the method can reveal overgrowth and cementation phenomena in carbonates not visible in white or polarized light. Generations of fractures can be distinguished by their luminescence, and diffuse structures in marbles can be seen which apparently were present as sharp features in the limestone prior to metamorphism. In several cases fossil organisms, which could not be recognized as organisms in polarized light because of extensive recrystallization, could be observed by luminescence. This is evidence in addition to that of Smith (*1*, *2*) that the luminescence technique will have paleontological applications also. Although this report is limited to carbonates, the luminescence technique will certainly be applicable to the petrology of all types of rocks (*1*, *2*).

ROBERT F. SIPPEL
EVERETT D. GLOVER
Field Research Laboratory,
Socony Mobil Oil Company,
Dallas, Texas

References and Notes

1. R. C. Stenstrom and J. V. Smith, *Geol. Soc. Amer. Spec. No. 76* (1964), p. 158.
2. J. V. Smith and R. C. Stenstrom, *Geol.* **73**, 627 (1965).
3. The instrument is described in detail in R. F. Sippel, *Rev. Sci. Instrum.* (in press).
4. H. W. Leverenz, *Introduction to the Luminescence of Solids* (Wiley, New York, 1950), p. 340.
5. W. L. Medlin, *J. Opt. Soc. Amer.* **53**, (1963).
6. ———, *J. Chem. Phys.* **30**, 451 (1959).
7. ———, *ibid.* **34**, 672 (1961).

7 July 1965

Paleozoic Reef in Pakistan

Abstract. *A Silurian, and perhaps Devonian, limestone belt in northern West Pakistan contains the first Paleozoic reefs found on the Indo-Pakistan subcontinent. The belt contains a rich fauna entirely new to Pakistan. Its presence indicates that this area was inundated in Silurian and Devonian times by seas bordered by reefs or containing reef platforms.*

The first Paleozoic reef belt on the Indo-Pakistan subcontinent has recently been recognized in northern West Pakistan. It is present in an east-west trending ridge, rising as much as 75 meters above the surrounding alluvial plain, between the towns of Nowshera and Risalpur about 40 kilometers east of Peshawar (latitude 34°N, longitude 72°E). The portion so far examined is about 8½ kilometers long, but low hills in the continuation of the strike both to the east and to the west probably are additional reef masses. Along this belt a series of individual reefs, ranging in thickness from less than 80 to as much as 250 meters, crops out. These are either separated by shale or connected by bedded limestone of lesser thickness than the reefs.

The reef limestone is massive, generally of pale red color, medium-to-coarse grained, highly fossiliferous, and partly dolomitized. It is underlain by about 30 meters of dolomite containing layers of brachiopods; the dolomite in turn rests on greenish gray, micaceous phyllite interbedded with layers of crinoidal limestone. At its upper limit the reef limestone grades into indistinctly bedded limestone containing few corals or brachiopods but many prominent cephalopods. This limestone is overlain by a gray, medium-grained, partly dolomitic quartzite. The entire sedimentary sequence strikes approximately east-west and dips 45° to 50°N.

The reef limestone contains a rich fossil association of tabular and spheroidal stromatoporoids, tabulate corals, including *Heliolites, Thamnopora, Favosites, Alveolites, Cladopora* (*1*), and *Syringopora*, rugose corals (*Mucophyllum, 1*), brachiopods including *Atrypa* and *Camarotoechia*, and large cephalopods of the family Michelinoceratidae.

All stromatoporoids and corals are so completely recrystallized that their skeletal structures have been thoroughly destroyed and little or nothing of them can be seen in thin section. It is generally only on suitably weathered limestone surfaces that traces of these skeletal structures can be seen in sufficient detail to allow at least generic identification. In the dolomitized rocks the fossil structures have been largely obliterated.

The reef-building organisms are found in many places in growth position; in other places overturned colonies of stromatoporoids and tabulate corals are seen; in some places the limestone is bedded and contains many fragments of reef-builders as well as other fossils. These bedded limestones have strikes deviating in various directions from the regional east-west strike and have dips ranging between 15° and 70°. Such beds are interpreted as reef-talus having a primary sedimentary dip which has been distorted by tectonic tilting.

The age of the reef limestone is Silurian or Early to Middle Devonian. Silurian and Devonian reef faunas have many genera in common and may be difficult to distinguish on the basis of the few specimens collected so far. *Mucophyllum* is most characteristic of Silurian strata, although its range extends into the Lower and, possibly, Middle Devonian (*1*). The fact that the only cephalopods are rather generalized michelinoceratids may point toward a Devonian age of the rock; for in a Silurian reef limestone a greater variety of cephalopod species and genera, such as are known from reefs of that age in Illinois and on the island of Gotland, might be expected. However, such assemblages may well exist in parts of the reef belt that have not been examined as yet.

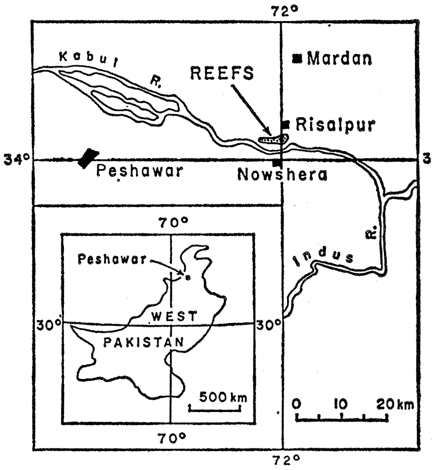

Fig. 1. Paleozoic reefs in Pakistan.

The limestone here described represents the first Paleozoic reef discovered in Pakistan and India and contains a fossil fauna that is entirely new to Pakistan. If a Silurian age is confirmed it will be the first documented fossiliferous exposure of rocks of that age in Pakistan. However, the possibility of an Early or Middle Devonian age cannot yet be ruled out entirely.

The reef limestones have long been utilized locally as building stone and are burnt for lime in kilns near Nowshera. Because much of the limestone is recrystallized, especially at the eastern extremity of the belt, it has also in former times been quarried as marble. Indeed, in the only reference to this rock in the geologic literature (*2*) it is described as a pink marble, formed by metamorphism of a ferruginous limestone. One of the effects of this metamorphism, according to Coulson, was the formation of bands of clear calcite that traverse the rocks. Coulson may well have been referring to the prominent cross sections of long, tabular stromatoporoids, which stand out as very light gray calcite bands in the pale red limestone matrix. In 1957 Kidwai (*3*) made a plane table map of the hills in order to evaluate the limestone reserves.

Fossil assemblages have also been collected recently from limestone localities in northern West Pakistan as much as 56 kilometers distant from the Nowshera reef. Some of these limestones seem to be correlative with the Nowshera reef, especially the Kala limestone north of the town of Swabi in the Mardan district, which in part represents a reef talus.

These limestones have in the past been assigned partly to the Precambrian and partly to the Carboniferous and Permian. The newly found fossils suggest that all the limestones which cover large areas of Swat state and Mardan district may have been deposited during the Silurian or Devonian, or possibly during parts of both periods, in a sea bordered by reefs or containing reef platforms.

The regional metamorphism in the Peshawar area increases toward the north so that the recrystallization and deformation of fossils in limestones tend to increase northward. Dolomitization of these limestones apparently increases toward the east. It is, therefore, unlikely that fossil assemblages as well preserved as those at Nowshera will be found in the limestones either to the east or to the north, although many less-well-preserved fossils have already been found.

No equivalents of these limestones have as yet been found south of Nowshera, but they may correlate with Paleozoic limestones recently found by A. Schreiber (*4*), of the German geological mission to Afghanistan, south of the Kabul River, about 70 kilometers northwest of Peshawar.

Both in Swat state and Mardan district these fossiliferous limestones are associated with extensive, black, fetid, fine-grained limestones and with vuggy, highly porous dolomites. The combination of reefs, fetid limestones, and porous dolomites has potential economic implications for the discovery of oil.

CURT TEICHERT*
KARL W. STAUFFER
U.S. Geological Survey,
Washington, D.C.

References and Notes

1. W. A. Oliver, Jr., private communication.
2. A. L. Coulson, *Rec. Geol. Survey India* **71**, pt. 3, 340 (1936).
3. A. H. Kidwai, "Marble deposits near Nowshera," unpublished report, Geological Survey of Pakistan.
4. A. Schreiber, private communication.

* Present address: Paleontological Institute, University of Kansas, Lawrence.

22 September 1965

Ultrasound Chemical Effects on Pure Organic Liquids

Abstract. *Molecular fragmentation of organic liquids was produced by cavitation due to ultrasound waves, even in the absence of water. The sonolysis of acetonitrile under argon yielded* N_2, CH_4, *and* H_2; *but under oxygen the products were* N_2, CO, CO_2, *and* H_2O. *Pure nonaqueous carbon tetrachloride also underwent sonolytic decomposition under either argon or oxygen, with the production of elemental chlorine.*

Intense ultrasonic waves cause chemical changes in water and in aqueous solutions if a permanent gas is present, by a mechanism involving cavitation (*1*). In pure water, sonolysis produces hydrogen atoms and hydroxyl radicals, as well as molecular hydrogen, oxygen, and hydrogen peroxide (*2, 3*). When dissolved substances are present, they may react with the H and OH radicals, causing further chemical changes in a manner similar to the "indirect action" of radiolysis (*3, 4*). In addition many volatile organic solutes in water (such as alcohols, aromatic compounds, or carbon tetrachloride) undergo a direct sonolysis inside the cavitation bubbles, with fragmentation of the molecule (*3, 5*).

These facts suggested the possibility that pure organic liquids might be decomposed by intense ultrasound even in the absence of water, although no such observation has been reported. Experiments were performed on high-purity acetonitrile and carbon tetrachloride; both liquids underwent sonolytic decomposition. Acetonitrile was chosen because of its wide use in physical chemistry as a nonaqueous solvent; CCl_4 was picked because it is customarily used for sonochemical studies in aqueous solution.

In the experimental procedure (*3*), a 10-ml glass bulb served as the sample cell, which was irradiated by an ultrasonic generator (800 kcy) and cooled by circulating water. Acetonitrile (4-ml samples) was first saturated with argon, then irradiated in a closed system for 2 to 10 hours; dissipation of acoustic power inside the cell was estimated to be 3 watts. Analysis of the gas phase by both gas chromatography and mass spectrometry showed that nitrogen, methane, and hydrogen were formed in molar ratios of 1:2:4. The yields of these gaseous products were about 10^{-8} mole liter^{-1} min^{-1}, which is about two orders of magnitude less than the yield of hydrogen peroxide obtained from water under the same experimental conditions. An attempt to detect less volatile products in the liquid phase was not successful.

Further experiments were made in which the argon atmosphere was modified by the addition of 10 percent of deuterium gas. Mass-spectrometric analysis showed that the ultrasonic treatment produced HD in substantial yield comparable with that of H_2, an indication that hydrogen atoms are a primary product in the sonolysis.

An oxygen atmosphere was substituted for argon. Comparative experiments showed that the yield of nitrogen from acetonitrile remained unchanged in the oxygen-saturated system, but the yield of hydrogen and methane fell to zero. In their place, new products appeared: namely, carbon monoxide, carbon dioxide, and water, in molar proportions of 6:2:1; the dissolved gas plays a major role in the sonochemical reaction. The mass spectrometry and gas chromatography techniques were here supplemented by O^{18}-tracer experiments of higher analytical sensitivity; parallel experiments were made under O^{18}—O^{18} and O^{16}—O^{16}, and the mass spectra of the gaseous products were compared.

For acetonitrile under argon, the sonolytic formation of methane and nitrogen in 2 : 1 ratio is consistent with the rupture of the C—C bond, giving methyl and cyanide radicals as intermediates. The production of hydrogen in high yield and the formation of H atoms as intermediates are evidence for efficient cleavage of the C—H bonds also, which is not surprising in view of the bond strengths (*6*).

Under oxygen, the sonolysis of acetonitrile results in oxidation to CO and CO_2 and in the formation of N_2 in relatively high yield. The products are different when acetonitrile is subjected to radiolysis (*7*). This demonstrates again the distinction (*3*) between sono-