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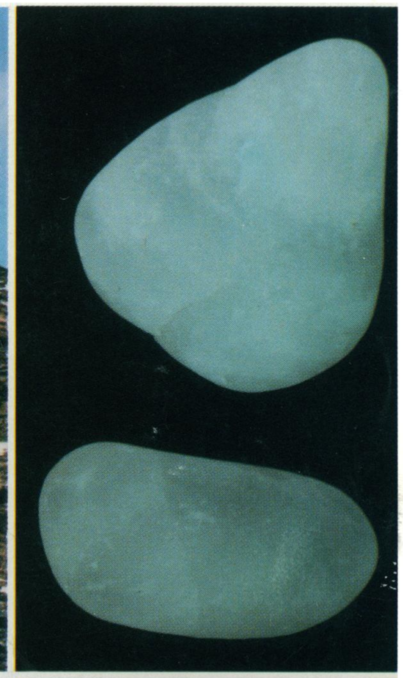

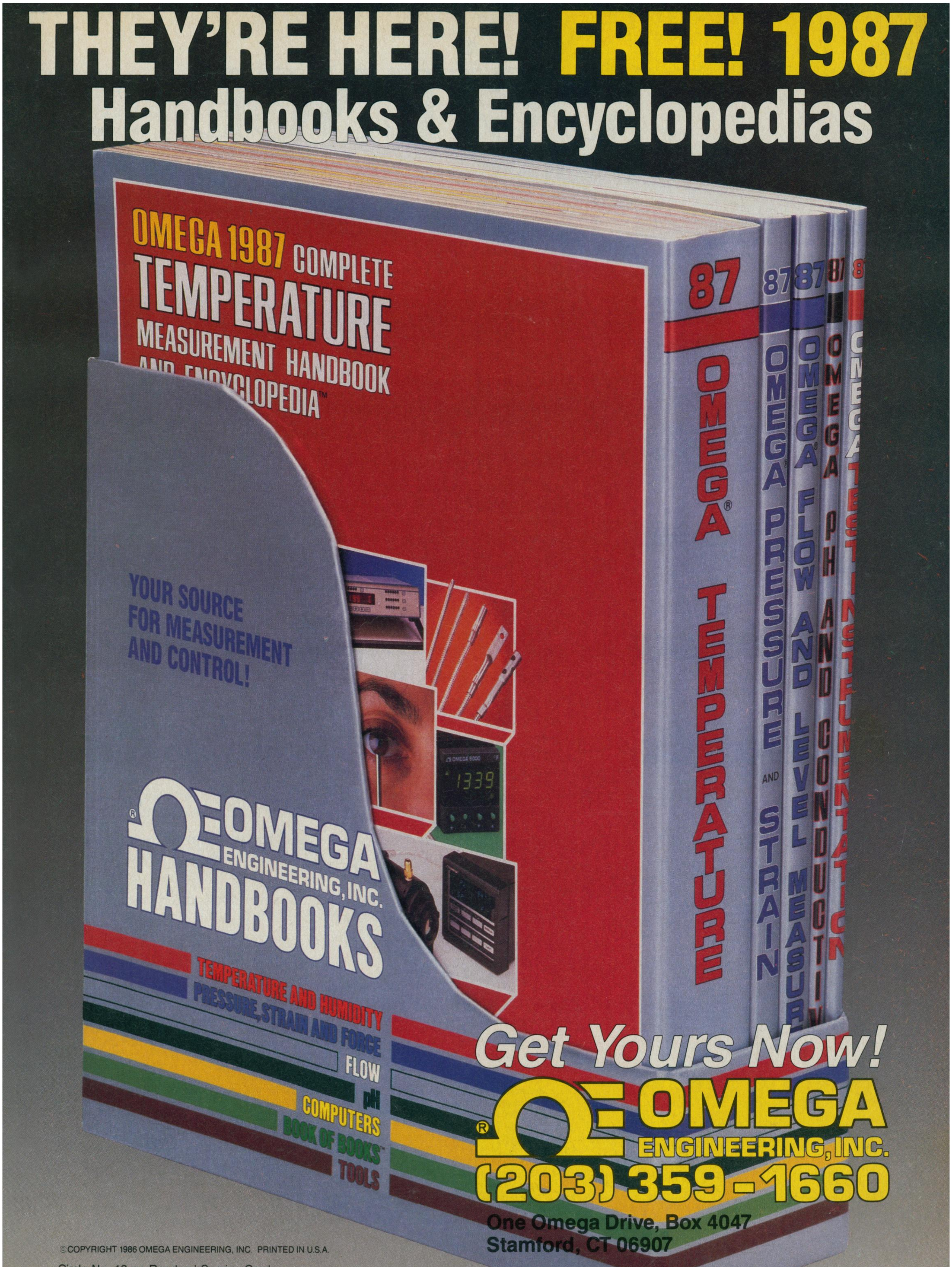
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COVER Remnants of uplifted marine terraces are common in the Southern Alps of New Zealand (bottom). Individual (upper left picture) is collecting widely scattered beach pebbles from an exhumed 320,000-year-old shore platform (altitude 1620 meters) at the base of a degraded sea cliff. Highly rounded quartz pebbles (11 to 12 millimeters in diameter) from notched ridge crest have frosted surfaces and impact marks made in a high-energy sedimentary environment. See page 1225. [W. B. Bull, University of Arizona, Tucson, AZ 85721, and A. F. Cooper, University of Otago, Dunedin, New Zealand]

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This Week in SCIENCE

Mountain-escalading marine terraces

TERRACES that were formed on the coastline (cover) are prevalent in New Zealand's Southern Alps; they were raised into mountains by crustal uplift where the Pacific and Australian plates converged (page 1225). The terraces, like flights of stairs, were dated by comparing them with terraces in New Guinea that have comparable spacing between "steps"; corals, sediments, and reefs found within the New Guinea terraces had previously been dated. Bull and Cooper plotted the altitudes of terraces and were able to determine the rate of uplift for them; the rate has increased from 3.2 meters per 1000 years to 7.8 meters. This change occurred some time around 135,000 to 140,000 years ago; the slower rate pertained for 200,000 years before that time. The increased rate may be the result of increased convergence between the two plates; if so, the rate would be expected to increase again as the plates continue to collide.

Fibroblasts in Werner's syndrome

SOME of the common signs of Werner's syndrome, a disease characterized by premature aging and death, may result from a defect in patients' fibroblasts (page 1240). Patients are of short statures with stocky trunks but thin limbs; they gray and bald prematurely and develop diabetes, leg ulcers, patchy skin, osteoporosis, and other problems. Fibroblasts from patients grow slowly in culture, divide at a slow rate, and typically die prematurely. Bauer *et al.* describe the growth characteristics of such fibroblasts to various growth factors and their metabolic responses. Patients respond with a normal mitogenic response when stimulated with fetal bovine serum. However, they do not respond as do normal fibroblasts to platelet-derived growth factor (PDGF) (or to fibroblast growth factor) even though they have normal numbers of receptors for the factor and apparently bind it with normal affinity. Normal fibroblasts respond to PDGF with increased production of messenger RNA for collagenase and with increased production of collagenase (an enzyme that degrades and remodels collagen and may be important in wound healing and other processes); Werner's fibroblasts produce high levels of the enzyme and RNA constitutively but show no increase in production upon PDGF stimulation. These differences may provide clues to the nature of the cellular defects that play a role in Werner's syndrome; they will also be useful for determining how various growth factors interact with cells.

Drug against drunkenness

THE drug Ro15-4513 blocks one of the important biochemical effects of ethanol and some of ethanol's behavioral effects in rats (page 1243). Such an agent would have major clinical significance if it could be shown to inhibit in humans some of the damaging neurobiological effects that are induced by ethanol. Ethanol stimulates uptake of chloride ion by γ-aminobutyric acid (GABA) receptors in brain tissue in vitro. Its action at the GABA-coupled chloride ion channel has been thought to underlie many of its behavioral properties; experiments with Ro15-4513 support this interpretation. Suzdak *et al.* found that ethanol-induced chloride uptake by GABA receptors was specifically blocked by Ro15-4513; the drug also inhibited ethanol-induced behaviors in rats—the signs of drunkenness (general sedation, staggered gait, impaired righting reflex) and anticonflict and anxiety-dispelling activities. Ro15-4513 is one of a group of drugs that is relatively nontoxic; this provides further encouragement for the possibility of developing from it a clinically effective ethanol antagonist. Kolata discusses the development of the drug and the potential benefits and problems that could accompany its use in humans as an antidote to intoxication (page 1198).

Anthropoid ancestors

REEVALUATION of the geology and fauna of the Jebel Qatrani Formation in the Fayum depression of Egypt—the source of the earliest African anthropoid primate fossils (monkeys and apes)—indicates that common ancestors of these primates existed perhaps 7 or 8 million years earlier than previously thought (page 1247). This region, once a tropical forest with a monsoonal climate, is rich in fossils of early anthropoids and of many typically African mammals. Dating of volcanic rocks overlying the Jebel Qatrani Formation places it and the fossils back to 31 million years ago, in the early Oligocene Epoch. The revised date expands the temporal gap between the primitive Egyptian anthropoids and monkeys and apes from East Africa. Fleagle *et al.* discuss the evolutionary significance of this new time scale.

Muscle disease

A military drill instructor in "superb physical condition" experienced several episodes of severe chest pain after exercise (page 1254). Fishbein describes the clinical work-up that led to the diagnosis of a lactate transporter deficiency disease in the patient. Lactate is the major organic acid that accumulates inside cells; it is generated in muscles during exercise and rest. Export of this acid is important for proper functioning of the contractile apparatus and energy-yielding pathways in muscles. The patient's striated muscles and red blood cells (both exporters of lactate) did not export lactate efficiently. This created an acidic intracellular environment that, in turn, could lead to degeneration or dissolution of muscle tissue, release of myoglobin into the urine, and high levels of creatine kinase in serum. This deficiency, presumed to be genetic, could affect all lactate transport proteins in the body. Instances of muscle cramps after exercise are common and may in other individuals similarly result from lactate transporter deficiencies.

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Energy Future

Events of 1986 have been traumatic for many people associated with the U.S. petroleum and natural gas industries. Prices at the wellhead have plunged, employment has been sharply curtailed, drilling has dropped to near longtime lows. Thus far, effects on production, consumption, and imports have not been great, but a continuation of present trends would lead to nationwide trauma at a later date. Because of longtime constants involved in developing energy sources, this country cannot afford complacency.

At one time, the United States was the world's lowest cost producer of petroleum and a substantial exporter. But the easy-to-find and inexpensive-to-produce oil has been found and exploited. There remains a large amount of oil in place (more than 300 billion barrels), but most of it is costly to produce: $10 to $15 a barrel and more.

When oil was selling above $30 a barrel in 1981 and there was a widespread expectation of even higher prices, 4561 rigs were drilling. In July 1986, with oil at about $10 a barrel, the number of active rigs dropped to less than 700. In November, when the price rose to $14, about 850 were drilling.

The large-scale drilling of 1980 to 1985 was barely sufficient to maintain a constant level of production. In 1986 production has dropped from about 9 million barrels a day (mbd) to 8.7. Experts agree that with prices at or near present levels the drop will continue. In the meantime, conservation is passé. Consumption is up, and imports have risen nearly 1 mbd. A Conoco report estimates that in the year 2000 oil imports will rise to 11 mbd. Imports of oil and its products were 4.8 mbd in 1983. Conoco also estimates that in 2000, the United States will be importing about 60 percent of its oil, mainly from the Middle East. Well ahead of that point, the stage would be set for a gigantic price squeeze. With a huge deficit in international trade, how would the United States pay for oil imports?

The drop in drilling is increasing U.S. energy vulnerability through a drop in natural gas reserves. Earlier, adequate gas supplies provided a cushion against shortages of oil. Vestiges of a "gas bubble" remain, but in the absence of large-scale drilling, reserves of gas are being drawn down twice as fast as they are being replaced. An abnormally cold winter could lead to shortages in deliverability.

During the next several years, additional nuclear plants will be generating electricity, but their capacities will be limited. The contributions of fusion and of renewable forms of energy will be comparatively negligible during the next decade. That leaves coal as the source of energy that could be exploited to minimize energy adversities. A considerable amount of oil and gas is burned merely to make heat. New technology permits coal to be burned cleanly for many of these applications. The cost of coal per million Btu's at mine mouth averages about $1. With residual oil at $12 a barrel, the cost of heat from it is $2 per million Btu's. During the last several years, the price of coal has been dropping. Productivity of mines has improved. Accident rates are lower. Competition among the 3000 coal mining companies is intense. Enormous reserves of coal are available.

Coal can be gasified to form methane. It can be liquefied to yield fluids for transportation. Fortunately, progress is being made in both of these applications. The Great Plains methane plant in North Dakota, though not a financial success, is a technical success operating at about 100 percent of design capacity: operators are on a learning curve, and have identified bottlenecks which, if corrected, could enable them to run at 120 to 140 percent of design capacity. Experiments designed to point the way to obtaining transportation fluids from coal are looking very promising. One approach is to co-process coal with residual oil, upgrading the mixture to useful fluids by hydrogenation. In a second approach hydrogenation is achieved through an improved two-step donor solvent procedure.

The United States could lessen oil and gas shortages during the next decade by instituting soon an import fee of $5 to $10 a barrel on oil. This would lead to development of more oil and gas while fostering conservation. The nation could achieve a longer term energy security by expediting advanced technology for utilization of coal.

—PHILIP H. ABELSON

Letters

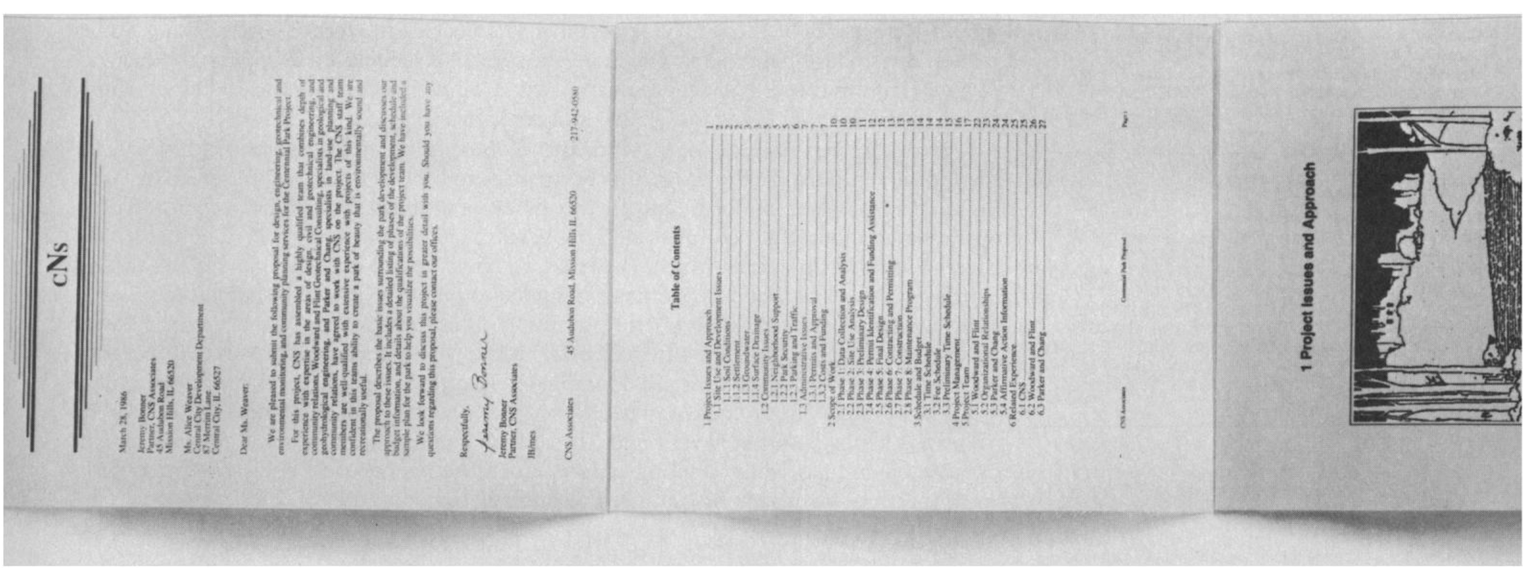
Cretaceous-Tertiary Dinosaur Extinction

Robert E. Sloan *et al.* (Reports, 2 May, p. 629) present several sets of data in support of their long held view that there was a simultaneous and gradual decline of dinosaurs and evolutionary radiation of ungulates near the Cretaceous-Tertiary boundary. Their interpretation is made without reference to taxonomic uncertainties and taphonomic biases. It appears to us that, when these matters are taken into consideration, the data of Sloan *et al.* are equally compatible with a hypothesis of abrupt extinction of dinosaurs followed by adaptive radiation of ungulates.

Sloan *et al.* conflate data on bone distribution in paleochannels and in paleosols of floodplains. Paleochannels and paleosols are such different depositional and preservational environments that we prefer to consider them separately. The apparent decline of dinosaur bone in paleosols toward the top of the Hell Creek Formation is accompanied by declining carbonate content of these paleosols, recently documented during fieldwork (by G.R.) in Bug Creek (*1*). Paleosols of the uppermost 2 meters of the Hell Creek Formation there are almost entirely noncalcareous. Bone is dissolved in acidic, noncalcareous soil environments (*2*), so this pattern of bone abundance could be preservational. Since calcareous fossils are more easily dissolved than are phosphatic ones, and small bones with their high surface-to-volume ratio are more readily destroyed than large bones (*2*), there should be a predictable sequence of last occurrences higher in the formation: land snails below mammal bones below large dinosaur bones. Such a sequence of disappearance for bones has been noted by several workers (*3*). The whole preservational sequence should be more rigorously documented.

Sloan *et al.* also report declining diversity of dinosaurs in a sequence of paleochannels, most of which are Paleocene in age (*4*). These dinosaurs are represented by isolated teeth, and reworking from older deposits is not adequately rebutted in their account. Incision of paleochannels into earlier deposits during a time of marine regression and tectonic uplift is well documented in the area of Bug Creek (*3*). Arguments against resorting on the basis of the degree of abrasion are unconvincing in light of experimental studies of bone transport in modern streams (*5*). Also unconvincing is the argument that dinosaur teeth in paleochannels are of Paleocene age and were contemporary with ungulate radiation, because these Paleocene channels lack remains of Cretaceous mammals. This would be expected if dinosaur remains were resorted from paleosols at a level within the Hell Creek Formation, where dinosaurs but not mammals were preserved because of differential dissolution. The declining abundance of dinosaurs in paleochannels could merely reflect increased cover of Cretaceous source beds by Paleocene floodplain deposits. This alternative interpretation is also open to further test, by searching for articulated dinosaur remains in Paleocene paleochannels, levee deposits, and paleosols. Until these are found, we regard as unproved the existence of Paleocene dinosaurs or the idea that dinosaurs were declining in diversity at the same time as an ungulate radiation.

Another line of evidence used by Sloan *et al.* is a compilation of dinosaur diversity showing gradual decline in numbers of dinosaur genera over the last 7 million years of the Cretaceous. Other compilations of dinosaur diversity for this time period (*6*) differ significantly from theirs, some showing declining diversity and others increasing diversity. One of us (G.D.L.) has prepared a compilation which takes into account taxonomic uncertainties between paleontologists



concerned with this issue. We find that a significant decline in dinosaur diversity is difficult to prove.

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Sloan *et al.* report gradual reduction in both diversity and population density of dinosaurs at the end of the Cretaceous. Their assertion of decreasing diversity during the last 9 million years of the Cretaceous is based on the numbers of genera in progressively younger assemblages. They found 30 genera in the combined Judith River–Oldman–St. Mary River formations; 23, 22, and 19 genera in progressively younger strata; and finally 12 genera in the upper 16 meters of the Hell Creek Formation. We disagree with the suggestion that diversity was declining because the total of 30 genera in the oldest fauna was obtained by summing total genera from a 2.5-million-year interval, while the other totals were drawn from faunas derived from about 1-million-year intervals (figure 1 of Sloan *et al.*).

A more reasonable approach would be to compare the number of dinosaurs present in the 2.5-million-year time interval at the end of the Cretaceous with the Judith River–Oldman–St. Mary River fauna. Figure 1 of Sloan *et al.* reveals 28 genera present during the last 2.5 million years of the Cretaceous. A decline from 30 to 28 genera seems very modest.

We performed a statistical test of dinosaur diversity changes on data taken from figure 1 of Sloan *et al.* We determined generic diversity at each of the time lines from 76 to 67 million years ago. We selected the two time lines with the highest diversities (23 and 27 genera at 75 and 74 million years ago, respectively) and compared them to diversities at the two most recent time lines (17 and 18 genera at 68 and 67 million years ago, respectively). We then compared the summed diversities of older and younger samples with the a priori hypothesis of no difference ($\chi^2 = 2.6$, d.f. = 1, $P > 0.10$) and found they did not differ significantly.

Sloan *et al.* also suggest that dinosaur abundance was declining through the Hell Creek Formation. On the basis of a chi-square test, they state that the highest level of the formation had a significantly lower dinosaur abundance than lower levels. However, using data from table 2 of Sloan *et al.* we compared the number of bones in each stratigraphic interval with the number that would be expected if each interval contained the average of 2.63 bones per square kilometer ($\chi^2 = 9.79$, d.f. = 5, $P > 0.05$). The test indicates that no sample (including the youngest) differed significantly from the others. In a second test, we compared the youngest interval with the combined collections of the older intervals ($\chi^2 = 2.86$, d.f. = 1, $P > 0.05$) and found no significant difference.

It appears to us that the data discussed above are consistent with constant diversity and constant abundance of dinosaurs through the last 9 million years of the Cretaceous. That the same data are open to the alternative interpretations of gradual decline and of relative constancy probably reflects the fact that the collections were made from many facies over many years and with many different purposes. Currently available information is not sufficient to establish whether or not the dinosaur extinction was gradual. Carefully designed fieldwork is needed to obtain new collections that specifically focus on patterns of dinosaur diversity at the end of the Cretaceous.

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Unequivocal evidence is required to support the assertion that dinosaurs were members of Paleocene faunas in Montana. We believe that possible reworking of dinosaur remains into younger channel deposits and their absence in nonchannel earliest Paleocene deposits are critical issues incompletely addressed by Sloan *et al.*

Bug Creek facies channel deposits (*1*) such as the Ferguson Ranch locality contain transported and reworked material (*2*). Behrensmeyer (*3*) analyzed the possibilities of mixing skeletal elements of members of temporally disjunct faunas. Channel lag deposits are concentrations of clasts, whether they are new additions or winnowed residue from reworked stream banks (*2*). The undocumented "minimal" abrasion of dinosaur teeth in Paleocene stream channel deposits (age determined palynologically) does not convincingly exclude the possibility of reworking. Limited abrasion is just as easily explained by minimal transport of exhumed teeth (and bones).

Three observations based on 16 years of fieldwork in eastern Montana require explanation. If dinosaurs lived during deposition of the Bug Creek facies channel fills, why have their articulated remains not been found in these deposits? Partial dinosaur skeletons commonly are found in undisputed Cretaceous channel fillings, for example, the type specimen of the *Tyrannosaurus rex*. Articulated remains do occur in the Bug Creek facies, but are invariably those of taxa not limited to the Cretaceous (for example, turtles and crocodiles) (*4*).

Intensive fieldwork focused on channel and overbank deposits of Paleocene age within the Z coal complex of the basal Tullock Formation has resulted in the discovery of many accumulations of nondinosaur fossil vertebrates, including articulated specimens (*4*). Purported contemporaneous dinosaur remains from the Bug Creek facies are known only from channel deposits that cut into and necessarily rework Cretaceous sediments.

The stratigraphically highest dinosaur fossils preserved in nonchannel deposits lie approximately 2 meters below the base of the Tullock Formation, and, where it has been identified palynologically, the Cretaceous-Tertiary boundary. We know of no vertebrate fossils from this interval, or within 1 meter above the Cretaceous-Tertiary boundary (excluding those in channels that cut through these strata). Thus the sample of dinosaur specimens from the uppermost 9 meters of the Hell Creek Formation (Sloan *et al.*, table 2) is actually derived from an interval with a thickness approximately 75% that of those with which it is being compared. How is this related to the alleged decrease in abundance of dinosaur remains?

The possibility that dinosaur specimens have been reworked and the apparent discrepancies between records from channel and overbank deposits demand further investigation.

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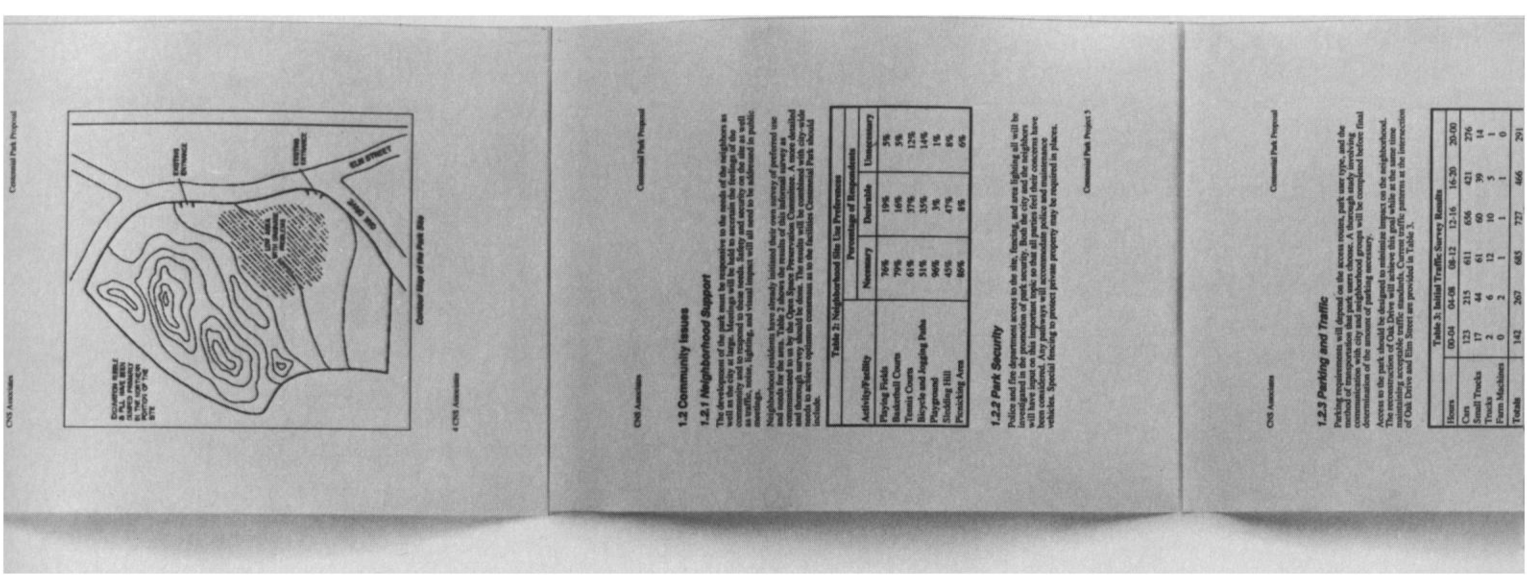

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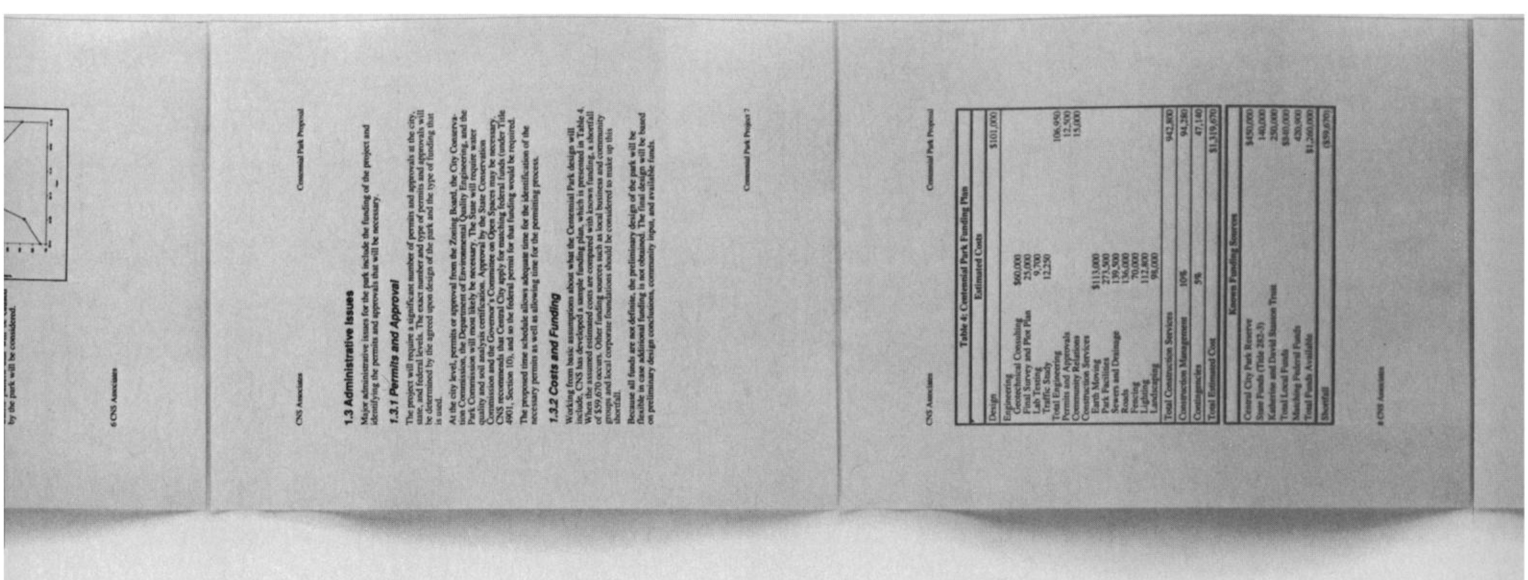
4. Forty-eight localities in the Z coal complex interval, 37 yielding articulated specimens (in the University of California collections); L. J. Bryant, thesis, University of California, Berkeley, CA (1985).

Response: There are six major events recorded in the upper Hell Creek Formation of McCone County, all within chron 29r [the 0.6-million-year reversed magnetic interval, including the Cretaceous-Tertiary (K-T) boundary], and at least four of them are discrete. The oldest is the latest Maastrichtian sea level lowering (*1*) and consequent minor unconformity; closely associated with this are the introductions of ungulates and of multituberculates of Asian origin and perhaps the introduction of *Leptoceratops* from Asia and *Alamosaurus* from South America. A lowering of sea level would make intercontinental migrations across a filter bridge easier. Also associated with this is part of the reduction of pollen taxa. Retallack and Leahy's interval of deep weathering follows. The next identifiable event is the K-T boundary, marked by the iridium-rich layer in some but not all sections, principally those in contemporary oxbow lakes. This is also marked by the abrupt termination of several Cretaceous pollen taxa. Immediately following this is a short stratigraphic interval with an enrichment of fern spores, in turn followed by the great increase in conifer pollen and wood. The next event is the deposition of the continuous upper Z coal, the top of the Hell Creek Formation, followed by the major change in sedimentation type that results in the typical and definitive Tullock shales of distinctly yellowish color. This color change is due to the deposition of many closely spaced layers of siderite cemented clay, separated by layers of light gray clay. These siderite bands are mainly absent from the Hell Creek Formation. We presume this change is due to the Danian sea level rise and consequent change in base level and water table. The final event is the terminal extinction of dinosaurs in Montana. The last dinosaurs occur in a channel that does not cut down into the Hell Creek Formation. Since our report was submitted we have demonstrated that Bug Creek West (BCW), Scmenge Point and Harbicht Hill (HH) are Paleocene channels using the same criteria that we used for Ferguson Ranch (FR). We have also located two more Paleocene localities, By George and Wounded Toe, within the Hell Creek Formation, and one not yet named in the basal Tullock Formation (*2*). The K-T boundary thus falls between Bug Creek Anthills (BCA) and BCW. Only one dinosaur genus disappeared at the K-T boundary, and 11 dinosaur genera survived into the Paleocene in Montana.

The possible sources for the fossils found in the channels are (i) reworking from older and lower channels, (ii) reworking from adjacent older floodplain deposits, (iii) being swept off the surface of the floodplains, and (iv) drowning in the channels. The question is, Are all of the dinosaur teeth in the Paleocene channels of sources (i) and (ii), or are at least some of them from source (iii)? Source (iv) could of course produce semiarticulated skeletons, but we have not found any in 18 field seasons. A possible reason for the lack of articulated skeletons of dinosaurs is the lower sedimentation rate of the Hell Creek Formation and the lower Tullock formations as compared with the Lance Formation or the Judith River Formation of Alberta containing the classic Oldman fauna. Depositional units in the lower Tullock Formation are only 1 to 10 centimeters thick, too thin for the burial of skeletons other than small vertebrates. The known Tullock fossils come dominantly from coals and the channel sands. The major



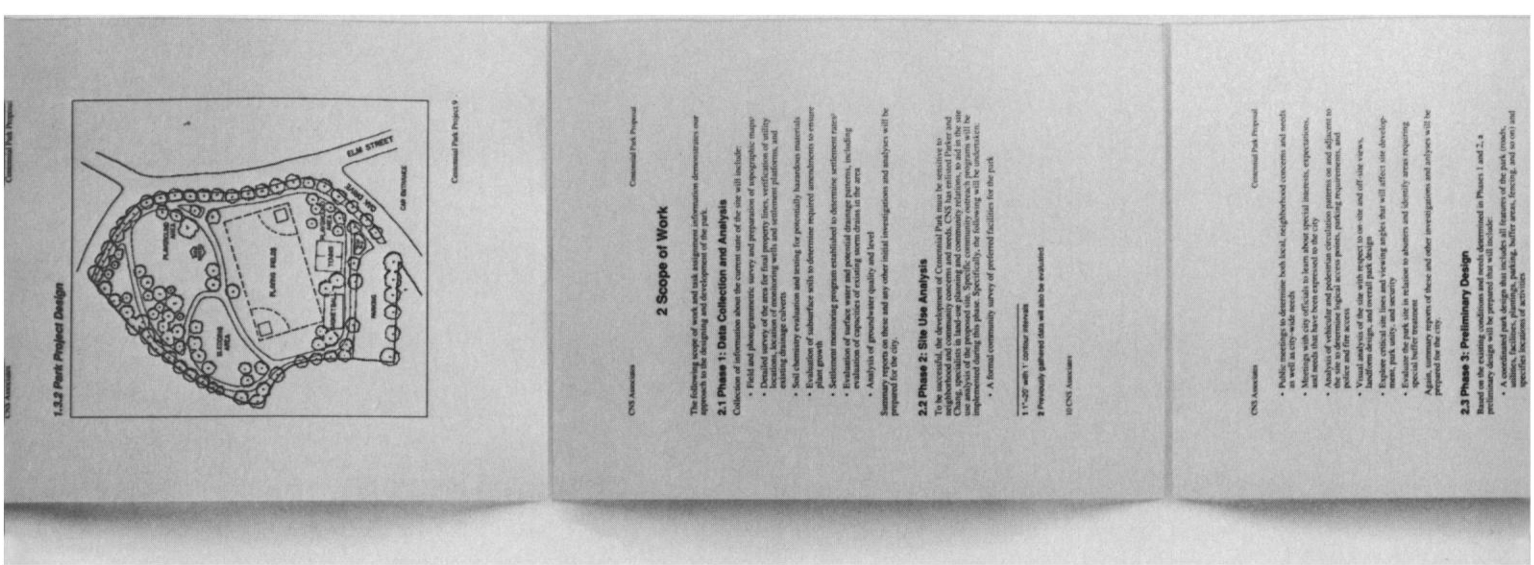
source of mammal remains (and we presume dinosaur teeth) in the Paleocene channels is (iii). All the listed channels have dinosaur teeth within them. A minor source for the mammal and dinosaur teeth is (i); we think this is no more than 5% of the included fossils. We think (ii) is unlikely because we have not found teeth in the floodplain shales despite many field seasons of prospecting. The deep cavities of small theropod teeth do not have floodplain sediments in them, only channel sands, as in the interiors of the turtle skulls.

We repeat our assertion that if dinosaur teeth are reworked, so must be the more common teeth of Cretaceous mammals. For example, *Didelphodon vorax*, the largest marsupial, is routinely known from most Cretaceous localities in the Hell Creek Formation, including BCA. It makes up on average, 2% of the number of mammalian specimens and is more common than any theropod dinosaur at most localities in the Hell Creek Formation. It is quite unknown from any of the Paleocene localities in either Garfield (*3*) or McCone counties. On the other hand *Meniscoessus borealis* is routinely present in all localities through FR, and in fact increases in abundance from BCA to BCW and HH. This is a strange kind of selective "reworking." One would expect reworking to homogenize the relict faunas. Instead, dinosaur teeth are enriched with respect to Lancian mammals in the Paleocene channels, and those mammals themselves differ from channel to channel. These faunas are not the result of a progressive dilution of reworked Cretaceous fossils.

Retallack and Leahy present useful new results on the distribution and types of paleosols in the Bug Creek area. We were aware of their work at the time of revision of our report, but could not in good conscience discuss it until they presented it. The FR channel cuts only 3 meters below the event Z, the K-T boundary. This is the interval that Retallack and Leahy point out as bleached by acid soil weathering, in which bones and teeth are missing in the floodplain silts and clays. The FR channel does not cut into a lower channel for at least 1.5 kilometers in the upstream direction. We do not see how the FR dinosaur teeth can be reworked.

On the matter of the bleached zone reducing the interval in which dinosaurs become scarce, we are in the process of reoccupying the University of Minnesota and Milwaukee Public Museum sites of dinosaurs and hand leveling the distance to the K-T boundary. Present results continue to show the trend stated in our report.

Sheehan and Morse suggest that it is more reasonable to combine all the Maastrichtian dinosaur faunas we cite as one unit of 3.3-million-years duration and compare them with the late Campanian faunas of 2.5-million-years duration on the basis of similar intervals of time. We do not think this is reasonable for the following reasons. The Oldman fauna includes some 320 semiarticulated dinosaur specimens (*4*) that have an approximate range in age of 1.5 million years. The slightly older Judith River fauna add three additional genera known only from isolated teeth and as yet not collected from the Oldman fauna, mainly because no extensive sediment-washing operations have been conducted except for those of Richard Fox of the University of Alberta, Edmonton, who has not reported on the reptilian remains. These taxa do occur later in the region. This means the augmented Oldman fauna is 30 genera over 1.5 million years. By combining the Lance, Hell Creek, and Scollard formation samples, the number of Lancian semiarticulated dinosaur specimens becomes 139 (*4*) over a total of 2 million years. To this we add the 52 Milwaukee Public Museum and University of Minnesota specimens and the genera known mainly from teeth. The Lancian faunas total 19 genera over a span of 2 million years. The compari-



son is thus between 30 genera and 19 genera, not 30 and 28. However, there is a great difference between the faunas of the lower and upper parts of the Hell Creek Formation. Our collections of teeth from the upper part of the Hell Creek Formation are significantly larger than any other collections in the world. While not all our specimens are counted as yet, they have been identified. We estimate that more than 3000 dinosaur teeth have been collected from only five of our localities in the upper 20 meters of the formation. Twelve genera are all we can identify in these collections. We invite others to produce a similar body of data from another area for comparison. Lumping data will only confuse the results. Fossils with formation occurrence data only and not stratigraphic position are of little use. We did err in the calculation of χ^2. The probability is slightly more than 0.05 rather than slightly less.

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Alachlor Removal from Drinking Water

A recent News & Comment article by Marjorie Sun (12 Sept., p. 1143) about the Environmental Protection Agency's (EPA's) proposal for alachlor contains the statement, "alachlor, for the most part, is not eliminated by purification at conventional city water treatment plants or even activated charcoal filters."

David Baker of Heidelberg College in Tiffin, Ohio, has observed significant removal of alachlor and other popular herbicides after water has been treated with granular activated carbon (GAC) filters (*1*). Laboratory-scale experiments by the Ontario Ministry of the Environment have demonstrated effective removal of alachlor with GAC filters and with powdered activated carbon (PAC). PAC (25 to 75 milligrams per liter) was successful in removing alachlor and other herbicides from raw water at several southwest Ontario plants in 1985 (*2*). PAC is commonly used at many community water systems for taste and odor control and, as the Canadian data demonstrate, could be used for herbicide removal without the need for installation of capital-intensive filters. Additional work in Louisiana funded by the EPA has shown quantitative removal of alachlor by GAC filters and substantial removal after ozonization (*3*).

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Erratum: In the summary of the article "What has happened to productivity growth?" by Martin Neil Baily (24 Oct., p. 443), the second sentence should have read, "Unless there is an increase in growth, American living standards will remain stagnant and problems such as the budget deficit will plague policy-makers."

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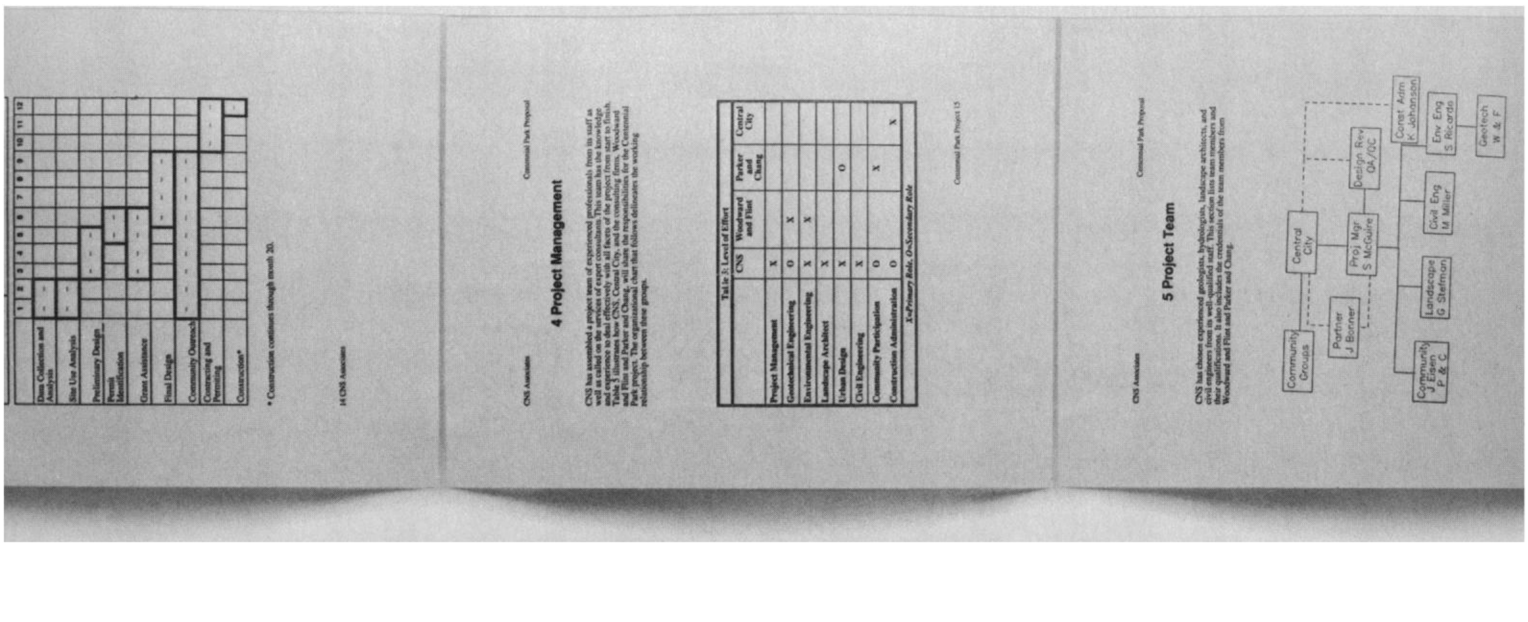

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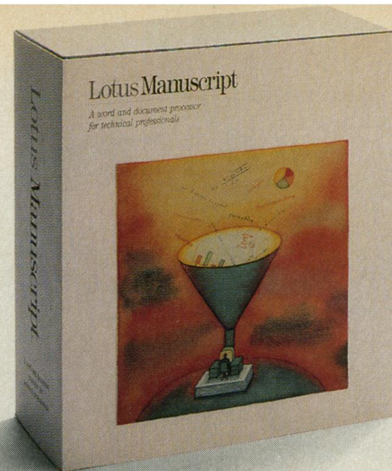

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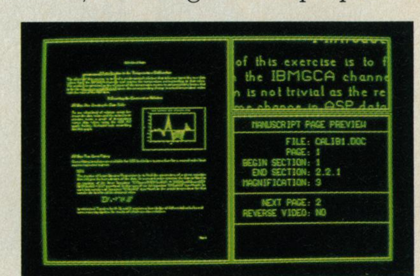

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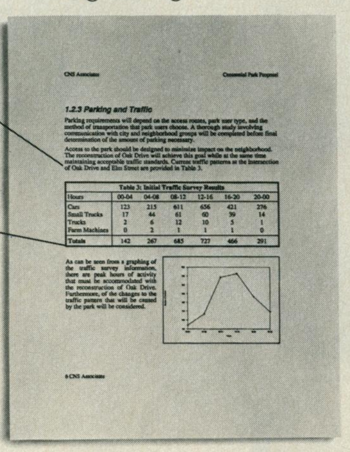

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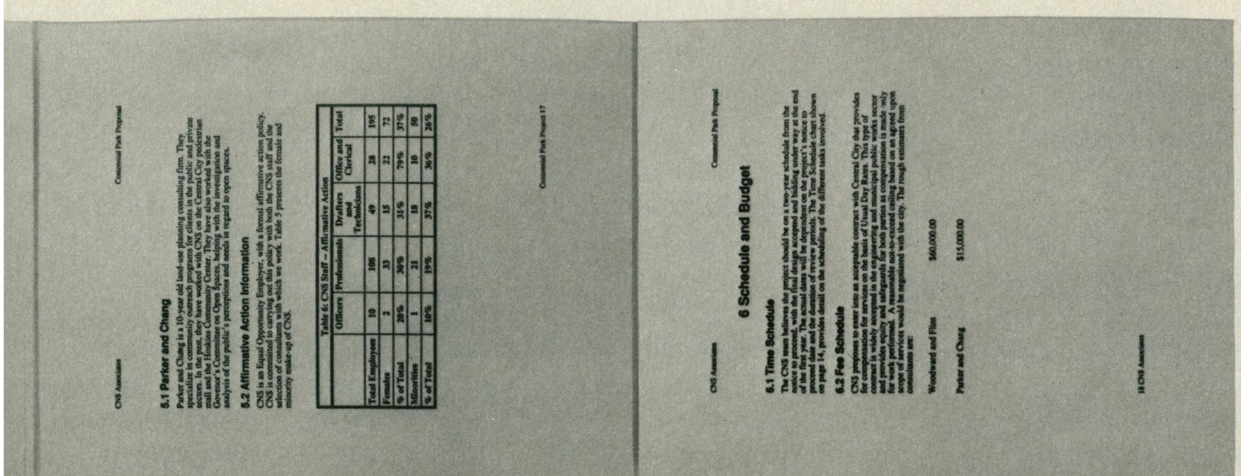

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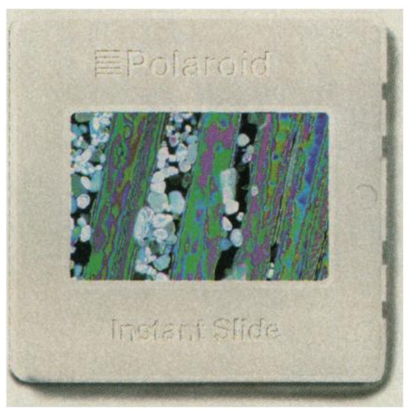

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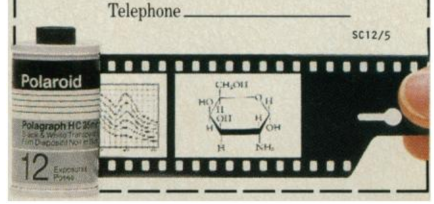

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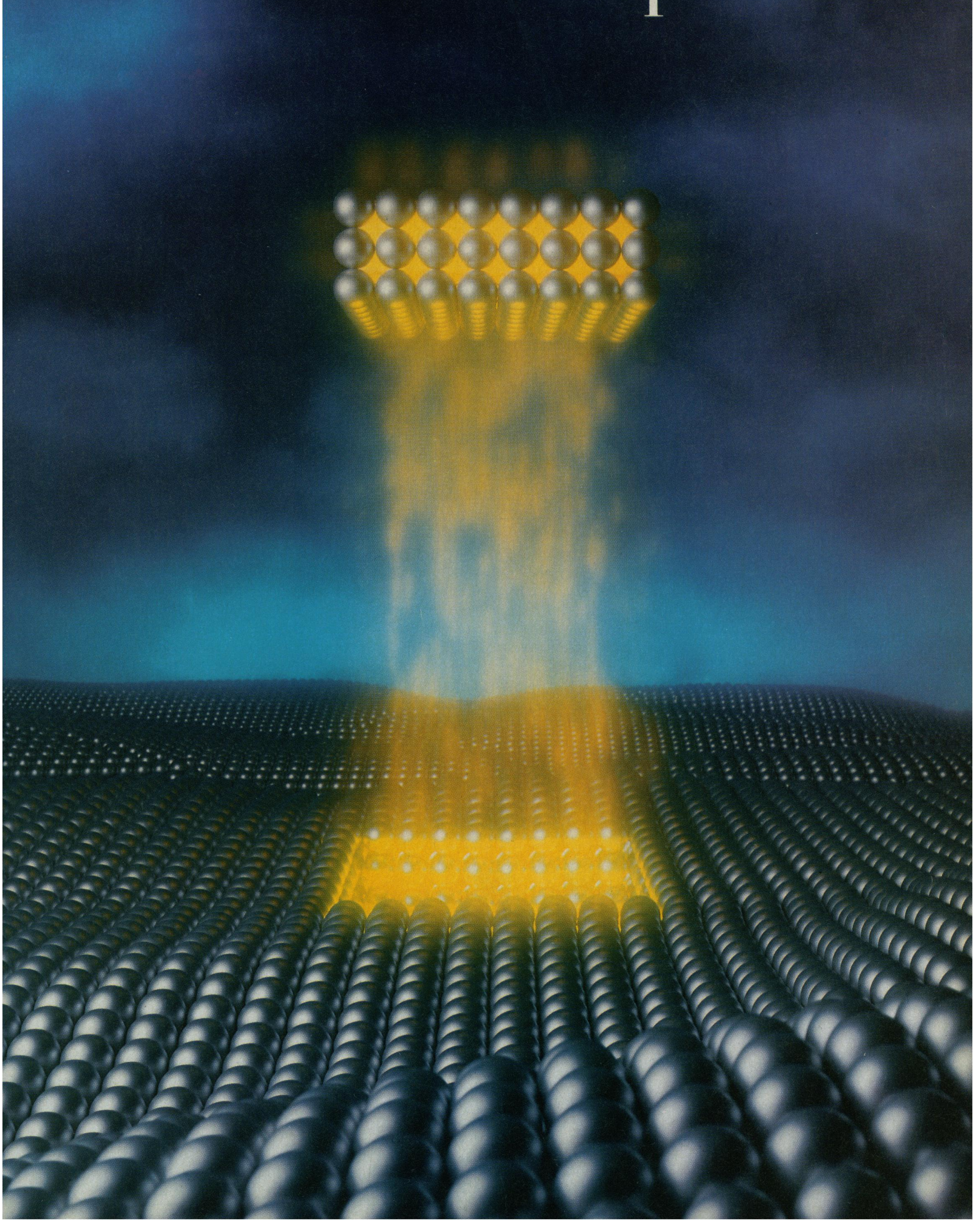


The Pressure Extrapolation

Modern automotive catalytic converters contain rhodium which promotes chemical reactions to remove pollutants from a car's exhaust. Scientists at the General Motors Research Laboratories have recently made discoveries about one such chemical reaction, the reaction between nitric oxide and carbon monoxide, pointing the way toward new or improved catalysts.

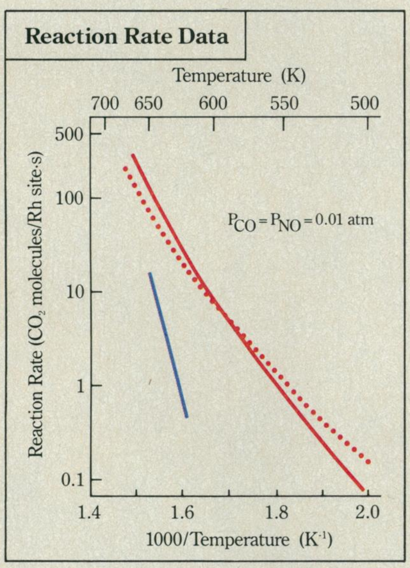


Figure 1: Rate comparisons for the NO-CO reaction. Measured data over single crystal Rh(111) (solid red line) and over supported Rh (blue line); model predictions (dotted red line).

Figure 2: Schematic representation of the elementary intermediate steps for the NO-CO reaction.

MOST FUNDAMENTAL catalytic studies using surface science techniques require an ultrahigh vacuum environment (10^{-13} atm). They are best suited for studying well characterized materials, such as metal single crystals. Catalytic reactions of practical interest, however, involve polycrystalline materials, in the form of small metal particles dispersed on supports. And they take place at atmospheric pressures rather than in an ultrahigh vacuum.

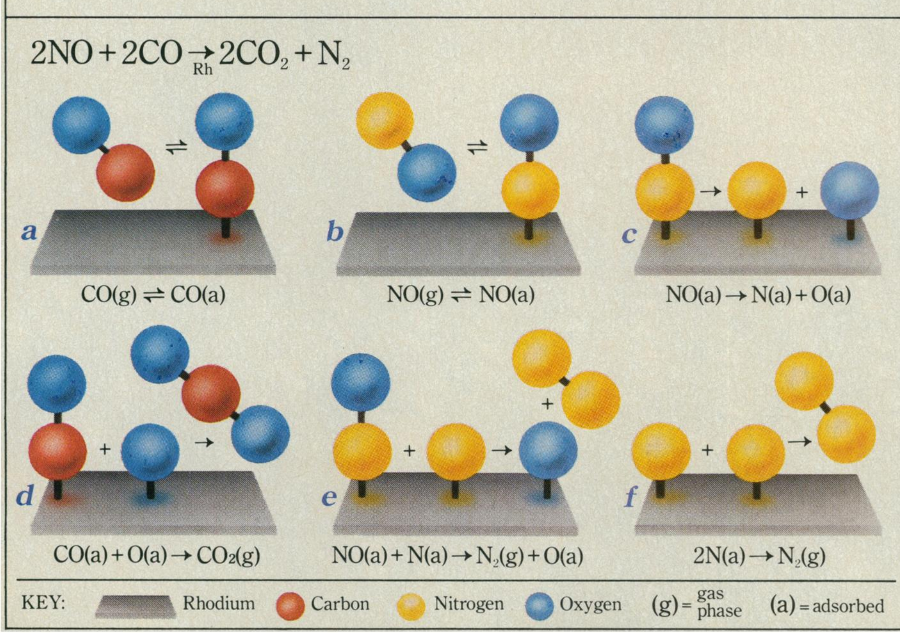
Now Dr. Galen B. Fisher and Dr. Se H. Oh have demonstrated how the wealth of chemical information obtained from ultrahigh vacuum (UHV) studies of ideal, single-crystal catalysts can be applied to the understanding of real-world systems that have different catalyst environments and that operate at much higher pressures.

These researchers concentrated their studies on the many chemical reactions that occur in modern automotive catalytic converters. One such reaction is the reduction of nitric oxide (NO) by carbon monoxide (CO) over a rhodium (Rh) catalyst to yield carbon dioxide (CO_2) and nitrogen (N_2) (Figure 2).

Dr. Fisher used various surface science spectroscopies in ultrahigh vacuum to study all of the elementary reactions over a rhodium single crystal [Rh(111)] that might be involved in this specific reaction. Over several years he measured the rates and determined the activation energies of each of these reactions. For most of these reactions, this was the first time these parameters had been measured. Based upon these results, Dr. Fisher hypothesized that the elementary reactions shown in Figure 2(a-f) were the significant steps involved in the NO-CO reaction and that nitrogen recombination and desorption (Figure 2f) was the rate-controlling step on Rh(111).

Dr. Fisher and Dr. Oh also initiated kinetic studies of this reaction at realistic reactant partial pressures and temperatures using two different catalysts—one was a rhodium single crystal [Rh(111)], and the other consisted of rhodium particles supported on alumina [Rh/Al_2O_3]. The rhodium concentrations on the support were similar to those used in an automotive catalytic converter. The studies with the single crystal at realistic, high pressures were done in collaboration with Dr. D. Wayne Goodman of Sandia National Laboratories.

At the same time, Dr. Oh devised a mathematical model for this reaction. The model consists



of steady-state conservation equations for the surface species, based on the reaction mechanism and the rate expressions for the individual reaction steps determined in Dr. Fisher's UHV studies. Overall reaction rates could then be computed from the surface concentrations satisfying the conservation equations. The reaction rates predicted by this model, which depend only on reactant partial pressures, are shown in Figure 1 (dotted red line).

The kinetics of the NO-CO reaction measured over a rhodium single crystal using realistic reactant partial pressures are shown in Figure 1 (solid red line). The agreement with the model predictions indicates that Drs. Fisher and Oh had correctly identified all of the intermediate reaction steps and confirms that, in this case, nitrogen recombination and desorption (Figure 2f) is the rate-controlling step on Rh(111). The fact that the agreement is so good also indicates that the rates of the elementary reactions measured under UHV conditions are still valid at realistic reactant partial pressures—a pressure extrapolation of more than ten orders of magnitude.

THE KINETICS of the NO-CO reaction measured over the supported rhodium catalyst (Figure 1, blue line), however, were much slower than predicted by the model. In addition, infrared studies have shown that NO is the predominant surface species on the catalyst, suggesting that in this case NO dissociation (Figure 2c) is the rate-controlling step. In fact, if the rate constant for NO dissociation measured under UHV conditions and used in the model is reduced by a factor of 2000, the kinetics of the NO-CO reaction measured over the supported rhodium catalyst are correctly predicted.

The difference between the kinetics of the NO-CO reaction measured over a rhodium single crystal and the kinetics measured over supported rhodium shows that this reaction depends on the environment of the rhodium in the catalyst. The reaction model strongly suggests that the NO dissociation reaction is the reaction step most sensitive to the rhodium environment.

"While our reaction model cannot tell us why NO dissociation is slower on supported rhodium," observes Dr. Oh, "it can help identify the kinds of studies necessary to clarify the origins of such sensitivity." Comparative kinetic studies can also provide useful insights for developing improved NO reduction catalysts. "Our studies have already told us," adds Dr. Fisher, "that one possible path to improving automobile catalysts is to make modifications that increase the NO dissociation rate."

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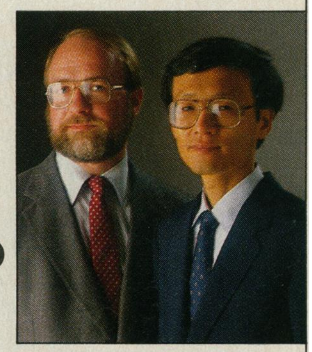

Dr. Galen B. Fisher (left) and Dr. Se H. Oh are both Group Leaders in the Physical Chemistry Department at the General Motors Research Laboratories.

Dr. Fisher holds the title of Senior Staff Research Scientist, and heads the Surface Chemistry and Corrosion Science Group. He attended Pomona College as an undergraduate and received his graduate degrees from Stanford University in Applied Physics. Before coming to General Motors in 1978, he did post-doctoral studies at Brown University and worked at the National Bureau of Standards. Since then, his research has been involved with surface science studies of various catalytic reactions.

Dr. Oh is a Senior Staff Research Engineer, heading the Catalytic Kinetics Group. He received his undergraduate degree from Seoul National University and holds a doctorate in Chemical Engineering from the University of Illinois. Dr. Oh did post-doctoral work at the University of Toronto prior to joining GM in 1976. Since then, he has been involved in measuring and modeling the kinetics of catalytic reactions.

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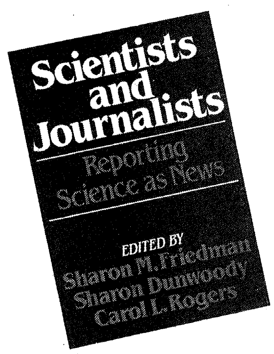

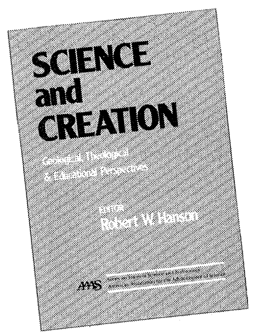

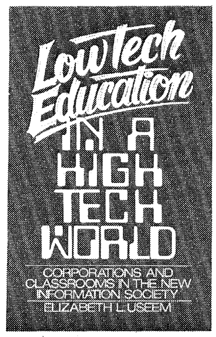

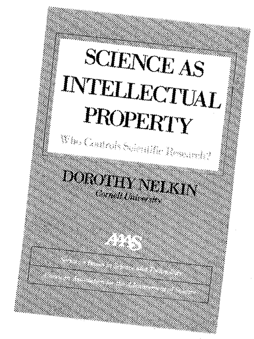

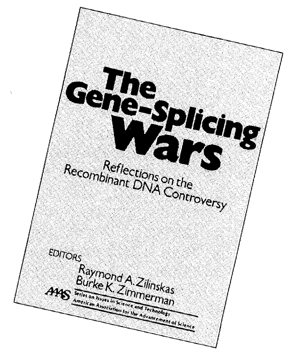

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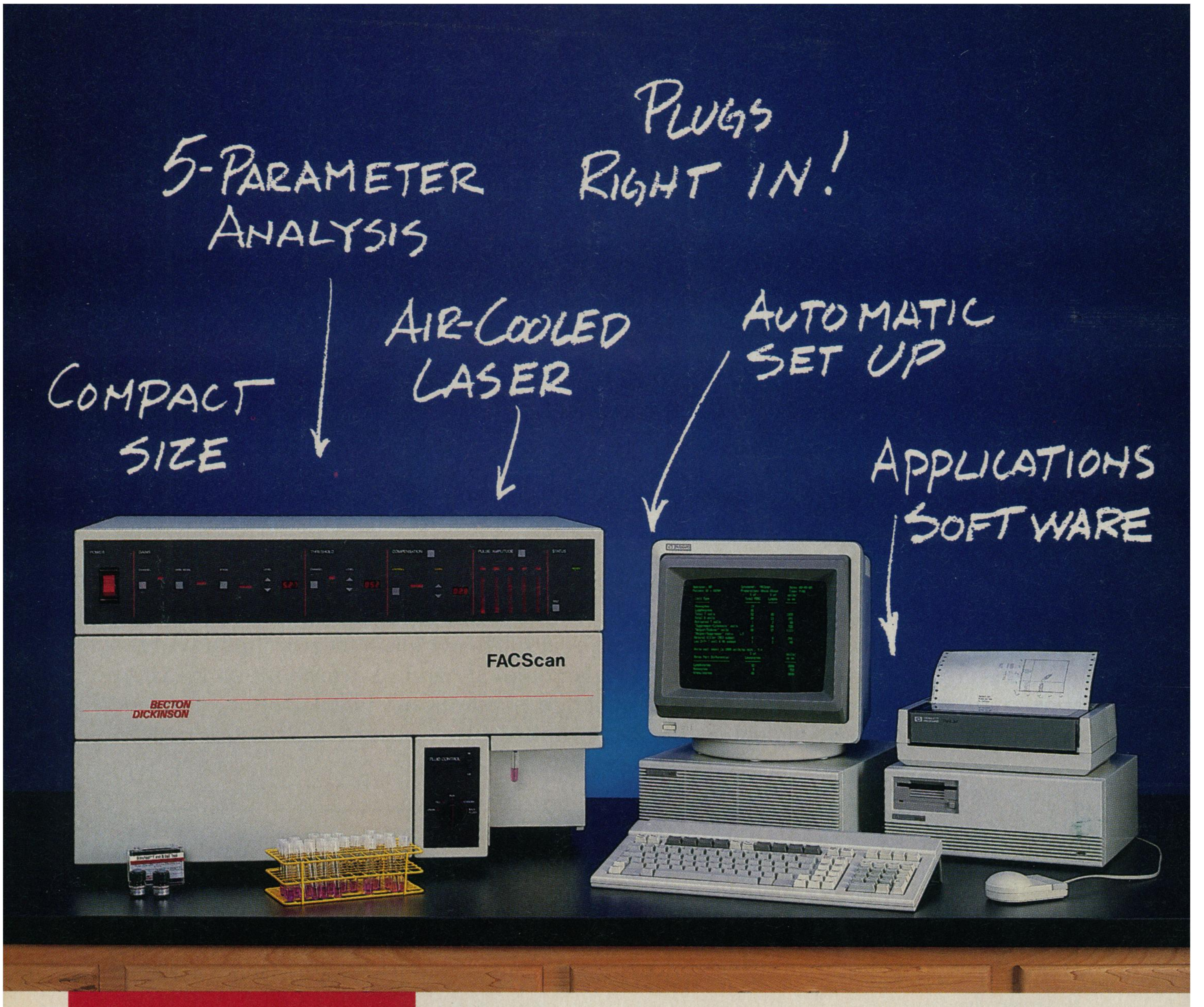

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