with the northern polar hood is shown in Fig. 1B. On all occasions when observations were made north of 45°N during winter, ozone was measured and the polar hood was always visible. The data plotted in Fig. 1B are the maximum amounts of ozone observed in the latitude range 50°N to 75°N. The amount measured varied, ranging all the way from the detection limit of 3 μ m-atm up to the largest value observed on Mars by Mariner 9, 57 µmatm. In spring when measurements were made of specific targets in the north, there was less ozone than in the winter and the polar hood was not readily visible.

The behavior of ozone over the south polar cap in summer is shown in Fig. 2A. Throughout the summer, the Mariner 9 observations show that there was no ozone over the remnant of the cap. Near the end of the summer the amount of ozone increased above the detection limit, reaching a value of 6 μ m-atm. Favorable viewing conditions were not attained during the fall in the south.

The behavior of ozone over the north polar cap during the winter and spring is shown in Fig. 2B. Toward the end of winter, when the polar hood cleared sufficiently to permit the cap to be seen by the Mariner 9 instruments, the amount of ozone measured was 16 μ m-atm. In the middle of spring the quantity of ozone above the polar cap was 10 µm-atm, and its magnitude decreased monotonically during the latter half of the northern spring. During the last two orbital operations of Mariner 9, just after the northern summer solstice, observations of the north polar cap showed that the ozone had disappeared.

The amount of ozone that was measured over the south polar cap in 1969, by the Mariner 7 ultraviolet spectrometer, was 10 μ m-atm (1). The season on Mars at that time was southern spring. This value is plotted in Fig. 2B at the corresponding seasonal time for comparison with the Mariner 9 data for the 1972 northern spring.

When ozone was observed in association with the polar hood in the fall and winter seasons, the ultraviolet spectrometer also detected increased reflectivity in the region from 3000 to 3500 Å compared to the reflectivity of the clear atmosphere. This increased reflectivity presumably is produced by the ice crystals of the polar hood. We have suggested elsewhere that

ozone with the appearance of the polar hood is experimental evidence for the suppression of ozone in the presence of water vapor (3). Current theoretical treatments (4) suggest that not only water vapor, but also hydrogen peroxide (which is a by-product of the photolysis of water vapor by sunlight in the presence of molecular oxygen) should have this effect. However, a full explanation of the present results will probably involve the effects of variations in atmospheric temperature and of the global transport of water vapor, in addition to photochemical considerations.

this correlation of the appearance of

Achieving an understanding of the presence and variation of ozone in the martian atmosphere is important for our knowledge of current conditions on Mars and the state of evolution of its atmosphere. In addition, this understanding of ozone photochemistry in a planetary atmosphere is relevant to the earth's atmosphere, where questions as to the stability of the earth's ozone in the presence of added impurities arise. On Mars, the Mariner observations show a 20-fold variation in the amount of ozone, depending on the presence or absence of another minor constituent, water vapor, in the atmosphere. In the evolution of the earth's primitive atmosphere, the formation of an ozone layer may have played an important role in the prebiotic chemistry that took place on the surface. The seasonal formation and disappearance of ozone in the contemporary martian atmosphere may be of consequence in any prebiotic chemistry that may be occurring there.

CHARLES A. BARTH CHARLES W. HORD A. IAN STEWART Department of Astro-Geophysics and Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder 80302

ARTHUR L. LANE Jet Propulsion Laboratory, California Institute of Technology, Pasadena 91103

MARY L. DICK

GAIL P. ANDERSON

Laboratory for Atmospheric and Space Physics, University of Colorado

References and Notes

- 1. C. A. Barth and C. W. Hord, Science 173, 197 (1971).
- 2. The amount of ozone is expressed in terms of micrometer-atmospheres, the thickness of the ozone column in micrometers when compressed to standard pressure and temperature on the earth; $1 \mu \text{m-atm} = 1 \times 10^{-4}$ cm-atm $= 2.69 \times 10^{15}$ molecules per square centimeter. The amount of ozone in the earth's atmosphere is approximately 0.3 cm-atm.
- amount of ozone in the earth's anticsphere is approximately 0.3 cm-atm.
 3. A. L. Lane, C. A. Barth, C. W. Hord, A. I. Stewart, *Icarcus* 18, 102 (1973).
 4. T. D. Parkinson and D. M. Hunten, J. Atmos.
- T. D. Parkinson and D. M. Hunten, J. Atmos. Sci. 29, 1380 (1972); M. B. McElroy and T. M. Donahue, Science 177, 986 (1972).
- The development of the ideas presented here was greatly stimulated by many conversations with all of the participants in the Mariner 9 mission. This research was supported by the National Aeronautics and Space Administration.
- 4 December 1972

Ice and Snow in Eolian Sand Dunes of Southwestern Wyoming

Abstract. Snow becomes incorporated in eolian sand dunes of southwestern Wyoming when snow cornices on dune crests begin to melt, slide down the lee slope, and are covered by sand during subsequent lee-slide deposition. In some cases burial is rapid enough to provide the insulation necessary to preserve the ice and snow within the dune throughout the year. Deformed laminae associated with the incorporated snow are preserved, and these features may be of value as paleoclimatic indicators in ancient sandstone.

Ice and snow are preserved throughout the year in colian dunes in the Killpecker dune field approximately 25 km east of Eden, Wyoming. Buried snow occurs as lenticular bodies whose maximum and intermediate axes lie in a plane more or less parallel with the major internal bedding of the dune. In September 1972, 4 months after the last snowfall in the area, two separate snow lenses were observed in one trench approximately 10 m downhill from the crest of a transverse dune 30 m high. The snow lens shown in Fig. 1 is 25 cm thick, extends 2.5 m laterally parallel to the crest of the dune, and is only 1.5 m beneath the dune surface. It is surrounded by relatively undisturbed laminae which, above the lens, conform to the convex upward boundary between sand and snow. A larger and somewhat more irregular body of snow was discovered in the same trench approximately 2.0 m below the dune surface, but its exact geometry and size are not known. A zone of completely frozen sand 10 cm thick surrounds this lens, and the adjacent laminae are slightly disrupted. To my knowledge, this is the first report of ice and snow preserved in eolian dunes, although Merk (1) has described an apparently temporary interment of snow in the Great Sand Dunes of Colorado.

Surface observations of the Killpecker dunes in the spring reveal that large snow cornices which formed on dune crests during the winter are covered by dry, blown sand which is remobilized after the thinner snow cover on the surrounding terrain has melted. Subsequent warming causes partial melting of the sand-covered cornices. They become unstable and slide down the lee side of the dune. Contortion and brecciation of laminae in the moist, cohesive sand covering the snow take place during melting and sliding. Disruption of laminae also occurs directly beneath the sliding cornice. The deformed mass of snow and sand (Fig. 2) may come to rest near the bottom of the lee slope or, more commonly, at some higher point on the slope where local equilibrium conditions between sand, wind, and dune geometry provide a slope somewhat less than the angle of repose of dry sand.

Observations in trenches and on the surface of dunes in September, before new snowfall, show that, where leeslope sand deposition has been rapid, some of these slumped snow cornices are buried and preserved within the dune. Collapse structures form in adjacent laminae where the depth of burial is such that melting can continue under prevailing climatic conditions. In some cases, however, the overlying sand provides sufficient insulation to prevent further melting and the snow becomes a permanent or semipermanent part of the dune.

The occurrence of ice and snow in the Killpecker dunes is one of only a few examples of perennially frozen ground in Wyoming. It is a surprising discovery because the ground is at an elevation of only 2043 m. With the exception of buried ice in Yellowstone National Park (2) and permafrost in peat deposits in the Beartooth mountains (3), the only other known perennially frozen ground in Wyoming is associated with modern glaciers or rock glaciers (4) at elevations in excess of 3000 m. Examples of frozen ground at lower elevations, such as the no longer existing "ice slough" discovered by early Wyoming settlers (5), are described only in pioneer journals and have not been precisely documented.

23 FEBRUARY 1973

Fig. 1. One of several snow lenses still preserved in eolian dune sand 4 months after the last snowfall. The lens is 25 cm thick, 2.5 m wide, and 1.5 m beneath the surface.

The Killpecker dune field is an excellent example of cold-climate dunes. Climatic records (6) from 1921 to 1960 for Farson, Wyoming, 33 km northwest of the dune field at approximately the same elevation, show that the warm month and cold month average temperatures are 17.8° and 12.2° C, respectively, and that the annual precipitation is 18 cm. Snowfall accounts for approximately 40 percent of the precipitation. Furthermore, a compilation of freeze probabilities (7) shows that a freeze at any time throughout the year is relatively common and that, on the average, there are only 59 days between the last spring occurrence and the first fall occurrence of freezing temperatures. Summary plots of temperature data (7) show that the Killpecker dune field lies in one of the coldest regions in Wyoming. The cold climate, along with the mechanism described above for the rapid burial of



Fig. 2. Deformed mass of sand and snow formed when a sand-covered cornice melted and slumped down the lee side of the dune. This photograph was taken 4 months before that shown in Fig. 1 at the same location. The trowel is 28 cm long.

snow, is responsible for this rather unique occurrence of perennially frozen ground.

One important implication of this discovery is that the process by which snow is incorporated into dunes and the melting of temporary snow in the dune may provide a mechanism for large-scale contortion and brecciation. Large-scale deformation in ancient sandstone of supposed eolian origin (for example, the Navajo, Entrada, and Casper formations) has perplexed geologists for many years. As a result of observational and experimental work, McKee (8) has related smallscale deformation to lee-side avalanching on dunes and large-scale recumbent folding in cross-bedded sand to surface drag, but there is still no adequate explanation for contortions on a scale of several meters and more. In fact, the apparent lack of eolian processes capable of producing such deformation of cohesive sand masses has led some observers to cite it as evidence for subaqueous deposition.

Although I did not observe deformation as large as that in some ancient eolian deposits, the contortion associated with cornice sliding (5 m wide and 0.5 m in amplitude) (Fig. 2) and the zone of brecciation (2 m wide and 0.3 m high) associated with volume change due to the melting of interred snow are much larger than any previously reported for modern dunes. Apparently depositional conditions and processes in cold-climate dunes produce internal structures not observed in more commonly studied warm-climate dunes (9).

It is premature to relate large-scale deformation in ancient eolian sandstone to the incorporation and melting of snow in cold-climate dunes. Sufficient modern analogies have yet to be documented. Furthermore, other mechanisms capable of producing these structures should be sought in order to evaluate the potential of such occurrences as paleoclimatic indicators. In any case, large-scale deformation in sand should not be interpreted as definite evidence of subaqueous deposition.

JAMES R. STEIDTMANN Department of Geology, University of Wyoming, Laramie 82070

References and Notes

- 1. G. P. Merk, thesis, University of Colorado . P. (1962). 2. J. ™
- J. M. Good, Contrib. Geol. 3, 92 (1964).
 W. G. Pierce, U.S. Geol. Surv. Prof. Pap. 424-B (1961), p. 154. N. Potter, Geol. Soc. Amer. Bull. 83, 3025 4.
- (1972) 5. J. D. Love, U.S. Geol. Surv. Prof. Pap. 495-C
- (1970), p. 121.
 6. C. F. Becker and J. D. Alyea, Univ. Wyo. Agr. Exp. Sta. Bull. No. 415 (1964); Univ. Wyo. Agr. Exp. Sta. Bull. No. 416 (1964).
- Wyo. Agr. Exp. Sta. Bull. No. 416 (1964).
 7. ______, H. Epperson, Univ. Wyo. Agr. Exp. Sta. Bull. No. 381 (1961).
 8. E. D. McKee, M. A. Reynolds, C. H. Baker, Jr., U.S. Geol. Surv. Prof. Pap. 450-D (1962), p. 155; E. D. McKee, J. R. Douglass, S. Rittenhouse, Geol. Soc. Amer. Bull. 82, 359 (1971) (1971)
- (1971).
 E. D. McKee, Sedimentology 7, 1 (1966); J. J. Bigarella, R. D. Becker, G. M. Duarte, Mar. Geol. 7, 5 (1969); E. D. McKee and J. J. Bigarella, J. Sediment. Petrol. 42, 670 (1972).
 I thank H. C. Haywood, D. J. Kirn, and J. E. McClurg for their assistance in the field
- 10. and J. D. Love, D. L. Steidtmann, and H. R. Sawyer for their help in manuscript preparation.

24 October 1972

Exhaust Catalysts: Appropriate Conditions for Comparing Platinum and Base Metal

Abstract. There are fundamental differences in the behavior of alumina-supported samples of a platinum and a copper-chromium catalyst for oxidation of carbon monoxide in a simulated automotive exhaust stream. Ignoring such differences can result in inappropriate comparisons between oxidation catalysts for automotive application.

The requirement that carbon monoxide and hydrocarbons be virtually eliminated from the exhaust of 1975 and later model automobiles has generated considerable interest in the development of an oxidation catalyst suitable for this task. Precious metals, notably platinum and palladium, have been reported to be especially well suited for catalyzing oxidation reactions in the auto exhaust environment (1). However, the high cost and relatively short supply of these metals have caused the search to continue for an oxidation catalyst which is inexpensive, plentiful, and as effective as the metals of the platinum group. Our studies of platinum and base metal catalyst systems have shown that the fundamental differences in their behavior have direct implications for both laboratory comparisons and automotive exhaust applications since the choice of experimental conditions can determine the outcome of the comparison. In light of this result, recent comparisons of various automotive emission control catalysts (2, 3)deserve some attention.

The catalysts used to oxidize CO in our experiments were among the most active of their respective classes. The base metal catalyst was a combination of copper (~ 8 percent by weight) and chromium (\sim 7 percent by weight) on an alumina support. Under the conditions of the experiments, these metals exist primarily in an oxidized form. The other catalyst, 0.3 percent by weight platinum on alumina, presumably retained the metallic state throughout the experiments. The catalysts were made by first impregnating 3-mm spheres of alumina with solutions of the appropriate metal salts and then drying and calcining.

Oxidation activity was measured in an integral flow reactor, with 7 cm³ of catalyst placed in a 19-mm (inside diameter) stainless steel pipe enclosed in a tube furnace. A feedstream blended to simulate exhaust gas (typically 2 percent CO, 2 percent O₂, 0.05 percent C_3H_6 , 10 percent H_2O , 10 percent CO_2 , and the balance N_2) was passed at flow rates ranging from 3.5 to 19 liter/ min through the catalyst bed as the furnace temperature was slowly raised. The exit stream was analyzed continuously for CO, O_2 , and hydrocarbons. Conversion and catalyst bed temperature were recorded simultaneously as the temperature increased.

Data on the relation between conversion and temperature for various inlet gas compositions were fitted to integrated forms of several different rate equations to establish the concentration dependence of the CO oxidation reaction. The rate over the base metal catalyst is best described by the expression

$$-d[\mathrm{CO}]/dt \equiv k_{\mathrm{bm}}[\mathrm{CO}]^{0.7} \qquad (1)$$

Symbols in brackets represent concentrations; t is time; and the coefficient $k_{\rm bm}$ is the rate constant. These kinetics are in reasonable agreement with those reported earlier for oxide catalysts (4) and are to be expected if the slow step in the reaction sequence is the extraction of an oxygen atom from the base metal oxide lattice by a CO molecule.

The rate over the Pt catalyst is best described by the expression

$$-d[\mathrm{CO}]/dt = k_{\mathrm{Pt}}[\mathrm{O}_2]/[\mathrm{CO}] \qquad (2)$$

This expression is also in agreement with previous work (5), and it is in SCIENCE, VOL. 179