

Loosened bonds

chemical transformations of organic compounds in the crust of the Earth.

Transition metals are the catalysts that Mango and co-workers are pursuing. They find that organic-rich source rocks, which are heat-treated to eliminate their inherent petroleum generation potential, have the catalytic ability to generate gas from hydrogen and *n*-alkenes. The gas produced has a composition strikingly similar to that of natural gas, methane being the predominant product (about 90 mol per cent). Their result contrasts with other experimental attempts to produce natural gas from organic matter at high temperatures in which the relative yields of methane are considerably lower. The implication is that something in the inorganic make-up of the source rock is the catalyst for the reaction, and Mango and co-workers suggest that it may be the unusually high concentrations of nickel and/or vanadium.

Although the actual catalytic culprit is not known, the results are consistent with the transition-metal catalysis scheme that Mango proposed¹ in 1992. It seems plausible that the catalytic process involves an oxidation-reduction couple, as something must be oxidized when carbon (in whatever form) is reduced to methane. Transition metals are one possibility, and the source of hydrogen in the natural setting is either the organic matter itself or reactions between minerals and water. So it is especially intriguing that Mango and co-workers found an increase in catalytic activity on adding a small amount of water to their experiments. As they note, however, there is apparently an effect of the concentration of H₂O on the results of the reaction.

The success of this bulk-rock study opens the door for controlled experiments to characterize the catalytic properties of the source rocks' various inorganic constituents: for instance, transition metal complexes in carbonaceous material or the structure of mineral surfaces. Mango and co-workers have not characterized in detail the mineralogy, petrology, texture or geochemical nature of the source rock before or after their laboratory work. Subsequent studies could be devised to investigate the likelihood that coupled organic and mineral transformation reactions provide the kick for methane generation.

On the other hand, the conditions imposed in the laboratory rarely include all the possibilities of the natural system. Some microbiologists^{10,11} seem to be comfortable with the idea that heat-loving microorganisms may thrive at temperatures as high as 150 °C. If so, then the biosphere could extend throughout the temperature range of the traditional 'oil window' in sedimentary basins. This raises the possibility⁹ that the metabolic processes of heat-and-pressure-loving organisms

(also known as hyperthermobarophiles) are the methane-forming catalysts in sedimentary rocks.

Current evidence cannot rule this idea out; indeed, the observation of anomalously high concentrations of methane in submarine hydrothermal vent fluids from the Juan de Fuca ridge¹² may provide some clues. Thermodynamic calculations¹² demonstrate that the concentration of methane is above that set by equilibrium involving H₂, H₂O and CO₂ at the temperatures of the vent fluids (317–368 °C). However, the concentrations of all four gases are consistent with equilibrium at about 275 °C. A catalysed approach towards equilibrium at any lower temperature, say 150 °C, would be consistent with even higher concentrations of methane, which might be diluted during mixing with fluids from other sources to provide the concentrations found in the vent fluids. The possibility of high-temperature methanogenesis is made more intriguing by the observation of particulate DNA in fluid samples from the same vents¹³.

At present, there is a bewildering choice of possible methane-forming catalysts in natural systems, all awaiting further experimental and theoretical investigations. Although still in their infancy, studies which go beyond the phenomenological and address the thermodynamic and kinetic constraints that lead to methane formation will modify thinking about geochemical processes involving fluids, aqueous solutions, gases, organic matter and volatile compounds in general. The applications could span an enormous variety of topics from petroleum geochemistry to sea-floor hydrothermal processes, and from life at high temperature to the study of the evolution of icy satellites in the outer Solar System. □

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- Mango, F. D. *Geochim. cosmochim. Acta* **56**, 553–555 (1992).
- Mango, F. D., Hightower, J. W. & James, A. T. *Nature* **368**, 536–538 (1994).
- Mango, F. D. *Science* **237**, 514–517 (1987).
- Mango, F. D. *Geochim. cosmochim. Acta* **54**, 23–27 (1990).
- Mango, F. D. *Geochim. cosmochim. Acta* **54**, 1315–1323 (1990).
- Mango, F. D. *Nature* **352**, 146–148 (1991).
- Price, L. C. *Geochim. cosmochim. Acta* **57**, 3261–3280 (1993).
- Sato, M. in *Fluid–Mineral Interactions: A Tribute to H. P. Eugster* (eds Spencer, R. J. & Chou, I.-M.) 271–283 (The Geochemical Society, San Antonio, 1990).
- Helgeson, H. C., Knox, A. M., Owens, C. E. & Shock, E. L. *Geochim. cosmochim. Acta* **57**, 3295–3339 (1993).
- Daniel, R. M. *Origins Life Evol. Biosphere* **22**, 33–42 (1992).
- Segerer, A. H. et al. *Origins Life Evol. Biosphere* **23**, 77–90 (1993).
- Lilley, M. D. et al. *Nature* **364**, 45–47 (1993).
- Deming, J. W. & Baross, J. A. *Geochim. cosmochim. Acta* **57**, 3219–3230 (1993).

PLASTIC packaging is splendidly hygienic for the food manufacturer, but a major nuisance as garbage. Biodegradable polymers, claimed to rot rapidly when thrown away, haven't solved the problem. Daedalus has a new suggestion.

He points out that the long-chain molecules of plastic materials are made by linking many monomer units together. Many such chains are quite capable of reversing this reaction, and coming apart again. The acetal resins and some nylons, for example, are liable to 'unzip' by repeated loss of the end monomer unit on the chain. Their molecules have to be stabilized by attaching a stable 'cap' on each end, to prevent the unzipping reaction from starting.

Daedalus is now designing a plastic film whose polymeric chains do not lie flat within it, but widthways across it, running from one face to the other. The end-groups on one face are firmly capped with a stable end-group. Those on the other face are more precariously capped with an end-group that is easily hydrolysed away by water, or oxidized by air. Formed into a two-layer 'sandwich', with the stable sides facing outwards and the unstable ones pressed together in the middle, such a film would be quite permanent. It could be used for bottles, bags, sachets and packaging of all kinds. But the act of opening the package would tear the film. Air or water would get at the vulnerable centre of the sandwich. The whole thing would then unzip rapidly back to monomer.

DREADCO's chemists are now trying to realize this vision. They are exploiting the known technique of electro-initiated polymerization. A polymer is grown on an electrode immersed in monomer solution; the applied voltage maintains a reactive charge on the end-group of each growing chain. On a flat electrode the parallel polymer chains should extend, like a fully dense microscopic growth of hair, into a sort of polymeric Langmuir–Blodgett film. When it is thick enough, the polymeric film will be removed from the solution, end-capped on the exposed face, stripped off the electrode, folded into sandwich form, and sealed. The process could even be run continuously on a rotating cylindrical electrode.

Autodestructive film will transform the packaging market. Packages will last exactly as long as required, and will then degrade automatically. A gaseous monomer would simply evaporate. But Daedalus would prefer a combustible liquid monomer which could be reclaimed later. Consumers could dump their old packaging in a barrel, and drain off the accumulating monomer as free motor fuel.

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