

Biochemical evolution. I. Polymerization on internal, organophilic silica surfaces of dealuminated zeolites and feldspars

(biological evolution/volcanic emissions)

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Contributed by Joseph V. Smith, December 29, 1997

ABSTRACT Catalysis at mineral surfaces might generate replicating biopolymers from simple chemicals supplied by meteorites, volcanic gases, and photochemical gas reactions. Many ideas are implausible in detail because the proposed mineral surfaces strongly prefer water and other ionic species to organic ones. The molecular sieve silicalite (Union Carbide; = Al-free Mobil ZSM-5 zeolite) has a three-dimensional, 10-ring channel system whose electrically neutral Si-O surface strongly adsorbs organic species over water. Three -O-Si tetrahedral bonds lie in the surface, and the fourth Si-O points inwards. In contrast, the outward Si-OH of simple quartz and feldspar crystals generates their ionic organophobicity. The ZSM-5-type zeolite mutinaite occurs in Antarctica with boggsite and tschernichite (Al-analog of Mobil Beta). Archean mutinaite might have become de-aluminated toward silicalite during hot/cold/wet/dry cycles. Catalytic activity of silicalite increases linearly with Al-OH substitution for Si, and Al atoms tend to avoid each other. Adjacent organophilic and catalytic Al-OH regions in nanometer channels might have scavenged organic species for catalytic assembly into specific polymers protected from prompt photochemical destruction. Polymer migration along weathered silicic surfaces of micrometer-wide channels of feldspars might have led to assembly of replicating catalytic biomolecules and perhaps primitive cellular organisms. Silica-rich volcanic glasses should have been abundant on the early Earth, ready for crystallization into zeolites and feldspars, as in present continental basins. Abundant chert from weakly metamorphosed Archean rocks might retain microscopic clues to the proposed mineral adsorbent/catalysts. Other framework silicas are possible, including ones with laevo/dextro one-dimensional channels. Organic molecules, transition-metal ions, and P occur inside modern feldspars.

Although extended Darwinian natural selection coupled with Mendel–Watson–Crick genetic inheritance/mutation provides a plausible framework for integrating the patchy paleontological record with the increasingly complex biochemical zoo of the present Earth, the actual chemical beginning of “life” still poses major challenges (1–11). How could the first replicating and energy-supplying molecules have been assembled from simpler materials that were undoubtedly available on the early proto-continents? Most cosmologists abhor spontaneous generation—or the wave of a magic wand from “God” or inheritance of “living” organisms from outer space. They search for a plausible integrated geological/biochemical framework that allows Oparin–Watson–Crick–Darwin biological evolution to begin on Earth using scientific features testable in a chemical laboratory and perhaps even observable in geologic

specimens. Bernal (1) preferred “life” to begin by catalytic assembly on a mineral surface, but all attempts to assemble an integrated scheme of physicochemical processes have significant weaknesses. Concepts of catalysis that use organic compounds dispersed in aqueous “soups” require a mechanism for concentrating the organic species next to each other on a catalytic substrate. After catalysis, the biochemically significant polymers such as polypeptides and RNAs must be protected from photochemical destruction by solar radiation and must not be heated too much. Only then could the energy-consuming replication/mutation of polymers yield the first primitive organisms. I am not concerned here with the subsequent irreversible forward march to increasing diversity of species immune to Earth’s slings and arrows, although mineral surfaces are important for lichens and bacteria.

The new concept is that certain materials have internal surfaces that are both organophilic and catalytic, allowing efficient capture of organic species for catalytic assembly into polymers in a protective environment. These physicochemical features are related to the state-of-the-art for zeolite catalysts in the chemical industry, the observed properties of naturally occurring zeolite and feldspar minerals, and a plausible framework for the accretion and early history of the Earth’s crust and atmosphere. The accompanying paper in this issue of *Proceedings* (12) on weathered feldspars contains relevant concepts and observations.

The present proposal does not provide a detailed recipe for catalytic formation of a replicating polymer. However, it may provide a conceptual framework from which plausible recipes will ensue from laboratory experiments and crystal-chemical modeling. Although all biochemical “life” might have developed from a single left-handed chance event that has essentially zero “probability” in terms of conventional ideas for chemical syntheses, multiple events of high probability are preferred, of which one event may have been the actual trigger. It would be wonderful, of course, if polypeptide chains, or even better RNA replicator/catalysts, turned up in actual experiments on the proposed organophilic materials. It would be even more thrilling if a fragment of the abundant chert or other sediments in surviving Archean terranes had survived metamorphism to preserve some convincing evidence of primary biocatalysis. Unless such encouraging evidence turns up, caution is warranted in proposing that “life” began merely as a trivial scientific event on a mineral catalyst. (From a philosophical viewpoint, this is only a very restricted scientific aspect of “life,” namely the assumed common ancestry and subsequent linkage of all biochemicals found in organisms. The complex debates on the cultural, societal, religious, and humanistic aspects of “life” are linked to the biochemistry but only at a simple level.)

First, the evidence from synthetic molecular sieves: general review (12). Silicalite, a molecular sieve invented by chemists

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at Union Carbide Corporation (13), can be as close to pure silica as the quality of the materials used for synthesis. Its three-dimensional channel system is bounded by 10-rings from a four-connected tetrahedral framework (14). All Si atoms are surrounded by four oxygen atoms, and the stereogeometry is such that the channels are lined by a three-connected net with the fourth Si-O bond pointing into the silica. Hence, there are no silanol (Si-OH) species projecting into the channels. Silicalite can adsorb molecules up to 6 Å across, including benzene. Figure 5 of Flanigen *et al.* (13) demonstrates that silicalite has a remarkable organophilic/hydrophobic nature, thus: "Traces of methanol, propanol, butanol, phenol, 1,4-dioxane, pentane and hexane have been removed from water" and "Silicalite possesses a remarkable stability for a 33% porous crystal. It is stable in air to over 1,100°C, and only slowly converts to an amorphous glass at 1,300°C. It is stable to most mineral acids but reacts with HF similarly to quartz."

The reason for the organophilic/hydrophobic nature is quite simple. Oil and water do not mix because the water molecules prefer ionic bonding and the organic molecules of the oil prefer van der Waals bonding. Hence, for a truly neutral surface, water molecules remain bonded to each other in an ionic environment, allowing the organic molecules to adsorb onto the neutral surface by van der Waals bonding. This verified experimental feature is the key to the present proposal. Any material with a truly neutral silica surface with no projecting silanols should be organophilic/hydrophobic. Quartz and various other silica polymorphs have outward bonds that become silanols in an aqueous system; hence, they are not organophilic like silicalite.

Silicalite matches the end-member of the ZSM-5 structural series of molecular sieve zeolites synthesized by chemists of Mobil R&D Corporation (15–18) and is a member of the pentasil structural group. As Al³⁺ replaces Si⁴⁺, the hydrophobic/organophilic nature weakens; the zeolite framework becomes more ionic, and the compensating extra-framework cations contribute to the electrostatic crystal field. Furthermore, after activation by heating, the molecular sieve becomes a powerful catalyst whose activity is linearly proportional to the Al substitution. The positions of the Al atoms at low concentration are not accurately known. Computer calculations indicate that disorder should be significant (19), but there should be some tendency for near-uniform spacing to minimize the electrostatic energy. Hence, I propose that a silicalite–ZSM-5 material that has just a trace of distributed Al could not only scavenge organic molecules but act as a catalyst for polymerization. Alternatively, an inhomogeneous silicalite–ZSM-5 intergrowth could capture organic molecules in the silicalite regions, ready for transfer to adjacent Al-bearing catalytic areas. Testifying to shape-selective sorption by silicalite is its use in column chromatography for isolation of monoethylalkanes from crude oils (20). The atomic positions of framework atoms and sorbed molecules, the synthesis of a wide range of Al/Si compositions, the removal and insertion of Al in secondary processes, and the infra-red characterization of hydroxyls, etc., are documented strongly (12). Silicalite is thermally unstable with respect to quartz, cristobalite, and tridymite, but more stable than silica glass or high pressure coesite and stishovite (21).

Although zeolite synthesis and catalysis are based on some general features that are well understood (22–32), most zeolites pose complex challenges that are resolved only at the empirical experimental level. The ZSM-5–silicalite series generally is synthesized with sodium and a templating agent, especially a tetrapropylammonium ion, but template-free syntheses are described (28, 29, 33). Silica gel was transformed into microcrystalline balls of silicalite (34) and into various ordered shapes (35). ZSM-5 crystals were de-aluminated by acid leaching/steaming/acid leaching and other methods (36–41). From the complex literature on adsorption of organic

molecules into the ZSM-5–silicalite and catalytic activity, the following representative papers are selected: linear decrease of hydrophobicity with Al substitution (42); methanol adsorption on acidic ZSM-5 and conversion to gasoline, xylene, etc. (43); water adsorption and evidence for insignificant interaction with a dehydroxylated silica surface (44, 45); dependence of relaxation time of CH₂ and CH₃ groups on chain length and degree of adsorption of amines and conversion to diamines upon heating (46); structural positions, diffuse-reflectance spectroscopy, and two-patch heterogeneous model for adsorption of benzene (47–51); structural perturbation of framework geometry of H-ZSM-5 by sorbed *p*-xylene and naphthalene (51–53); adsorption of CO on H-ZSM-5 and a hydrothermal product (54); and nature of silanol groups, defects, and structural heterogeneities in relation to water and benzene adsorption (55–58).

Based on this overall concept of a van der Waals silica-rich surface, Pandora's box of ≈4,000 minerals was examined for potential candidates as biochemical adsorbent/catalysts. In general, most ionic minerals, including clay minerals, are unpromising. The obvious candidates come from three mineral families: zeolites, feldspars, and silicas.

From the family of zeolitic and related silica-rich species, I select:

- mutinaite, as above,
- tschernichite, the Al-bearing analog of the Mobil high silica zeolite Beta (59–67), which has a remarkable polytypic domain structure with a 10-ring, three-dimensional channel system,
- boggsite, with a 10- to 12-ring, three-dimensional channel system, which occurs with tschernichite in Columbia basalt (68),
- faujasite, the natural analog of Linde Type Y, the main industrial catalyst with a 12-ring, three-dimensional channel system; can be de-aluminated by various processes (not referenced in detail); known only as a very rare mineral until discovery in sedimentary beds of diagenetic tuffs in Jordan (69),
- mordenite, an easily de-aluminated, common, high silica natural zeolite, with industrial analogs, whose one-dimensional channel can be blocked by either faulting or an Al-complex (70–90),
- mesoporous silicas with nanometer channels and mainly hydrophilic surfaces but some organophilic behavior (91–103),
- all-silica analog (Chevron SSZ-24) of Union Carbide aluminophosphate AIPO-5, for which one might envisage unipolar segments of aluminophosphate interleaved with nonpolar silica down the 12-ring cylindrical channel (104–105), and
- theoretical chiral frameworks in the database of the Consortium for Theoretical Frameworks, University of Chicago, being prepared for publication.

Zeolites would have grown from volcanic ash, as in the present Earth, would have been transformed by ion exchange, heating, and recrystallization, and ultimately would have transformed to the more stable feldspars. In brief, the type of zeolite generated from volcanic ash depends on the chemical composition of the ash and the fluids that are involved in the zeolite growth, the temperature, and the subsequent metamorphism (106, 107). Large pore zeolites are rare (61–63, 68, 108) and would tend to transform into small pore zeolites and feldspars. Layered Na-silicate hydrates like magadiite might have been precursors to high silica zeolites including mordenite (109). Silica minerals and feldspars would have occurred in outcrops of volcanic, plutonic, sedimentary, and metamorphic rocks. The origin of abundant, silica-rich cherts, commonly interleaved with iron oxides in banded iron formations from the

Archean, is unclear (110), but detailed chemical microscopy is warranted. Whatever the details, there must have been abundant opportunities for the formation of silica-rich organophilic surfaces on the early Earth.

Feldspars must have been exposed to the atmosphere on the proto-continents (111), based on the survival of various metamorphosed volcanic and granitic rocks (110) back to ≈ 4 Gybp (Giga year before present). An extraordinary range of grooved and honeycombed surfaces must have been produced by weathering (8, 112, 113), whose chemical and physical nature would have some communality with that of the present day. It is worth exploration the possibility that the honeycombs contained organophilic spots, perhaps at dimples where the topologic linkage would resemble that of silicalite. Such mixed organophilic/hydrophilic-catalytic spots might be protected from direct ultraviolet radiation. Significant substitution of B, Mg, P, Ti, Mn, Fe, Cu, Zn, etc., for Al and Si in the framework and of NH_4 in alkali sites of feldspars (112, 114) might be useful for provision of elements needed in biomolecules. Fourier transform infrared spectroscopy of anorthite macrocrysts from island arc basalts has revealed the $-\text{CH}_2-$ stretching band, which disappeared on heating to ≈ 510 K (115). Hydrocarbons are present along with microcrystals of Cu metal in related anorthite macrocrysts (116). Other reported lattice-stabilized species include: CH_3 , C_2H_5 , NO_2 , and O^- (114). The thermoluminescence of feldspars is bleached rapidly by sunlight (8).

Silica has an enormous range of structural types that continues to grow as new synthesis procedures are developed. The stable minerals quartz (low temperature), cristobalite-tridymite polytypic series (high temperature), coesite, and stishovite are compact, and their surfaces are expected to be ionic, except perhaps at defects. Melanophlogite is a clathrasil that encloses volcanic species, but its tight windows are not conducive to biochemical polymerization. Silicalite presently does not have a mineral analog, but a search should be made for Al-poor mutinaite in which de-alumination might have occurred. Fluorine-rich silicic volcanic ash might be a suitable starting material for crystallization of a silicalite-mutinaite.

To conclude, my ideas on the geological background are placed in the context of a review (117) of the heterogeneous growth of meteorites and planets, especially the Earth and Moon. The specialist literature on the origin of life and molecular evolution contains many ideas and experimental data that link up nicely with the above literature from the chemical industry and mineralogy: early solar system (118); carbonaceous chondrites (119, 120); heavy meteorite bombardment (121, 122); geological setting of earliest life forms (123); ancient sediments (124, 125); hot springs and oceans (126, 127); prebiological activity in volcanic processes (128, 129); alteration of obsidian to zeolites (130); adsorption of small molecules, including amino acids and growth of peptide chains, on macroporous silica (131–136); asymmetric adsorption by quartz (137); synthesis of amino acids on X- and Y-type faujasite zeolites (138); energy from feldspar and silica radioactivity and strain (139); heterogeneous chemistry on minerals (140); synthesis of oligopeptides with Beta, mordenite, faujasite, and kaolinite (141); models for prebiotic synthesis of RNA on aluminous zeolites (142) and montmorillonite (143); binding of adenine to montmorillonite and hydroxylapatite (144); instability of adenine in water (145); possible role of catalytic RNA (146–151); molecular replication (152); *in vitro* evolution of nucleic acids (153); origin and amplification of biomolecular chirality (154); chiral symmetry breaking during self-assembly of monolayers from chiral purine (155); kinetic cooperativity in prebiotic catalysts (156); crucial stages in origin of animate matter (157); and sequence of biological chirality (158).

In brief, the Earth grew heterogeneously from a mess of materials assembled from the condensed solar nebula. The first materials from the inner solar system were mainly similar

to reduced enstatite-iron meteorites (159). Later materials from the outer solar system resembled oxidized olivine-rich meteorites, together with various ices. Melting began early, and heat was lost rapidly to space via volcanism and atmospheric processes. The impact history is unclear because the lunar record does not transfer directly to the Earth. Early atmospheres were swept away; the earliest surviving zircon grain dates to ≈ 4.3 Gybp; and the earliest metamorphosed rocks date to ≈ 4 Gybp (160). Volcanism in the next 0.5 Gy would be 5–10 times more intense than now, as biological evolution took off. Most of the numerous patches of continental crust, a few hundreds of kilometers across, would be separated by small ephemeral oceans, and sink into the crust by polygonal tectonics, to be reworked into a plum pudding mantle. Surviving pieces of reduced and oxidized mantle would continue to melt, and new pieces of mixed mantle would be melting to yield a cornucopia of volcanic rocks ranging from olivine-rich komatiites through basalts to feldspar/silica-rich rhyolites. The mantle has provided diamonds with N lamellae and a wide range of reduced mineral inclusions. Volcanic glass with ≈ 70 – 75% SiO_2 would be particularly reactive. Miller-type electrical activity in some of the volcanic explosion debris might have converted reduced C-N-H species from the mantle into amino acids, etc. Star dust and other fine condensates from comets and asteroids would have entered the atmosphere at various velocities, some to be flash-melted and some to survive. In general, the atmosphere was not strongly reduced, could have been slightly oxidizing on average, and contained substantial CO and CO_2 (161–163). For brief periods after impacts and major volcanic eruptions, a range of atmospheric gas mixtures would have been available for photochemical and electrical reactions. Ultimately, pieces of crust would have become sufficiently refractory to survive as the cratonic nuclei of present continents (164), perhaps because CO_2 flushed out the water. Ephemeral lakes and oceans might have had a wide range of exotic compositions before reaction with mineral buffers in basalts and sediments. Finally, there would have been wide excursions of temperature and precipitation from day to day, season to season, pole to equator, and ocean to mountaintop comparable to the present range, certainly covering the range for zeolite synthesis, adsorption, and catalysis.

Hence, it is plausible to consider that sedimentary layers of volcanic ash would have been soaked in solutions carrying a wide range of ions and molecules. Crystallization to zeolites, layer silicates, feldspars, carbonates, etc., would have occurred in ways similar to those of today. High silica zeolites like mordenite, tschernichite, and mutinaite might have become de-aluminated during hot/cold/wet/dry cycles to generate catalytic reactors for concentration and polymerization of organic species. More exotic is the possibility that feldspar crystals in granite tors exposed to the atmosphere became weathered by hot/cold/wet/dry cycles and that the honeycombed weathering crusts became sufficiently organophilic in local spots to pull in C-N-H species directly from the atmosphere. Even more exotic is the possibility that the catalytic reactors generated amino acids directly from gases in the atmosphere, thus obviating any need for meteoritic input or electrochemical reactions in the atmosphere. Perhaps all types of inputs were useful. All of these ideas can be tested at the conceptual and experimental level, as detailed in later papers. Perhaps some indicative evidence remains in Archean chert and other sediments; western Australia may offer the best hope of finding silica relics retaining microscopic clues to early catalysis through only a low grade metamorphic haze (165–166).

If the assembly of (for example) RNA species on an organophilic catalytic surface becomes reproducible under controlled conditions in many laboratories, thus meeting the standard scientific aim of universal reproducibility, would there be philosophic and religious consequences? This is a very challenging question with no simple answer. Did left-handed

life really began only once, or did life succeed after many syntheses of replicable/catalytic biomolecules? Moreover, was there merely a fortuitous imbalance of laevo over dextro protomolecules on the early Earth, with ultimate capture of the sequence of biological evolution by lucky laevo; or was predominance of laevo forced by circularly polarized light from the cosmos (154), operating in conjunction with the lunar orbit. Clearly, there would remain many uncertainties in the actual evolution of biochemical life, even if an inorganic beginning had become more physically possible.

This idea was originally triggered in 1986 by correspondence with Euan Nisbet (University of Saskatchewan, Canada) about his proposal (123) that RNA should be linked with hydrothermal systems and zeolites and by my criticism of October 1986 that a hydrophilic zeolite had problems that an organophilic species like sicalite would not. The recent discovery of mutinaite by Ermanno Galli and colleagues at Ferrara and of the wonderful honeycombs in feldspars from the Shap granite by Ian Parsons and Martin Lee gave sufficient plausibility to warrant preparation of this paper. I thank Ian Parsons (Edinburgh, Scotland), Peter Buseck (Tempe, AZ), and Werner Baur (Chicago) for discussions on feldspars, zeolites, and silica minerals and for word-by-word review; I also thank many chemists from Union Carbide Corporation/UOP (especially Edith Flanigen, Lyle Patton, John Sherman, Steve Wilson, Robert Broach, and the late Donald Breck) for the opportunity to consult on industrial zeolites and to give a talk on the present idea. The symbiosis between industrial chemistry/engineering and academic geosciences testifies to the creative power of crossing the disciplines. Joseph J. Pluth works closely with me on the crystallography and chemical interpretation of zeolites. This paper is part of the Synchrotron-X-ray Micrometer/Electron-Nanometer Project, which couples the Center for Advanced Radiation Sources at the University of Chicago with the Facility for High Resolution Electron Microscopy at Arizona State University. My research work on zeolites was funded by Union Carbide Corporation/UOP, National Science Foundation/Chemistry Division, American Chemical Society/Petroleum Research Foundation, Exxon Educational Foundation, Mobil Research Foundation, and Chevron Corporation. My ideas on the origin of the Earth/Moon system developed during the Apollo Program funded by National Aeronautics and Space Administration, and I am indebted to Brian Windley (Leicester, UK) and Barry Dawson (Edinburgh, Scotland) for sharing their catholic knowledge of the ins and outs of the crust and mantle. William Cochran, Helen Megaw, William Taylor, and many research students, including Jack Zussman at the Cavendish/Crystallographic Laboratory of Cambridge University, excited my specific interests in the crystallography of life and the structure of minerals. J. D. Bernal (London) and W. L. Bragg (Manchester and Cambridge) have left a wonderful legacy of ideas on the origin and development of life.

- Bernal, J. D. (1967) *The Origin of Life* (Weidenfeld & Nicholson, London).
- Oparin, A. I. (1968) *Genesis and Evolutionary Development of Life* (Academic, New York).
- Calvin, M. (1969) *Chemical Evolution: Molecular Evolution Toward the Origin of Living Systems on the Earth and Elsewhere* (Clarendon, Oxford).
- Watson, J. D. (1976) *Molecular Biology of the Gene*, (Benjamin, New York), 3rd ed.
- Miller, S. L. & Orgel, L. E. (1974) *The Origins of Life on Earth* (Prentice-Hall, Englewood Cliffs, NJ).
- Mayr, E. (1982) *The Growth of Biological Thought: Diversity, Evolution, and Inheritance* (Harvard/Belknap, Cambridge, MA).
- Cairns-Smith, A. G. (1982) *Genetic Takeover and the Mineral Origins of Life* (Cambridge Univ. Press, Cambridge, UK).
- Dyson, F. J. (1985) *Orgins of Life* (Cambridge Univ. Press, Cambridge, UK).
- Cairns-Smith, A. G. & Hartman, H., eds. (1986) *Clay Minerals and the Origin of Life* (Cambridge Univ. Press, Cambridge, UK).
- Fox, S. W. (1988) *The Emergence of Life* (Basic, New York).
- Kauffman, S. A. (1993) *The Origins of Order: Self-Organization and Selection in Evolution* (Oxford Univ. Press, Oxford).
- Smith, J. V. (1998) *Proc. Natl. Acad. Sci. USA* 95, 3366–3369.
- Flanigen, E. M., Bennett, J. M., Grose, R. W., Cohen, J. P., Patton, R. L., Kirchner, R. M. & Smith, J. V. (1978) *Nature (London)* 271, 512–516.
- Price, G. D., Pluth, J. J., Smith, J. V., Bennett, J. M. & Patton, R. L. (1982) *J. Am. Chem. Soc.* 104, 5971–5977.
- Kokotailo, G. T., Lawton, S. L., Olson, D. H. & Meier, W. M. (1978) *Nature (London)* 272, 437–438.
- Olson, D. H., Haag, W. O. & Lago, R. M. (1980) *J. Catal.* 61, 390–396.
- Olson, D. H., Kokotailo, G. T., Lawton, S. L. & Meier, W. M. (1981) *J. Phys. Chem.* 85, 2238–2243.
- von Ballmoos, R. & Meier, W. M. (1981) *Nature (London)* 289, 782–783.
- Ricchiardi, G. & Newsam, J. M. (1997) *J. Phys. Chem.* 101, 9943–9950.
- Hoering, T. C. & Freeman, D. H. (1984) *J. Chromatogr.* 316, 333–341.
- Johnson, G. K., Tasker, I. R. & Howell, J. V. (1987) *J. Chem. Thermodyn.* 19, 617–632.
- Flanigen, E. M. (1973) *Adv. Chem. Ser.* 121, 119–139.
- Lok, B. M., Cannan, T. R. & Messina, C. A. (1983) *Zeolites* 3, 282–291.
- Csicsery, S. M. (1984) *Zeolites* 4, 202–213.
- Jacobs, P. A. & Martens, J. A. (1987) *Synthesis of High-Silica Aluminosilicate Zeolites*, (Elsevier, Amsterdam).
- Lowe, B. M. (1988) in *Innovation in Zeolite Materials Science*, eds. Grobet, P. J., Mortier, W. J., Vansant, E. F. & Schulz-Ekloff, G. (Elsevier, Amsterdam), pp. 1–12.
- Milton, R. M. (1989) *Am. Chem. Soc. Symp. Ser.* 398, 1–10.
- Schwieger, W., Bergk, K., Freude, D., Hunger, M. & Pfeiffer, H. (1989) *Am. Chem. Soc. Symp. Ser.* 398, 274–290.
- Szostak, R. (1989) *Molecular Sieves: Principles of Synthesis and Identification*, (Van Nostrand Reinhold, New York).
- Flanigen, E. M. (1991) *Stud. Surf. Sci. Catal.* 58, 13–34.
- Kessler, H. (1992) in von Ballmoos, R., Higgins, J. B. & Treacy, M. M. J., eds. *Proceedings from the 9th International Zeolite Conference* (Butterworth-Heinemann, Boston), pp. 73–91.
- Helmkamp, M. M. & Davis, M. E. (1995) *Annu. Rev. Mater. Sci.* 25, 161–192.
- Shiralkar, V. P. & Clearfield, A. (1989) *Zeolites* 9, 363–370.
- Franklin, K. R. & Lowe, B. M. (1987) *Zeolites* 7, 135–142.
- Mann, S., Burkett, S. L., Davis, S. A., Fowler, C. E., Mendelson, N. H., Sims, S. D., Walsh, D. & Whilton, N. T. (1997) *Chem. Mater.* 9, 2300–2310.
- Fyfe, C. A., Gobbi, G. C. & Kennedy, G. J. (1983) *Chem. Lett.* 10, 1551–1554.
- Skeels, G. W. & Flank, W. H. (1983) *Am. Chem. Soc. Symp. Ser.* 218, 369–382.
- Lohse, U., Thamm, H., Noack, M. & Fahlke, B. (1987) *J. Inclusion Phenom.* 5, 307–313.
- Handreck, G. P. & Smith, T. D. (1990) *Zeolites* 10, 746–752.
- Alsdorf, E., Feist, M., Gross, T., Jerschewitz, H. J., Lohse, U. & Schwieger, M. (1990) *Z. Phys. Chem.* 271, 267–275.
- Kornatowski, J., Baur, M. H., Pieper, G., Rozwadowski, M., Schmitz, W. & Cichowlas, A. (1992) *J. Chem. Soc. Faraday Trans.* 88, 1339–1343.
- Nakamoto, H. & Takahashi, H. (1982) *Zeolites* 2, 67–68.
- Jacobs, P. A. & von Ballmoos, R. (1982) *J. Phys. Chem.* 86, 3050–3052.
- Scholle, K. F. M. G. J., Veeman, W. S., Post, J. G. & Van Hooff, J. H. C. (1983) *Zeolites* 3, 214–218.
- Pope, C. G. (1987) *J. Colloid Interface Sci.* 116, 221–223.
- Meinhold, R. H., Parker, L. M. & Bibby, D. M. (1986) *Zeolites* 6, 491–497.
- Taylor, J. C. (1987) *Zeolites* 7, 311–318.
- Talu, O., Guo, C. & Hayhurst, D. (1989) *NATO ASI Ser. Ser. E* 158, 53–62.
- Wang, H. P., Yu, T., Garland, B. A. & Eyring, E. M. (1990) *Appl. Spectrosc.* 44, 1070–1073.
- Mentzen, B. F. & Lefebvre, F. (1997) *Mater. Res. Bull.* 32, 813–821.
- Reischman, P. T., Schmitt, K. D. & Olson, D. H. (1988) *J. Phys. Chem.* 92, 5165–5169.
- Van Koningsveld, H., Tuinstra, F., Van Bekkum, H. & Jansen, J. C. (1989) *Acta Crystallogr. B* 45, 423–431.
- Van Koningsveld, H. & Jansen, J. C. (1996) *Microporous Mater.* 6, 159–167.

54. Szanyi, J. & Paffett, M. T. (1996) *Microporous Mater.* **7**, 201–218.
55. Hill, S. G. & Seddon, D. (1985) *Zeolites* **5**, 173–178.
56. Hunger, M., Kärger, J., Pfeifer, H., Caro, J., Zibrowius, B., Bülow, M. & Mostowicz, R. (1987) *J. Chem. Soc. Faraday Trans.* **83**, 3459–3468.
57. Zhdanov, S. P., Kosheleva, L. S. & Titova, T. I. (1988) *Dokl. Akad. Nauk. SSSR* **303**, 1171–1176 (Russian).
58. Chiang, A. S. T., Lee, C. K., Rudzinski, W., Narkiewicz-Michalek & Szabelski, P. (1997) *Stud. Surf. Sci. Catal.* **104**, 519–572.
59. Newsam, J. M., Treacy, M. M. J., Koetsier, W. T. & de Gruyter, C. B. (1988) *Proc. R. Soc. London Ser. A* **420**, 375–405.
60. Higgins, J. B., LaPierre, R. B., Schlenker, J. L., Rohman, R. C., Wood, J. D., Kerr, G. T. & Rohrbaugh, W. J. (1988) *Zeolites* **8**, 446–452, correction **9**, 398.
61. Smith, J. V., Pluth, J. J., Boggs, R. C. & Howard, D. G. (1991) *J. Chem. Soc. Chem. Commun.*, 363–364.
62. Boggs, R. C., Howard, D. G., Smith, J. V. & Klein, G. L. (1993) *Am. Mineral.* **78**, 822–825.
63. Galli, E., Quartieri, S., Vezzalini, G. & Alberti, A. (1995) *Eur. J. Mineral.* **7**, 1029–3102.
64. van der Waal, J. C., Rigutto, M. S. & van Bekkum, H. (1994) *J. Chem. Soc. Chem. Commun.*, 1241–1242.
65. de Menoral, L. C., Buckermann, W., Figueras, F. & Fajula, F. (1996) *J. Phys. Chem.* **100**, 465–467.
66. Kunkeler, P. J., Moeskops, D. & van Bekkum, H. (1997) *Microporous Mater.* **11**, 313–323.
67. Yang, C. & Xu, Q. (1997) *Zeolites* **19**, 404–410.
68. Pluth, J. J. & Smith, J. V. (1990) *Am. Mineral.* **75**, 501–507.
69. Ibrahim, K. & Hall, A. (1995) *Eur. J. Mineral.* **7**, 1129–1135.
70. Barrer, R. M. & Murphy, E. V. T. (1970) *J. Chem. Soc. A*, 2506–2514.
71. Barrer, R. M. & Klinowski, J. (1975) *J. Chem. Soc. Faraday Trans.* **3**, 690–698.
72. Kühl, G. H. (1977) *Am. Chem. Soc. Symp. Ser.* **40**, 96–107.
73. Karge, H. G. (1980) *Z. Phys. Chem.* **122**, 103–116.
74. Klinowski, J., Thomas, J. M., Anderson, M. W., Fyfe, C. A. & Gobbi, G. C. (1983) *Zeolites* **3**, 5–7.
75. Ratz, F., Freund, E. & Marcilly, C. (1983) *J. Chem. Soc. Faraday Trans.* **79**, 2299–2309.
76. Ripmeester, J. A., Majid, A. & Hawkins, R. E. (1983) *J. Inclusion Phenom.* **1**, 193–198.
77. Hays, G. R., Van Erp, W. A., Alma, N. C. M., Couperus, P. A., Huis, R. & Wilson, A. E. (1984) *Zeolites* **4**, 377–383.
78. Ratz, F., Freund, E. & Marcilly, C. (1985) *J. Chem. Soc. Faraday Trans.* **81**, 299–310.
79. Bodart, P., Nagy, J. B., Debras, G., Gabelica, Z. & Jacobs, P. A. (1986) *J. Phys. Chem.* **90**, 5183–5190.
80. Musa, M., Tarina, V., Stoica, A. D., Ivanov, E., Plostinaru, D., Pop, E., Pop, G., Ganea, R. & Birjega, R. (1987) *Zeolites* **7**, 427–432.
81. Meyers, B. L., Fleisch, T. H., Ray, G. J., Miller, J. T. & Hall, J. B. (1988) *J. Catal.* **110**, 82–95.
82. Goovaerts, F., Vansart, E. F., De Hulsters, P. & Gelan, J. (1989) *J. Chem. Soc. Faraday Trans.* **85**, 3687–3694.
83. Karge, H. G. & Dondur, V. (1990) *J. Phys. Chem.* **94**, 765–772.
84. Miller, J. T., Hopkins P. D., Meyers, D. L., Ray, G. J., Roginski, R. T., Zajac, G. W. & Rosenbaum, N. H. (1992) *J. Catal.* **138**, 115–128.
85. Sawa, M., Niwa, M. & Murakami, Y. (1992) *Zeolites* **12**, 175–179.
86. Van Niekerk, M. J., Fletcher, J. C. Q. & O'Connor, C. T. (1992) *J. Catal.* **138**, 150–163.
87. Rudolf, P. R. & Garces, J. M. (1994) *Zeolites* **14**, 137–146.
88. Warzywoda, J., Dixon, A. G., Thompson, R. W. & Sacco, A., Jr. (1995) *Microporous Mater.* **5**, 1019–1025.
89. Datka, J., Gil, B. & Kubacka, A. (1996) *Zeolites* **17**, 428–433.
90. Alberti, A. (1997) *Zeolites* **19**, 411–415.
91. Beck, J. S., Vartuli, J. C., Kennedy, G. J., Kresge, C. T., Roth, W. J. & Schramm, S. E. (1994) *Chem. Mater.* **6**, 1816–1821.
92. Vartuli, J. C., Kresge, C. T., Leonowicz, M. E., Chu, A. S., McMullen, S. B., Johnson, I. D. & Sheppard, E. W. (1994) *Chem. Mater.* **6**, 2070–2077.
93. Edler, K. J. & White, J. W. (1995) *J. Chem. Soc. Chem. Commun.* **2**, 155–156.
94. Chen, C., Xiao, S. & Davis, M. E. (1995) *Microporous Mater.* **4**, 1–20.
95. Llewellyn, P. L., Schueth, F., Grillet, Y., Rouquerol, F., Rouquerol, J. & Unger, K. K. (1995) *Langmuir* **11**, 574–577.
96. Inagaki, S., Koiwai, A., Suzuki, N., Fukushima, Y. & Kuroda, K. (1996) *Bull. Chem. Soc. Jpn.* **69**, 1449–1457.
97. Huo, Q., Margolese, D. I. & Stucky, G. D. (1996) *Chem. Mater.* **8**, 1147–1160.
98. Schmidt, R., Stocker, M., Hansen, E., Akporiaye, D. & Ellestad, O. H. (1995) *Microporous Mater.* **3**, 443–448.
99. Sayari, A. (1996) *Chem. Mater.* **8**, 1840–1852.
100. Tanev, P. T. & Pinnavaia, T. J. (1996) *Science* **271**, 1267–1269.
101. Velev, O. D., Jede, T. A., Lobo, R. F. & Lenhoff, A. M. (1997) *Nature (London)* **389**, 447–448.
102. Corma, A. (1997) *Chem. Rev.* **97**, 2373–2419.
103. Tanev, P. T., Liang, Y. & Pinnavaia, T. J. (1997) *J. Am. Chem. Soc.* **119**, 8616–8624.
104. Van Nordstrand, R. A., Santilli, D. S. & Zones, S. I. (1988) *Am. Chem. Soc. Symp. Ser.* **368**, 236–245.
105. Richardson, J. W., Jr., Smith, J. V. & Han, S. (1990) *J. Chem. Soc. Faraday Trans.* **86**, 2341–2342.
106. Hay, R. (1966) *Geol. Soc. Am.* **85**, special paper.
107. Munson, R. A. & Sheppard, R. A. (1974) *Mineral Sci. Eng.* **6**, 19–34.
108. Rinaldi, R., Smith, J. V. & Jung, G. (1975) *Neues J. Mineral. Monat.* 433–443.
109. Surdam, R. C. & Eugster, H. P. (1976) *Geol. Soc. Am. Bull.* **87**, 1739–1752.
110. Windley, B. F. (1984) *The Evolving Continents* (Wiley, New York), 2nd ed.
111. Smith, J. V. (1981) *Phil. Trans. R. Soc. London A* **301**, 401–422.
112. Smith, J. V. & Brown, W. L. (1988) *Feldspar Minerals 1* (Springer, Berlin), 2nd Rev. and Extended Ed.
113. Inskeep, W. P., Nater, E. A., Bloom, P. R., Vandervoort, D. S. & Erich, M. S. (1991) *Geochim. Cosmochim. Acta* **55**, 787–800.
114. Petrov, I. (1994) *Am. Mineral.* **79**, 221–239.
115. Kimata, M., Shimizu, M., Saito, S., Nishida, N., Arakawa, Y. & Shimoda, S. (1993) *Neues J. Mineral. Monat.* 408–416.
116. Kimata, M., Nishida, N., Shimizu, M., Saito, S., Matsui, T. & Arakawa, Y. (1995) *Mineral. Mag.* **59**, 1–14.
117. Smith, J. V. (1982) *J. Geol.* **90**, 1–48.
118. Gaffey, M. J. (1997) *Origins Life Evol. Biosphere* **27**, 185–203.
119. Deamer, D. W. & Pashley, R. M. (1989) *Origins Life Evol. Biosphere* **19**, 21–28.
120. Hartman, H., Sweeney, M. A., Kropp, M. A. & Lewis, J. S. (1993) *Origins Life Evol. Biosphere* **23**, 221–227.
121. Oberbeck, V. R. & Fogleman, G. (1990) *Origins Life Evol. Biosphere* **20**, 181–195.
122. Gogarten-Boekels, M., Hilario, E. & Gogarten, J. P. (1995) *Origins Life Evol. Biosphere* **25**, 251–264.
123. Nisbet, E. G. (1985) *J. Mol. Evol.* **21**, 289–298.
124. Schidlowski, M. (1994) *Origins Life Evol. Biosphere* **24**, 267–268.
125. Schopf, J. W. (1994) *Origins Life Evol. Biosphere* **24**, 263 (abstr.).
126. Segerer, A. H., Burggraf, S., Fiala, G., Huber, G., Huber, R., Pley, U. & Stetter, K. O. (1993) *Origins Life Evol. Biosphere* **23**, 77–90.
127. Macleod, G., McKeown, C., Hall, A. J. & Russell, M. J. (1994) *Origins Life Evol. Biosphere* **24**, 19–41.
128. Markhinin, E. K. & Podkletnov, N. E. (1977) *Origins Life* **8**, 225–235.
129. Basiuk, V. A. & Navarro-González, R. (1996) *Origins Life Evol. Biosphere* **26**, 173–194.
130. Kawano, M. & Tomita, K. (1997) *Clays Clay Minerals* **45**, 365–377.
131. Otroschenko, V. A., Vasilyeva, N. V. & Kopilov, A. M. (1985) *Origins Life* **15**, 115–120.
132. Basiuk, V. A., Gromovoy, T. Y., Golovaty, V. G. & Glukhov, A. M. (1990–1) *Origins Life Evol. Biosphere* **20**, 483–498.
133. Basiuk, V. A., Gromovoy, T. Y., Glukhov, A. M. & Golovaty, V. G. (1991) *Origins Life Evol. Biosphere* **21**, 129–144.
134. Gromovoy, T. Y., Basiuk, V. A. & Chuiko, A. (1991) *Origins Life Evol. Biosphere* **21**, 119–128.
135. Basiuk, V. A. (1992) *Origins Life Evol. Biosphere* **22**, 333–348.
136. Basiuk, V. A., Gromovoy, T. Y. & Khil'chevskaya, E. G. (1995) *Origins Life Evol. Biosphere* **25**, 375–393.
137. Bonner, W. A., Kavasmaneck, P. R., Martin, F. S. & Flores, J. J. (1975) *Origins Life* **6**, 367–376.
138. Poncelot, G., van Assche, A. T. & Fripiat, J. J. (1975) *Origins Life* **6**, 401–406.

139. Coyne, L. M. (1985) *Origins Life* **15**, 161–206.
140. Lahav, N. (1994) *Heterogeneous Chem. Rev.* **1**, 159–179.
141. Zamaraev, K. I., Romannikov, V. N., Salganik, R. I., Wlassoff, W. A. & Khramtsov, V. V. (1997) *Origins Life Evol. Biosphere* **27**, 325–337.
142. Nisbet, E. G. (1986) *Episodes* **9**, 83–90.
143. Ferris, J. P. & Ertem, G. (1993) *J. Am. Chem. Soc.* **115**, 12270–12275.
144. Winter, D. & Zubay, G. (1995) *Origins Life Evol. Biosphere* **25**, 61–81.
145. Shapiro, R. (1995) *Origins Life Evol. Biosphere* **25**, 82–98.
146. Pace, N. R. & Marsh, T. L. (1985) *Origins Life* **16**, 97–116.
147. Orgel, L. E. (1986) *J. Theor. Biol.* **123**, 127–149.
148. Lahav, N. (1993) *Origins Life Evol. Biosphere* **23**, 329–344.
149. Ferris, J. P. (1996) *Origins Life Evol. Biosphere* **26**, 232.
150. Joyce, G. F. (1996) *Origins Life Evol. Biosphere* **26**, 233.
151. Szathmáry, E. (1997) *Nature (London)* **387**, 662–663.
152. Orgel, L. E. (1992) *Nature (London)* **358**, 203–209.
153. Joyce, G. F. (1994) *Curr. Opin. Struct. Biol.* **4**, 331–336.
154. Bonner, W. A. (1991) *Origins Life Evol. Biosphere* **21**, 59–111.
155. Sowerby, S. J., Heckl, W. M. & Petersen, G. B. (1996) *J. Mol. Evol.* **43**, 419–424.
156. Ricard, J., Vergne, J., Decout, J. & Maurel, M. (1996) *J. Mol. Evol.* **43**, 315–325.
157. Lifson, S. (1997) *J. Mol. Evol.* **44**, 1–8.
158. Popa, R. (1997) *J. Mol. Evol.* **44**, 121–127.
159. Javoy, M. (1995) *Geophys. Res. Lett.* **22**, 2219–2222.
160. Holland, H. D. (1997) *Science* **275**, 38–39.
161. Towe, K. M. (1981) *Precambrian Res.* **16**, 1–10.
162. Walker, J. C. G. (1985) *Origins Life Evol. Biosphere* **16**, 117–127.
163. Kasting, J. F. (1990) *Origins Life Evol. Biosphere* **20**, 199–231.
164. de Wit, M., Roering, C., Hart, R. J., Armstrong, R. A., de Ronde, C. E. J., Green, R. W. E., Tredoux, M., Peberdy, E. & Hart, R. A. (1992) *Nature (London)* **357**, 553–562.
165. Buick, R., Thornett, J. R., McNaughton, N. J., Smith, J. B., Barley, M. E. & Savage, M. (1995) *Nature (London)* **375**, 574–577.
166. Barley, M. A., Pickard, A. L. & Sylvester, P. J. (1997) *Nature (London)* **385**, 55–58.