to an OPTIMA (Micromass, Manchester, UK) stable-isotope mass spectrometer through a cupric oxide/nichrome wire oxidation furnace, a copper reduction furnace and a liquid-nitrogen carbon dioxide/water cold trap²¹. The GC and GC/MS analyses were performed using a Hewlett Packard 5890A GC and a Hewlett Packard GC/MSD.

position of other amino acids²⁷. Explanations for the abundances beyond this first report will require additional experimentation and analysis; in particular, establishing the $\delta^{15}N$ values of additional components in this complex mixture.

The common amino acids that contain asymmetric centres are not racemic, and all show, to varying degrees, an excess of the Lenantiomer^{7,8}. The δ^{15} N values could be determined for both enantiomers of alanine and glutamic acid. It is clear that these values are extraterrestrial (Table 1), and are essentially identical for the respective enantiomers of each amino acid within the present error of the measurement at the enrichments observed ($\pm 1\%$). The D/L value for alanine in this stone is 0.5 (Fig. 1), which is similar to that reported for alanine in the hydrolysed water extract of a previous stone (0.6; ref. 7). A similar value was obtained for yet a third stone (M.H.E. and J. A. Silfer, unpublished results). The D/L value for glutamic acid is consistent with our previously reported value of 0.3; ref. 7. Even if one assumes, for example, that the slight ¹⁵N depletion in the L-alanine relative to D-alanine is real, it cannot be accounted for by a contribution from known terrestrial sources. If the original concentrations of the L-alanine and D-alanine had been identical, the excess L-alanine required to produce a D/L value of 0.5 would have to have an isotopic composition of approximately +55‰ to deplete L-alanine in this acid-hydrolysed water extract. To our knowledge, no terrestrial organic sources have been reported with this level of 15N excess. Similarly, one can estimate the contribution of commonly observed terrestrial nitrogen (-10 to +10‰) to the isotope composition of the alanine, and its impact on the D/L value. This range of isotopic compositions would change the presumed initial value from 1.0 to 0.9. Thus it is clear that the δ^{15} N values reported here for Murchison amino acids are indigenous and have not been compromised by a terrestrial overprint.

An additional concern might be that the L-alanine or L-glutamic acid excess are the result of exotic co-eluting compounds. However, GC/MS and GC/C/IRMS analyses indicate no obvious co-elutions. Previous GC/MS analyses using a GC column with an entirely different stationary phase resulted in very similar L-enantiomer excesses⁷, also diminishing the likelihood of co-elutions. Moreover, if as yet unspecified compounds are co-eluting with the L-enantiomers, they would have to have similar structures (that would produce the same fragmentation ions on GC/MS), chemistry (for identical GC retention times) and isotopic compositions (δ^{15} N values) to enhance only the L-enantiomers. It should be noted that an L-enantiomer excess for several exotic amino acids has also recently been reported²⁸, although a stable-isotope assessment of their extraterrestrial origins was not attempted.

Table 1 Amino-acid abundances and δ ¹⁵ N values	

Amino acid	Concentration (nmol g ⁻¹)	δ ¹⁵ N (‰)*
α-Aminoisobutyric acid	20.1	+184
Sarcosine	ND†	+129
Isovaline	8.0‡	+66
Glycine	24.5	+37
β-Alanine	12.8	+61
p-Alanine	-§	+60
L-Alanine	10.4‡	+57
L-Leucine	2.5§	+60
D,L-Proline	ND†	+50
D,L-Aspartic acid	4.7§	+61
p-Glutamic acid	-\$	+60
L-Glutamic acid	10.8§	+58

^{*}The δ^{15} N values are an average of four GC/C/IRMS analyses, the average error being about ±1%s. Values are reported relative to the standard, atmospheric N₂: δ^{15} N(%s) = $(f^{15}$ N/ f^{14} N, f^{15} N, f^{14} N, f^{15} N,

 $\parallel \delta^{15} N$ value reflects contribution of both enantiomers.

Our report of non-racemic amino acids is in conflict with the initial report of higher amino-acid D/L values for the Murchison meteorite¹⁰. However, we emphasize that our amino-acid distributions and relative abundances for all three stones are in general agreement with those initial and subsequent findings²⁶. This would not be expected if contamination occurred. It is also important to recognize that the amino acids present in the Murchison meteorite stones may not reflect the distribution at the initial time of synthesis. Organic and inorganic reactions may have altered amino-acid distributions over a period of unknown duration when the meteorite parent body (from which Murchison was derived) probably retained an aqueous phase⁹. Given this caveat, it is possible that different stones may contain components that do not reflect identical alteration histories. But although previous authors have attributed an apparently slight L-excess to biological contamination¹⁰, we believe, as will be discussed below, that the stable-isotope values point to an alternative explanation.

The moderate-to-extreme ¹⁵N enrichments observed for amino acids in the Murchison meteorite establish their indigenous nature and, as previously suggested, point to a possible interstellar source for their precursors if not for some of the compounds themselves. Given the current hypotheses that (1) an enantiomeric excess is likely to have been a precondition for the origin of life on Earth (for example, refs 1, 2) and (2) the Earth's initial inventory of organic matter was derived from meteorite and comet bombardment⁶, the occurrence of an excess of the L-enantiomers in the Murchison meteorite provides the first evidence for a source of this chirality deemed essential for life's origin. The origins of the excess in the L-enantiomers presently remains unclear. The excess may have resulted from the alteration of initially abiotic, racemic mixtures by a process such as preferential decomposition by exposure to circularly polarized light¹. The extent to which such processes would have altered the stereochemistry of amino acids during the billion years preceding the first fossil evidence of life on Earth is unknown. But if amino-acid precursors (and perhaps some amino acids themselves) are probably interstellar⁹, this would certainly increase the time for exposure of organics to circularly polarized light before the formation of our Solar System. The preliminary report of a biotic signature in an Antarctic stone of martian origin²⁹, and the recent suggestion of life on Earth several hundred million years earlier than indicated by fossil evidence³⁰, certainly raises questions as to how pervasive life was in the early Solar System and the time required for its origin(s), in particular if chirality was a precondition for life. Stable-isotope analysis of amino-acid enantiomers, if present in the martian stone, may help to authenticate their origin(s)³¹, given the unique isotope signatures observed for Mars by the Viking mission³².

Received 17 September 1996; accepted 14 July 1997.

- 1. Bonner, W. A. The origin and amplification of biomolecular chirality. Orig. Life 21, 59-111 (1991).
- 2. Goldanskii, V. I. & Kuzmin, V. V. Chirality and cold origin of life. Nature 352, 114 (1991).
- 3. Cohen, J. Getting all turned around over the origins of life on Earth. Science 267, 1265-1266 (1995).
- Oró, J. Comets and the formation of biochemical compounds on the primitive Earth. Nature 190, 389–390 (1961).
- Chyba, C. F., Thomas, P. J., Brookshaw, L. & Sagan, C. Cometary delivery of organic molecules to the early Earth. Science 249, 366–373 (1990).
- Chyba, C. F. & Sagan, C. Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. Nature 355, 125–132 (1992).
- Engel, M. H. & Nagy, B. Distribution and enantiomeric composition of amino acids in the Murchison meteorite. Nature 296, 837–840 (1982).
- Engel, M. H., Macko, S. A. & Silfer, J. A. Carbon isotope composition of individual amino acids in the Murchison meteorite. Nature 348, 47–49 (1990).
- Cronin, J. R. & Chang, S. in The Chemistry of Life's Origins (eds Greenberg, J. M. et al.) 209–258 (Kluwer Academic, Amsterdam, 1993).
- 10. Kvenvolden, K. et al. Evidence for extraterrestrial amino acids and hydrocarbons in the Murchison meteorite. Nature 228, 923–926 (1970).
- Epstein, S., Krishnamurthy, R. V., Cronin, J. R., Pizzarello, S. & Yuen, G. U. Unusual stable isotope ratios in amino acid and carboxylic acid extracts from the Murchison meteorite. *Nature* 326, 477–479 (1987).
- Engel, M. H., Macko, S. A. & Nagy, B. in Organic Geochemistry, Principles and Applications (eds Engel, M. H. & Macko, S. A.) 685–695 (Plenum, New York, 1993).
- Hoppe, P., Amari, S., Zinner, E. & Lewis, R. S. Isotopic compositions of C, N, O, Mg and Si, trace element abundances, and morphologies of single circumstellar graphite grains in four density fractions from the Murchison meteorite. Geochim. Cosmochim. Acta 59, 4029–4056 (1995).

being about 17-78. Since $1 - 10^{-1}$ and $1 - 10^{-1}$ and 1 -

[‡]The value for isovaline includes a contribution from valine that co-eluted with isovaline during HPLC analysis.

[§] Concentrations reported for L-alanine, L-leucine, D,L-aspartic acid and L-glutamic acid represent the total contribution of both enantiomers for the respective amino acids.

letters to nature

- Pizzarello, S., Krishnamurthy, R. V., Epstein, S. & Cronin, J. R. Isotopic analyses of amino acids from the Murchison meteorite. Geochim. Cosmochim. Acta 55, 905

 –910 (1991).
- Pizzarello, S., Feng, X., Epstein, S. & Cronin, J. R. Isotopic analyses of nitrogenous compounds from the Murchison meteorite: Ammonia, amines, amino acids, and polar hydrocarbons. *Geochim. Cosmochim. Acta* 58, 5579–5587 (1994).
- Fogel, M. L. & Cifuentes, L. A. in Organic Geochemistry, Principles and Applications (eds Engel, M. H. & Macko, S. A.) 73–98 (Plenum, New York, 1993).
- Yuen, G., Blair, N., Des Marais, D. J. & Chang, S. Carbon isotopic composition of low molecular weight hydrocarbons and monocarboxylic acids from the Murchison meteorite. *Nature* 307, 252–254 (1984).
- Gilmour, I. & Pillinger, C. Isotopic differences between PAH isomers in Murchison. Meteorites 27, 224–225 (1992).
- Hare, P. E., St John, P. A. & Engel, M. H. in Chemistry and Biochemistry of the Amino Acids (ed. Barrett, G. C.) 415–425 (Chapman & Hall, London, 1985).
- Merritt, D. A. & Hayes, J. M. Nitrogen isotopic analyses by isotope-ratio-monitoring gas chromatography/mass spectrometry. J. Am. Soc. Mass Spectrom. 5, 387–397 (1994).
- Macko, S. A., Uhle, M. E., Engel, M. H. & Andrusevich, V. Stable nitrogen isotope analysis of amino acid enantiomers by gas chromatography/combustion/isotope ratio mass spectrometry. *Anal. Chem.* 69, 926–929 (1997).
- Silfer, J. A. Stable carbon and nitrogen isotope signatures of amino acids as molecular probes in geologic systems. Thesis, Univ. Oklahoma (1991).
- Silfer, J. A., Engel, M. H., Macko, S. A. & Jumeau, E. J. Stable carbon isotope analysis of amino acid enantiomers by conventional isotope ratio mass spectrometry and combined gas chromatography/ isotope ratio mass spectrometry. *Anal. Chem.* 63, 370–374 (1991).
- Silfer, J. A., Qian, Y., Macko, S. A. & Engel, M. H. Stable carbon isotope compositions of individual amino acid enantiomers in mollusc shell by GC/C/IRMS. Org. Geochem. 21, 603–609 (1994).
- Grady, M. M., Wright, I. P., Swart, P. K. & Pillinger, C. T. The carbon and oxygen isotopic composition of meteoritic carbonates. *Geochim. Cosmochim. Acta* 52, 2855–2866 (1988).
- Shock, E. L. & Schulte, M. D. Summary and implications of reported amino acid concentrations in the Murchison meteorite. Geochim. Cosmochim. Acta 54, 3159–3173 (1990).
- Vallentyne, J. R. Biogeochemistry of organic matter-II. Thermal reaction kinetics and transformation products of amino compounds. Geochim. Cosmochim. Acta 28, 157–188 (1964).
- Cronin, J. R. & Pizzarello, S. Enantiomeric excesses in meteoritic amino acids. Science 275, 951–955 (1997).
- McKay, D. S. et al. Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001. Science 273, 924–930 (1996).
- 30. Mojzsis, S. J. et al. Evidence for life on Earth before 3,800 million years ago. Nature **384**, 55–59 (1996)
- Engel, M. H., Goodfriend, G. A., Qian, Y. & Macko, S. A. Indigeneity of organic matter in fossils: A test using stable isotope analysis of amino acid enantiomers in Quaternary mollusk shells. *Proc. Natl Acad. Sci. USA* 91, 10475–10478 (1994).
- 32. Kieffer, H. H., Jakosky, B. M. & Snyder, C. W. in Mars (eds Keiffer, H. H., Jakosky, B. M., Snyder, C. W. & Matthews, M. S.) 1–33 (Univ. Arizona Press, Tucson, 1992).

Acknowledgements. We thank S. Fulkerson for his support of this work, and V. Andrusevich and T. Brockwell for their assistance with the analyses. This work was supported by the US NSF. Instrument time and travel funds were provided by Micromass Inc.

Correspondence and requests for materials should be addressed to M.H.E. (e-mail: AB1635@OU.EDU).

Creating electrical contacts between metal particles using directed electrochemical growth

Jean-Claude Bradley, Hsuing-Ming Chen, Jeffrey Crawford, Jennifer Eckert, Karima Ernazarova, Thomas Kurzeja, Muduo Lin, Michael McGee, Wolfgang Nadler & Samuel G. Stephens

Drexel University, Department of Chemistry, 32nd and Chestnut Streets, Philadelphia, Pennsylvania 19104, USA

Electrical connections in microelectronics are usually established by means of photolithography to define the conducting channels. But methods that do not involve lithography have been explored, such as the use of electrodeposition¹ or electropolymerization²-6 to grow random structures of conducting material between two electrodes. This approach has been used to make diodes, transistors and signal amplifiers based on conducting polymers²-3. Template-based²-1² and thermal plating¹³ strategies have also been used to direct the growth of electrically conducting media. One advantage of these approaches over photolithography is the possibility of forming contacts in three dimensions and so achieving enhanced data-processing densities. Previous electrochemical approaches have required that the electrodes to be connected are physically linked to the external voltage source. Here we show that electrodissolution and electrodeposition pro-

cesses in an applied electric field can be exploited to create directional growth of copper deposits between copper particles that are not connected to an external circuit. Moreover, the particles distort the electric field in such a way as to focus the diffusion of copper ions and consequently the direction of 'wire' growth, enabling the particles to be connected to one another in a directional and controllable manner. This suggests that appropriately directed electric fields may be used to connect an array of such particles into an arbitrary circuit pattern.

An electric field induces polarization in conductive particles. Beyond a critical polarization, the overpotential at the surface of the particle becomes sufficiently elevated to induce electrochemical reactions. Because each particle serves as both anode and cathode, the process is referred to as bipolar electrochemistry¹⁴⁻²⁴. This phenomenon has been investigated using fluidized or packed bed electrodes for applications in metal recovery14-17, electrosynthesis¹⁸⁻²¹ and ultramicroelectrode²²⁻²⁴ studies. The technique is particularly well suited for electrochemistry in low-conductivity media. We use bipolar electrochemistry to form electrical contacts between metal particles physically isolated from an external circuit. This work is an extension of our previous interest in toposelective (site-selective) modifications of colloids using electric fields²⁵. In the present work, toposelective electrodissolution and electrodeposition are spatially coupled to generate copper deposits (referred to as 'wires') at predictable and highly selective locations.

The initial experimental conditions consist of aligning two copper particles perpendicular to two Pt electrodes in an aqueous medium (Figs 1 and 2). On application of an electric field, electrochemical oxidation of copper to cupric ions²⁶ occurs on one particle while electrochemical reduction of water occurs at the other particle. After a certain time the concentration of copper in the interparticle space increases to a level that allows electrodeposition to compete with the reduction of water. The result is the formation of fractal 'wires' which grow towards the nearest point on the other particle's surface. Once the wire spans the gap, electrical contact is achieved and all electrochemical phenomena between the particles instantly cease because the potential difference has been abolished. If one of the particles is placed near the cathodic feeder electrode, a wire will form between the particle and the electrode. This can easily be avoided by ensuring that the distance between the cathodic feeder electrode and the nearest particle is much larger than the interparticle distance.

The growth time and wire morphology can be readily controlled simply by changing the applied field intensity. At fields <15 V cm⁻¹ no wire formed within a period of 5 minutes (Fig. 3). A threshold field intensity for wire growth is expected as a minimum overpotential must be reached to ensure copper electro-oxidation and water reduction on the surface of the particles. At higher field intensities, the wire growth time rapidly decreased presumably owing to the accelerating release of copper ions and the increased electrophoretic force on these ions towards the particle acting as the cathode. Above about 35 V cm⁻¹ the wire growth time was not significantly reduced with increasing field intensities. Such growthspeed independence on voltage has been observed in electrodeposition studies at very low metal ion concentrations²⁷. Typical nonbipolar electrodeposition experiments are governed by a complex interplay of diffusion, migration and electroconvection^{27–42}. It is thus surprising to find that the growth speed of the wire can be independent of voltage, even though the intense and inhomogeneous fields near the particles are almost certainly inducing powerful and complex convective flows.

As expected from the proposed mechanism, copper ions are initially generated by the anodic particle and must cross the interparticle gap. During this induction period no visible phenomena can be observed. We stress that this induction period is different from that observed in typical electrodeposition, which is thought to involve the building up of space charges or uniform