Huston provided valuable help with site selection. We thank the Organization for Tropical Studies at Duke University and in particular D. A. and D. B. Clark and the staff of the La Selva Biological Station for logistical support. Financial support was provided by the NSF.

Received 11 August; accepted 15 November 1988.

1. Natn. Acad. Sci. *Nitrates: An environmental Assessment* (NRC, Washington, DC, 1978).
2. Robertson, G. P. *Environment* **28**, 16-21 (1986).
3. Banin, A., Lawless, J. C. & Whitter, R. C. *Adv. Space Res. Proc. COSPAR* **XXV**, 141-153 (Pergamon, New York, 1984).
4. Duxbury, J. M., Bouldin, D. R., Terry, R. E. & Tate, R. L. *Nature* **298**, 462-464 (1982).
5. Firestone, M. K. *Agronomy Monogr.* **22**, 289-320 (1982).
6. Sahrawat, K. L. & Keeney, D. R. *Adv. Soil Sci.* **4**, 103-148 (1986).
7. Tiedje, J. M. in *Biology of Anaerobic Microorganisms* (ed. Zehnder, A. J. B.) 179-244 (Wiley, New York, 1988).
8. Melillo, J. M., Aber, J. D., Steudler, P. A. & Schimel, J. P. *Ecol. Bull. (Stockholm)* **35**, 217-228 (1983).
9. Robertson, G. P. & Tiedje, J. M. *Soil Sci. Soc. Am. J.* **48**, 383-389 (1984).
10. Robertson, G. P. & Rosswall, T. *Ecol. Monogr.* **56**, 43-72 (1986).
11. Dickinson, R. E. & Cicerone, R. J. *Nature* **319**, 109-114 (1986).
12. Rasmussen, R. A. & Khalil, M. A. K. *Science* **232**, 1623-1624 (1986).
13. Sancho, F. & R. Mata. *Estudio detallado de suelos: Estacion Biologica La Selva* (Organization for Tropical Studies, Duke Univ., North Carolina, 1988).
14. Sollins, P., Sancho, F., Sanford, R. L. & Parker, G. G. in *La Selva: Ecology and Natural History of a Neotropical Rain Forest* (eds McDade, L., Bawa, K., Hespenheide, H. & Hartshorn, G.) (Sinauer Press, Chicago) (in the press).
15. Radulovich, R. & Sollins, P. *Soil Sci. Soc. Am. J.* **51**, 1386-1388 (1987).
16. Hartshorn, G. S. in *Costa Rican Natural History* (ed. Janzen, D. H.) Ch. 7 (Univ. of Chicago Press, 1983).
17. Harcombe, P. A. in *Recovery and Restoration of Damaged Ecosystems* (eds Cairns, J., Dickson, K. L. & Herricks, E. E.) 347-378 (Univ. of Virginia Press, Charlottesville, Virginia, 1977).
18. Robertson, G. P., Vitousek, P. M., Matson, P. A. & Tiedje, J. M. *Plant & Soil* **97**, 119-127 (1987).
19. Tiedje, J. M. in *Methods of Soil Analysis, Part 2.* (eds Miller, R. H. & Keeney, D. R.) 1011-1026 (Am. Soc. Agron., Madison, Wisconsin, 1982).
20. Parkin, T. B., Kaspar, H. F., Sexstone, A. J. & Tiedje, J. M. *Soil Biol. Biochem.* **16**, 323-330 (1984).
21. Ryden, J. C. & Skinner, J. H. *Soil Biol. Biochem.* **19**, 753-757 (1987).
22. Tiedje, J. M., Simkins, S. & Groffman, P. M. *Plant & Soil* (in the press).
23. Folorunso, O. A. & Rolston, D. E. *Soil Sci. Soc. Am. J.* **48**, 1214-1219 (1984).
24. Smith, M. S. & Tiedje, J. M. *Soil Sci. Soc. Am. J.* **43**, 951-955 (1979).
25. Groffman, P. M., Tiedje, J. M., Robertson, G. P. & Christensen, S. *Advances in Nitrogen Cycling in Agricultural Ecosystems* (ed. Wilson, J. R.) 174-192 (Commonwealth Agric. Bur., Sidney, Australia, 1988).
26. Robertson, G. P. *J. Ecol.* (in the press).
27. Keller, M., Kaplan, W. A., Wofsy, S. C. & DaCosta, J. M. *J. geophys. Res.* **93**, 1600-1604 (1988).
28. Livingston, G. P., Vitousek, P. M. & Matson, P. A. *J. geophys. Res.* **93**, 1593-1599 (1988).
29. Sanchez, P. *Properties and Management of Soils in the Tropics* (Wiley, New York, 1976).
30. Uehara, G. & Gillman, G. *The Mineralogy, Chemistry and Physics of Tropical Soils with Variable Charge Clays* (Westview, Boulder, Colorado, 1981).
31. Gorham, E., Vitousek, P. M. & Reiners, W. A. *A. Rev. ecol. Syst.* **10**, 53-88 (1979).
32. Robertson, G. P. & Tiedje, J. M. *Soil Biol. Biochem.* **19**, 187-193 (1987).
33. Matson, P. A. & Vitousek, P. M. *Global Biogeochemical Cycles* **1**, 163-170 (1987).
34. Hahn, J. & Crutzen, P. J. *Phil. Trans. R. Soc. Lond.* B **296**, 521-541 (1982).
35. Singh, H. B. *Envir. Sci. Technol.* **21**, 320-327 (1987).
36. Cicerone, R. J. *Science* **237**, 35-41 (1987).

Origin of Messel Oil Shale kerogen

K. Goth*, J. W. de Leeuw†, W. Püttmann‡ & E. W. Tegelaar†

* Forschungsinstitut Senckenberg, Senckenberganlage 25, 6000 Frankfurt am Main, FRG
† Delft University of Technology, Faculty of Chemical Technology and Materials Science, Organic Geochemistry Unit, de Vries van Heystplantsoen 2, 2628 RZ Delft, The Netherlands
‡ Lehrstuhl für Geologie, Geochemie und Lagerstätten des Erdöls und der Kohle, RWTH Aachen, Lochnerstrasse 4-20, 5100 Aachen, FRG

Despite many investigations concerning the insoluble organic matter in sediments (kerogen), its chemical nature and origin are only poorly understood. Here we report the results of a combined microscopy and chemical study of the Messel Oil Shale which shed light on the mechanism of kerogen formation. Scanning electron microscopy revealed the overwhelming presence of cell-wall remains of *Tetraedron-like* microalgae which are virtually indistinguishable from those of the widely occurring extant *Tetraedron minimum* (Chlorococcales). Flash-pyrolysis gas chromatography/mass spectroscopy indicated the presence of an insoluble, non-hydrolysable highly aliphatic biopolymer in both fossil and extant *Tetraedron* species. The bulk of the Messel Oil Shale kerogen probably consists of selectively preserved cell-wall material of *Tetraedron* algae, mainly made up of this newly discovered biopolymer. We therefore suggest that this polymer, and similar types of recently discovered highly aliphatic biopolymers in other algae and plant cuticles, are important precursors of *n*-alkanes in crude oils.

The Messel Oil Shale (near Darmstadt, West Germany) represents an organic-matter-rich lacustrine deposit of Mid-Eocene (~48-Myr) age[1]. This sediment (in particular, its fossil content) has been studied extensively by palaeontologists and organic geochemists[2], but despite these efforts, the origin and nature of the bulk of the organic matter is poorly understood.

Microscopic examinations of a large number of samples, obtained from outcrops within the open-cast mine at the aforementioned location as well as samples from cores, revealed that the organic matter in the Messel Oil Shale (~30% on a dry-weight basis) is mainly concentrated in distinct laminae. These organic-rich laminae alternate with laminae that are rich in clay and which also contain minor amounts of terrestrially derived organic debris (Fig. 1). Such units of microlaminae are commonly ~0.1-0.2 mm thick and their abundant occurrence throughout the Messel Oil Shale sequence suggests a cyclic sedimentation pattern (K.G., manuscript in preparation). The lack of vertical circulation within the lake, probably caused by density stratification, prevented bioturbation, thus permitting the preservation of these laminae. The occurrence of pyrite and siderite[3,4] supports the suggestion of an oxygen-depleted deep water body. Further evidence for density stratification is provided by the presence of porphyrins related to the bacteriochlorophyll *d* series, which originate from the anaerobic phototrophic bacteria *Chlorobiaceae*[5].

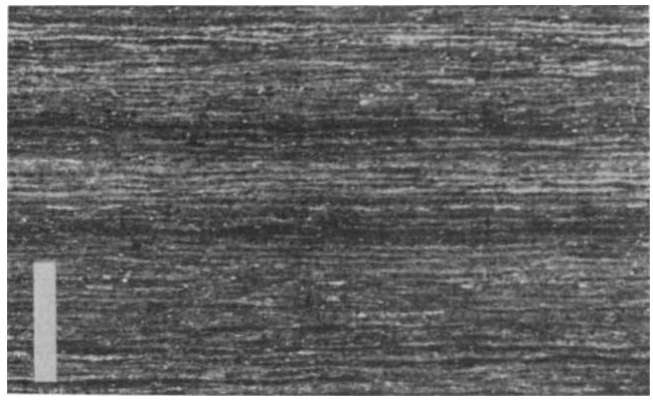

Fig. 1 Cross-section of a typical laminated oilshale from the Messel Formation. Light-coloured microlaminae are composed of *Tetraedron* remains, and dark layers represent background sediment. Scale bar, 2.0 mm.

Examination of a large number of the organic-rich laminae by scanning electron microscopy (SEM) revealed a predominance of small sculptured bodies, relatively uniform in size (5-10 μm, Fig. 2), which are considered to be the cell-wall remains of unicellular algae[4]. A sharp delineation was observed between the base of these nearly pure algal laminae and the inorganic laminae. This alternating sequence results from the sedimentation of algal debris, originating in annual blooms of these organisms, superimposed on the mainly inorganic, terrestrially derived background (K.G., manuscript in preparation).

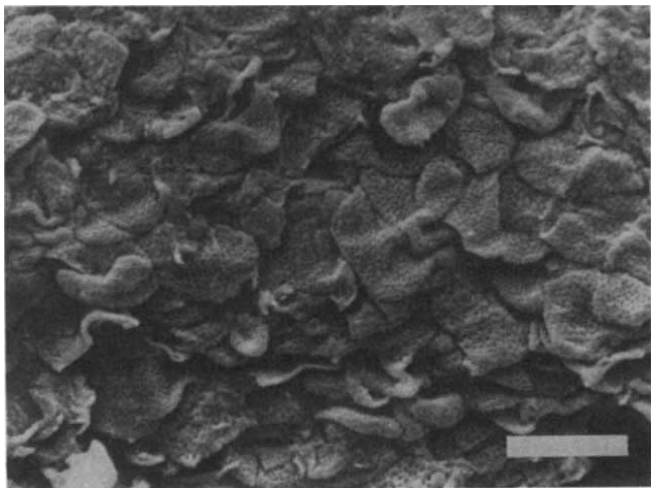

Fig. 2 Scanning electron micrograph image of a *Tetraedron* microlamina from the Messel Oil Shale. Note the dense packing of cell-wall remains. Scale bar, 10 μm.

The cell-wall remains comprise the most common biogenetic component and are thus believed to represent the predominant part of the organic matter in the Messel Oil Shale (K.G., manuscript in preparation). Their accumulation in distinct layers made it possible to obtain almost pure samples of algal-derived organic matter by physically removing the algal laminae from the background sediment using a sharp scalpel. The algal cells are pillow-shaped, with either a wart- or net-like surface structure (Fig. 3*a*)[4,6]. Transmission electron microscopy (TEM) studies of cross-sections revealed internally homogeneous wavy cell walls varying in thickness from 0.04 μm between, and 0.2 μm at, the corrugations. All these features (size, shape, surface pattern, preserved wall structure) are very similar to a species of the extant chlorococcal genus *Tetraedron* (K.G., manuscript in preparation).

The outer morphology of the Messel fossils is virtually indistinguishable from the extant *Tetraedron minimum* (Fig. 3*b*). Its single cells are quadrangular and flattened (pillow-like), 5–20 μm long and 3–8 μm thick. The angles are rounded, tapering into a short papilla[7,8] with surfaces covered either by small verrucae or by an irregular network, depending on the cell size. The thick cell wall is composed of three layers[9]. This cosmopolitan species occurs abundantly in the plankton of slightly eutrophized fish-ponds, lakes and rivers[7,8].

Tetraedron cell-wall remains appear to be by far the most important constituents of the organic matter in the Messel Oil Shale. We therefore attempted to chemically characterize the insoluble cell-wall material of the extant *T. minimum* and its fossil counterpart using flash-pyrolysis gas chromatography/mass spectrometry (Py-GCMS), to shed light on the formation and structure of the Messel shale kerogen. It must be noted that the assumed contribution of several other types of microbial organisms, such as dinoflagellates and chlorobium-type bacteria, to the organic matter of the Messel Oil Shale is based mainly on lipids, which comprise at most 5% of the organic matter[5,10].

The Py-GCMS total-ion chromatogram of a Messel Oil Shale sample, highly enriched with *Tetraedron* cell-wall remains, and that of the isolated cell walls of *T. minimum*, are shown in Fig. 4. Both chromatograms are dominated by homologous series of straight-chain α,ω-alkadienes, alk-1-enes and alkanes ranging from C_6 to C_{31}. The longer-chain alkanes show a slight preference for odd, rather than even, carbon number. The strong similarities between both pyrolysates indicates the presence of an insoluble, non-saponifiable aliphatic macromolecular structure in the cell walls of the extant *T. minimum* and its fossil counterpart. Based on these results, the *Tetraedron* cell-wall polymer appears to be similar to the insoluble, non-hydrolysable highly aliphatic biopolymers present in plant cuticles[11–13] and all three races of *Botryococcus braunii* algae[14,15]. It should be noted, however, that in the extant *T. minimum* this macromolecular structure comprises only a minor part (~5 wt%; E.W.T., unpublished results) of the total biomass, whereas it is abundantly present in the *Tetraedron*-enriched Messel sample. During diagenesis, the labile components (for example, polysaccharides) of the *Tetraedron* cells are presumably degraded, leading to relative enrichment of the aliphatic cell-wall biopolymer in the Messel Oil Shale kerogen. The selective preservation and relative enrichment of similar biopolymers has been observed previously (refs 14, 15, and E.W.T., J. H. F. Kerp and J.W. de L., manuscript in preparation).

On the basis of the accumulating evidence for the direct contribution of *in situ* insoluble organic substances to kerogen[11–18] and of the abundant presence of *n*-alkanes and *n*-alkenes in the pyrolysates of almost any oil-prone kerogen[19], it is suggested that the selective preservation of resistant macromolecular structures represents an alternative mechanism for the formation of kerogen (E.W.T., J. H. F. Kerp and J.W. de L., manuscript in preparation). This contrasts with the currently accepted theory whereby kerogen results from an abiological random polymerization of monomers derived from the biodegradation of biopolymers, such as polysaccharides and proteins, and from existing aliphatic lipid moieties[20,21].

Kerogens with a suitable hydrogen/carbon ratio are believed to generate oil at high temperature and pressure[20]. It has been speculated that *n*-alkanes present in crude oils are thermally derived from the aliphatic lipid moieties through defunctionalization[20]. Maturation experiments have already shown, however, that the insoluble, non-hydrolysable highly aliphatic biopolymer, isolated from the cuticular membranes of the extant *Agave americana* (E.W.T. *et al.*, manuscript in preparation), yield long-chain alkanes under thermal stress, indicating the oil potential of these aliphatic biopolymers.

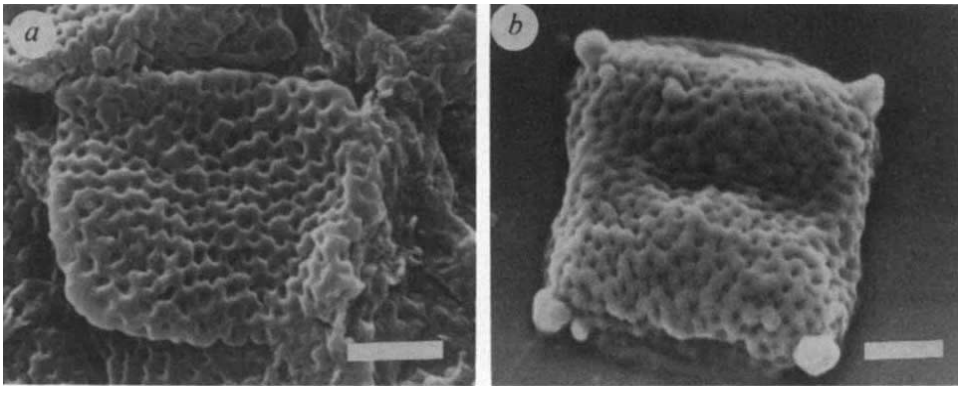

Fig. 3 Scanning electron photomicrographs of single *Tetraedron* cells. *a*, *Tetraedron sp.* from the Eocene Messel Oil Shale; scale bar, 2 μm. *b*, Extant *T. minimum* (strain SAG 44.81); scale bar, 2 μm. Notice the similarity in the surface patterns. Papillar processes at the cell angles do not occur or are not preserved in the Messel *Tetraedron sp.*

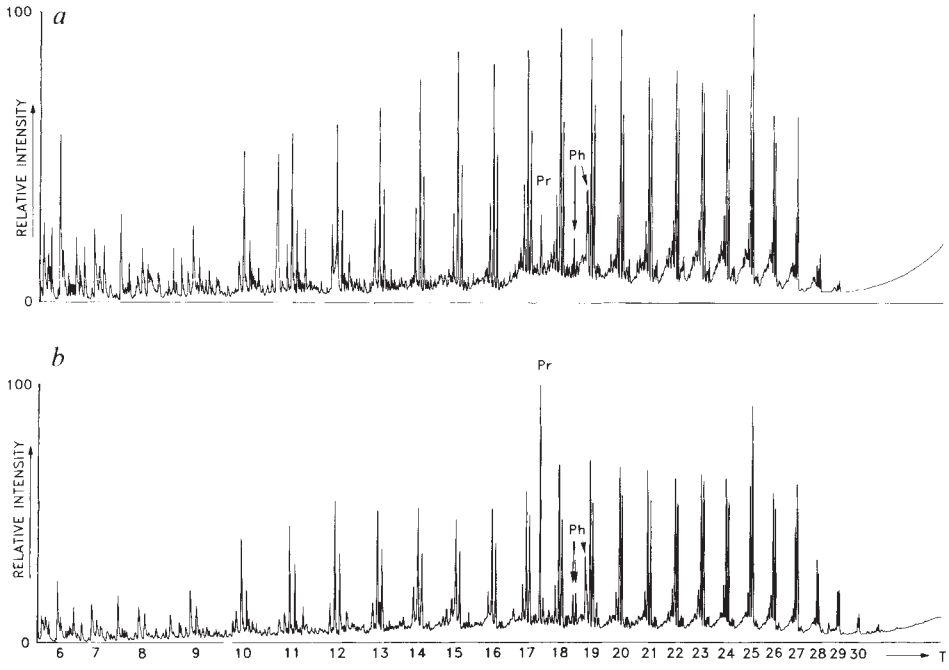

Fig. 4 Total-ion chromatograms of Py-GCMS analyses of *a*, isolated cell wall of *T. minimum*, and *b*, *Tetraedron*-enriched Messel Oil Shale. Isolation of the cell walls of *T. minimum* was achieved by extraction, saponification and acid hydrolysis, carried out according to methods described previously (refs 22, 23 and M. E. C. Moers *et al.*, manuscript in preparation). Details of the Py-GCMS analyses have been described before[24]. Instrumental conditions were: Curie-point temperature 770 °C; Gas-chromatographic separation was achieved on a fused silica column (length = 25 m; inner diameter = 0.31 mm) coated with chemically bonded CPSil 5; temperature programme of the GC oven comprised heating from 0 to 320 °C at 3 °C min^{-1}, then holding at 320 °C for 20 min; mass spectra were obtained at an ionization voltage of 70 eV. Peak identification is as follows: the numbers refer to the homologous series of α,ω-alkadienes, *n*-alk-1-enes and *n*-alkanes; Pr denotes pristenes, probably originating from bound tocopherol[25]; Ph denotes phytadienes, probably originating from chlorophylls[26].

Several studies are currently being performed to elucidate the structures of these types of resistant aliphatic biopolymers and to determine the extent of their occurrence.

The unusually good preservation of organisms in the Messel Oil Shale thus enables scientists to investigate interrelationships of fundamental importance in geosciences. The plans for rubbish disposal at the former open-cut mine in Messel should therefore be abandoned to prevent a unique site from being lost forever.

The unialgal culture for the SEM and geochemical studies was obtained from the collection of algae of the Institute for Plant Physiology, University of Göttingen (strain SAG 44.81, *T. minimum*). We would like to thank Dr Mollenhauer of the Algological Department of the Research Institute, Senckenberg, who was engaged in the cultivation of *Tetraedron* strains, and M. Baas of the TU Delft for technical assistance. This work was partly supported by the Deutsche Forschungsgemeinschaft (DFG) (Projekt Schaarschmidt 178/6) and the Netherlands Foundation for Earth Science Research (AWON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Received 25 July; accepted 3 November 1988.

1. Tobien, H. *Notizbl. hess. Landesamt. Bodenforsch.* **96,** 111–119 (1968).
2. Von Koenigswald, W. & Michaelis, W. *Geol. Jb. Hessen* **112,** 5–26 (1984).
3. Irion, G. *Natur Mus., Frankf.* **107,** 213–218 (1977).
4. Goth, K. *Cour. Forsch.-Inst. Senckenberg* **85,** 209–211 (1986).
5. Hayes, J. M., Takigiku, R., Ocampo, R., Callot, H. J. & Albrecht, P. *Nature* **329,** 48–51 (1987).
6. Püttmann, W. & Goth, K. *Cour. Forsch.-Inst. Senckenberg* **102** (in the press).
7. Kováčik, L. *Arch. Hydrobiol. Suppl.* **46,** 354–391 (1975).
8. Komárek, J. & Fott, B. *Das Phytoplankton des Süßwassers, 7.Teil, 1.Hälfte, Chlorophyceae (Grünalgen) Ordnung: Chlorococcales* 695–700 (Schweizerbart, Stuttgart, 1983).
9. Kováčik, L. & Kalina, T. *Arch. Hydrobiol. Suppl.* **46,** 433–444 (1975).
10. Ourisson, G., Mattern, G. & Albrecht, P. *J. chem. Soc.* D **22,** 1570–1571 (1970).
11. Nip, M., Tegelaar, E. W., de Leeuw, J. W., Schenck, P. A. & Holloway, P. J. *Naturwissenschaften* **73,** 579–585 (1986).
12. Nip, M. *et al.* in *Advanced Organic Geochemistry 1985* (eds Leythaeuser, D. & Rullkötter, J.) 769–778 (Pergamon, Oxford, 1986).
13. Nip, M. *et al Geochim. cosmochim. Acta* (in the press).
14. Largeau, C., Derenne, S., Casadevall, E., Kadouri, A. & Sellier, N. in *Advanced Organic Geochemistry 1985* (eds Leythaeuser, D. & Rullkötter, J.) 1023–1032 (Pergamon, Oxford, 1986).
15. Derenne, S., Largeau, C., Casadevall, E., Tegelaar, E. W. & de Leeuw, J. W. *Fuel Process. Tech.* (in the press).
16. Chappe, B., Albrecht, P. & Michaelis, W. *Science* **217,** 65–66 (1982).
17. Philp, R. P. & Calvin, M. *Advanced Organic Geochemistry 1975* (eds Campos, R. & Goni, J.) 735–752 (Enadisma, Madrid, 1976).
18. Philp, R. P. & Calvin, M. *Nature* **262,** 134–136 (1976).
19. Van de Meent, D., Brown, S. C., Philp, R. P. & Simoneit, B. R. T. *Geochim. cosmochim. Acta* **44,** 999–1013 (1980).
20. Tissot, B. P. & Welte, D. H. *Petroleum Formation and Occurrence.* (Springer, Berlin, 1984).
21. *Kerogen—Insoluble Organic Matter from Sedimentary Rocks* (ed. Durand, B.) (Technip, Paris, 1980).
22. Holloway, P. J. in *CRC Handbook of Chromatography, Lipids* Vol. 1 (ed. Mangold, H. K.) 321–334 (CRC, Boca Ranton, 1984).
23. Holloway, P. J. in *CRC Handbook of Chromatography, Lipids* Vol. 1 (ed. Mangold, H. K.) 347–380 (CRC, Boca Ranton, 1984).
24. Tegelaar, E. W. *et al. J. anal. appl. Pyrolysis* (in the press).
25. Goossens, H., de Leeuw, J. W., Schenck, P. A. & Brassell, S. C. *Nature* **312,** 440–442 (1984).
26. Van de Meent, D., de Leeuw, J. W. & Schenck, P. A. *Adv. org. Geochem. 1979* (eds Douglas, A. G. & Maxwell, J. R.) 469–474 (Pergamon, Oxford, 1980).

The critical slip distance for seismic faulting

C. H. Scholz

Lamont-Doherty Geological Observatory and Department of Geological Sciences, Columbia University, Palisades, New York 10964, USA

Experimentally based friction laws[1,2] have been found to predict virtually the entire range of observed behaviour of natural faults[3,4]. These laws contain a critical slip distance, *L*, which plays a key role in determining the degree of fault instability, the size of the zone of earthquake nucleation, the frictional breakdown width, and the proportion of pre- and post-seismic slip to co-seismic slip. In laboratory measurements *L* is found to be about 10^{-5} m, but modelling results show that it must be about 10^{-2} m if natural earthquake behaviour is to be simulated. The discovery that fault surfaces are fractal over the scale range 10^{-5}–10^{5} (refs 5, 6), even for faults with large net slip, has confused the problem of scaling this parameter from laboratory experiments to natural faults, because fractal surfaces have no characteristic length. Here I show that geometrically unmated fractal surfaces, when in contact under