Structures in Carbonate Rocks Made Visible by Luminescence Petrography

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Reports

Structures in Carbonate Rocks Made Visible by Luminescence Petrography

Abstract. *Using a simple device which should bring the luminescence-petrography technique within the grasp of all interested petrographers, we have examined approximately 250 thin sections of carbonate rocks and minerals. Many new phenomena became apparent.*

When thin sections of rock or mineral are examined microscopically by the luminescent light produced by impact of a broad beam of low-energy electrons, structures are frequently evident which are invisible under ordinary white or polarized light. These luminescent structures can give important clues to the origin or history of the material. We report here and illustrate previously unobserved luminescent structures of the following types: (i) growth structures in infillings of sparry calcite which give the complete growth history of the minerals, (ii) similar structures in dolomite which make the origin (growth from solution) clear; (iii) vein structures in large crystalline calcite which are in perfect optical continuity with the host mineral and are thus undetectable by other methods; (iv) growth structures of most unexpected complexity in optical grade calcite (Iceland spar).

The use of electron-excited luminescence as a petrologic tool was suggested by J. V. Smith (*1, 2*). Although he used the microprobe for his observations, he also suggested the possibility of designing a simple electron emitter, to be used with an ordinary petrographic microscope, to bring the luminescence technique within the grasp of essentially all petrographers. The phenomena reported here were observed with a simple device of this sort, built in our laboratory. Surprisingly, this instrument (*3*) has proved superior to the microprobe for luminescence observations. Specific points of superiority are:

1) The luminescence features may be compared much more easily with features apparent in normal petrographic practice.

2) Ordinary uncoated and unpolished thin sections may be used.

3) Much larger areas of the specimen (up to 10 by 15 mm) can be illuminated by the electron beam and examined with low power objectives.

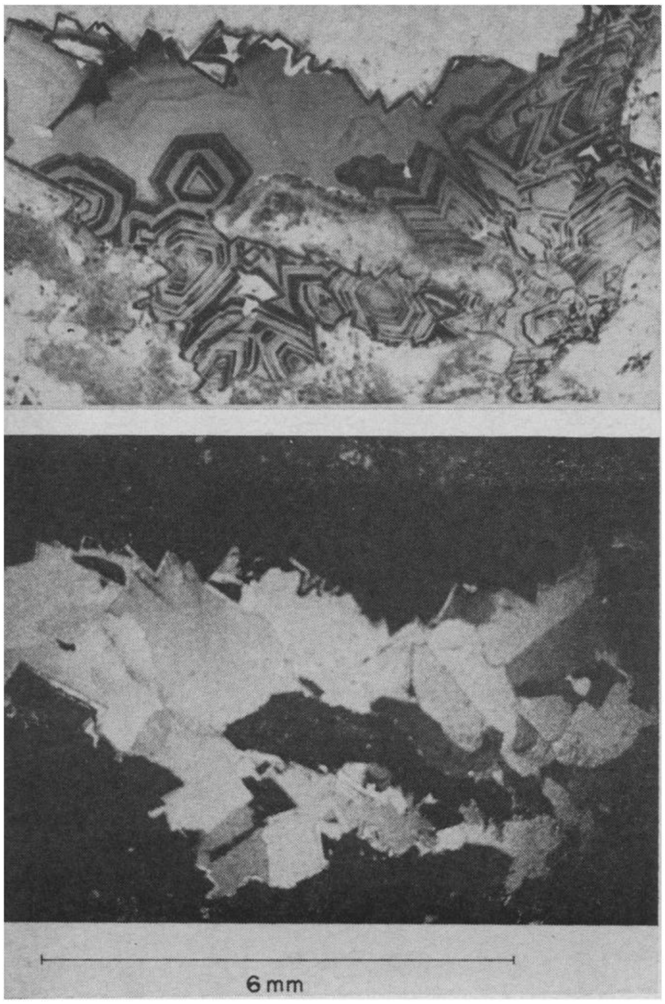
To date, approximately 250 thin sections of carbonate have been examined with the instrument. Of these, approximately 40 were dolomites, 70 were calcites of Iceland spar quality, and the rest were limestones. We report here and illustrate some of the most striking phenomena we found.

It is well known that the orange cathodoluminescence of calcite is due to the presence of divalent manganese (*4*). Medlin (*5*) has investigated the Mn^{++} transitions involved, in terms of the emission spectrum. It is also known that Fe^{+++}, Co^{++}, and Ni^{++} quench the Mn^{++} luminescence in calcite (*6*). Most carbonate rocks which we have examined show this same orange luminescence, and Smith (*2*), using the microprobe, has shown that areas high in iron content do not luminesce. We have observed several additional features. Although most carbonate rocks show orange luminescence, most calcites of Iceland spar quality do not. Without exception, Iceland spar crystals lacking orange luminescence show a definite blue luminescence which is always quite uniform in distribution. The absence of zoning in this blue luminescence is evidence that an activator ion is not responsible. The most reasonable tentative explanation is that the blue luminescence arises from transitions in an unidentified defect center. Blue luminescence is also observed occasionally in regions of carbonate rocks. A definite green luminescence is frequently seen in linear distributions in Iceland spar and as irregular blobs in some specimens. Because of the variable distribution of this luminescence, we attribute it to an unidentified activator impurity.

Medlin (*7*) attributed the thermoluminescence of dolomite also to Mn^{++} ions and described the spectral distribution as the same as calcite—a band peaking at 6600 Å and appearing orange (*5*). In calcites and, in particular, in dolomite we find significant spectral shifts. Although many specimens do luminesce in the orange, it is by no means unusual to find a specimen which shows a significant shift to the yellow or to the red. The extremes which have been found to date are one specimen which luminesced brilliant yellow and another which luminesced a deep red. The total shift possible thus seems to be at least 1000 Å. The cause of this shift is at present not understood.

In luminescence, structures become visible which are entirely absent when ordinary petrographic methods of observation are used. Four such types of structure are shown in black and white. The matching pictures taken with crossed Nicols are of rather poor quality because ordinary unpolished thin sections were used and the pictures were taken in the instrument. Thus, immersion oil could not be used.

Figures 1, 2, and 3 are of calcite infillings in a dolomite from Kline, New Mexico. In each figure, the lower photograph shows what one can observe under polarized light with crossed Nicols. The central, light regions are the infillings of calcite and the dark, outer regions are dolomite. Individual grains of calcite of rather irregular shape may be distinguished. The upper photograph in each figure is of the same area of the specimen, showing the luminescent structures which become visible under electron bombardment. Everything visible in the luminescence photographs was produced on the film by the luminescence from the rock itself; no auxiliary light was used. The dark regions in the photographs luminesced a brilliant orange in calcite and a deep red in dolomite. Evidently the luminescent banding in the calcite is produced by variations in the concentration of Mn^{++} activator ions or quenching



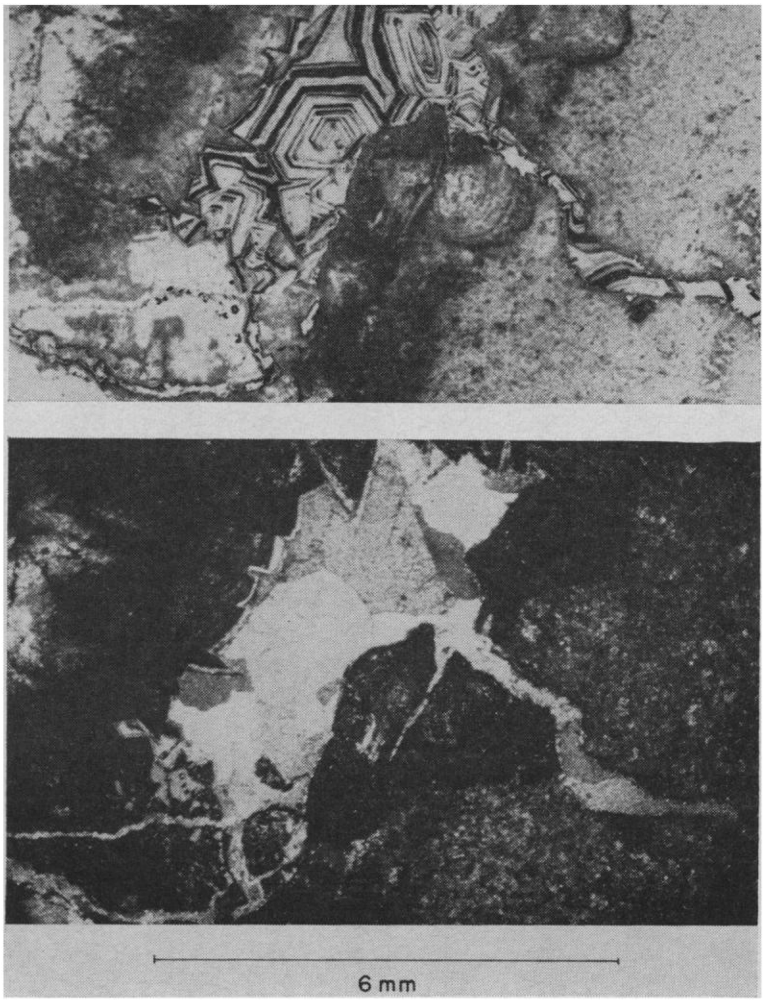
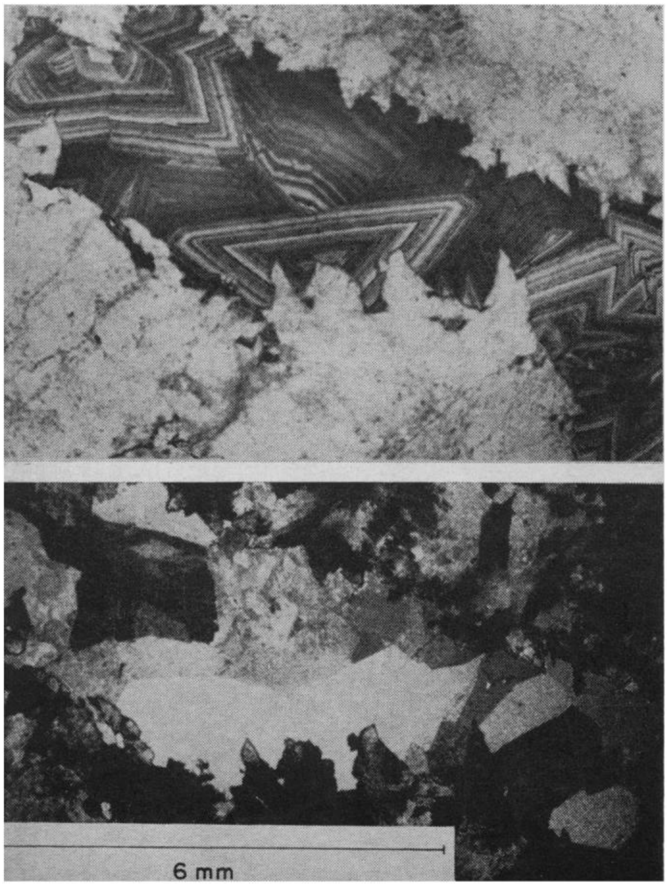
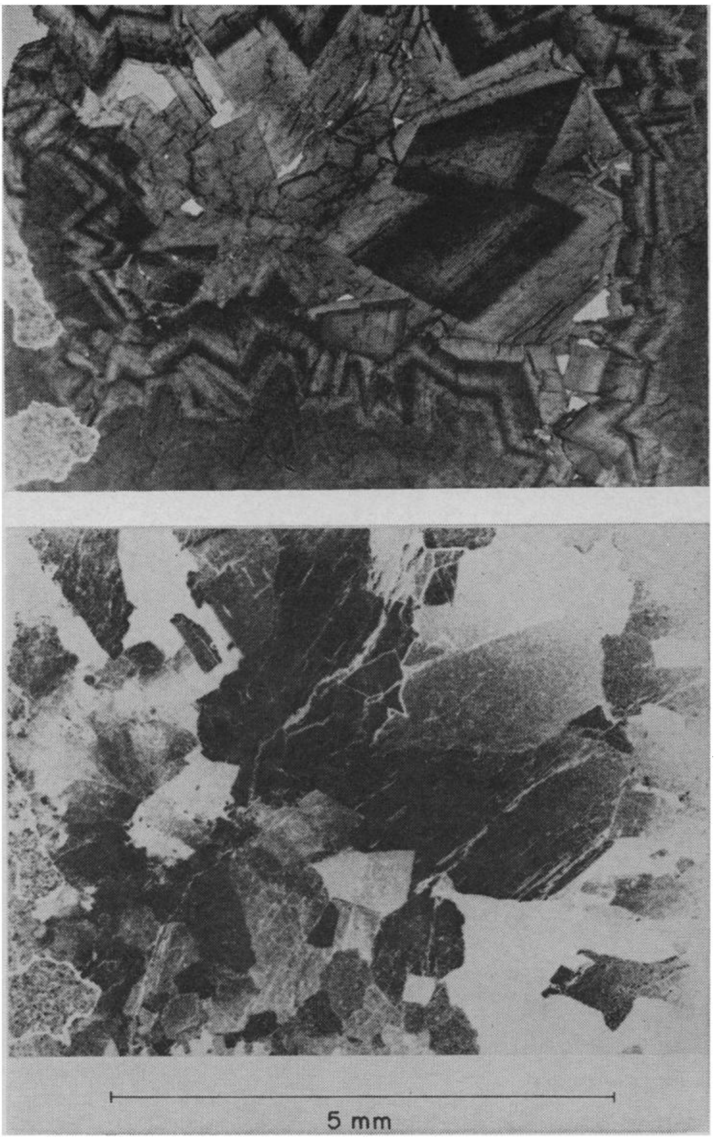


Fig. 1 (above left). Calcite infilling in dolomite. The top photograph was taken by luminescence from the specimen only. The bottom photograph is of the same region of the same specimen, taken with crossed Nicols. All the luminescence photographs are negatives. The dark areas correspond to bright luminescence and the light areas to dim luminescence. Fig. 2 (above right). Calcite infilling in dolomite. A region as photographed by luminescence (top) and with crossed Nicols (bottom). Fig. 3 (below left). Calcite infilling in dolomite. A region as photographed by luminescence (top) and with crossed Nicols (bottom). Fig. 4 (below right). Calcite infilling in dolomite. This photograph was taken by luminescent light, using higher magnification. Under the microscope this single grain revealed 50 distinguishable growth bands.





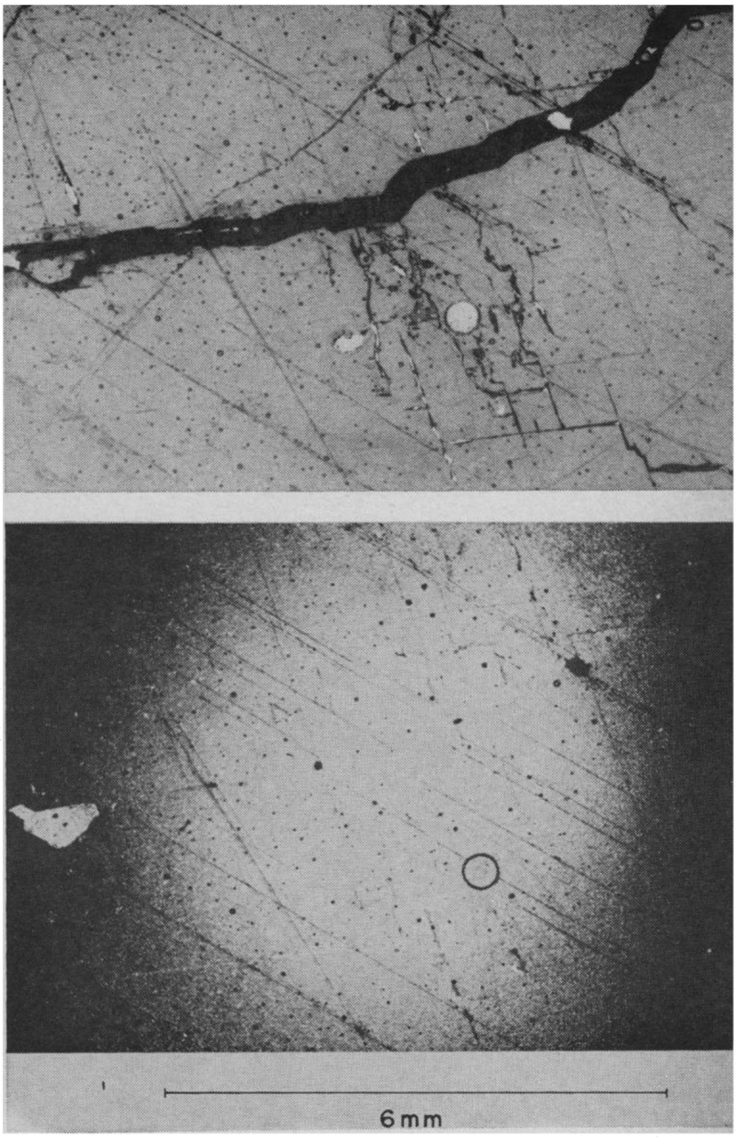


Fig. 5 (above left). Dolomite. A region as photographed by luminescence (top) and with crossed Nicols (bottom) (see text). Fig. 6 (above right). Calcite. A region as photographed by luminescence (top) and with crossed Nicols (bottom) (see text).

ions, or both, present in the solutions from which the crystals grew. We assume that, as waters moved through the rock, variations in the water concentration of these ions were responsible for variations in the amounts incorporated in the growing calcite crystals. Notice particularly that the succession of bands can be correlated from grain to grain, and in some cases grains from different thin sections may be correlated (see particularly Figs. 1 and 2). Thus, we have a detailed history of the growth of the crystals. The most obvious point is that the crystals tend to grow in regular geometric forms, as long as they do not approach the irregular outlines of the enclosing vug. As the crystals grow larger, perhaps in some cases because fluid passages become more constricted and thus introduce a varying supply of ions in solution, the straight leading edges of the growing crystals tend to become irregular, and the crystals adopt a less geometric appearance (see particularly Fig. 1). It appears that the main reason for the irregular appearance of the fully grown crystals is simply the effect of the irregular shape of the confining walls of the vug in which the crystallization has occurred. Notice (particularly in Fig. 1) that some of the crystals appear to alter their habit as the growth proceeds. Figure 4 is a luminescence photograph at higher magnification of an infilled grain of calcite (in the same material). Here is essentially a single grain approximately 2 mm in its largest dimension. This luminescent structure, reflecting the chemical zoning which produced it, permits one to recreate the various stages in the growth history of this mineral. Variations in the growth rate along the leading edges of the growing crystal have been recorded in minutest detail.

Figure 5 shows a dolomite filling in dolomite where the origins of the dolomite can scarcely be argued. The bottom photograph gives no evidence of a particular mode of formation, but the luminescence photograph shows clearly the same type of growth banding as seen before in the calcites. Clearly we have here a vug in which the dolomite grew from solution.

The cover of this issue shows a specimen of carbonatite from Magnet Cove, Arkansas. In the top photograph one can see bladed apatite crystals in a matrix of large crystalline calcite. In fact, all the calcite visible in this crossed Nicols photograph is a single crystal. The bottom photograph (luminescence) reveals a brilliant orange vein running through the calcite, which luminesced a much dimmer shade of orange. This vein can be traced as a series of broken line segments right through the apatite, which luminesced a light violet color. Because the vein calcite is in perfect optical continuity with the matrix cal-

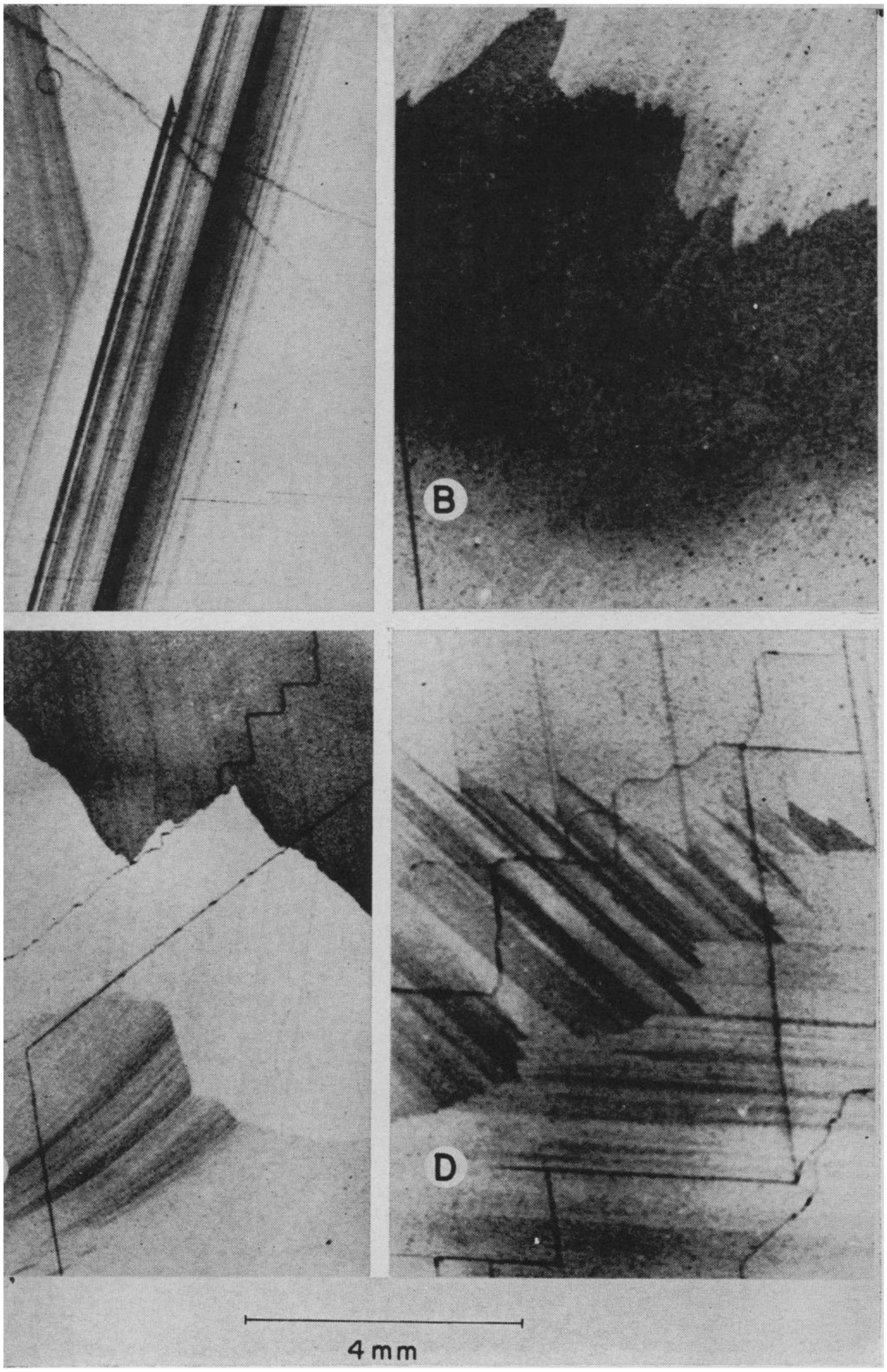


Fig. 7. Four specimens of calcite of Iceland spar quality. Luminescence photographs: *A*, growth banding in orange luminescence; *B*, irregular region of green luminescence; *C*, structure visible in orange luminescence; *D*, growth banding in orange luminescence.

cite, the entire phenomenon is invisible under polarized light. A similar phenomenon was discovered in a calcite specimen from a lead, zinc, silver mine at Monterrey, Mexico (Fig. 6). In this case, however, some evidence of the existence of such a vein may be seen in polarized light. Notice in the lower photograph that certain of the fine diagonal fractures do not line up but are offset. The reason for this is clearly seen in the luminescence photograph of the specimen. Obviously we have here a dilation vein filling of calcite which, as in the prior case (see cover of this issue) is in perfect optical continuity with the surrounding calcite and is thus invisible with ordinary optical methods. Again the vein is brilliant orange, and the surrounding calcite luminesces a much duller color.

In Fig. 7 are luminescence photographs of four specimens of optical grade calcite (Iceland spar). The thin sections were large, approximately 25 mm in each direction. No white-light pictures are included since no detail could be seen other than the cleavage cracks which are also visible in the luminescence pictures. In each case, the plane of the thin section is also the cleavage surface of calcite, and the other directions of cleavage may be seen in some cases from the fractures, some of which occurred during bombardment. The orange linear banding in the upper left photograph (a specimen from Marble Falls, Texas) is perhaps the easiest to understand. Apparently there was a sudden change in habit during the growth of this portion of the crystal. The upper right photograph is of a yellow calcite from Chihuahua, Mexico. The irregular blob (dark region in the photograph) luminesced light green. This green luminescence extended into the upper region of the photograph as a sequence of fine lines. The irregular distribution of the green luminescence is evidence that an activator ion is responsible. Perhaps the most reasonable explanation for this puzzling irregularity is that the crystal grew in a confining fracture, ultimately filling it and adopting the irregular shape of the confining walls. The walls may have then been further removed by a widening of the fracture, permitting renewed growth of the crystal. The lower left picture shows a calcite from Clear Lake, Montana, which shows a similar phenomenon but in orange luminescence. The lower right photograph shows a linear banding, again in orange luminescence, in a specimen from Eagle Picher, Oklahoma.

Experience with some seventy Iceland spar specimens shows that such complex structures occur in only about 10 percent of the specimens. Most Iceland spars show dull blue luminescence, and it is fairly common to find patterns of green lines superimposed on the blue luminescence. About 10 percent are manganese-activated and luminesce a uniform orange.

The pictures shown here were selected merely to illustrate some of the new phenomena which become visible in luminescence petrography. The number of such phenomena is large indeed, not only in carbonates but also in most other rock types. In addition to the new types of structures illustrated here, we have found that 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*).

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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.

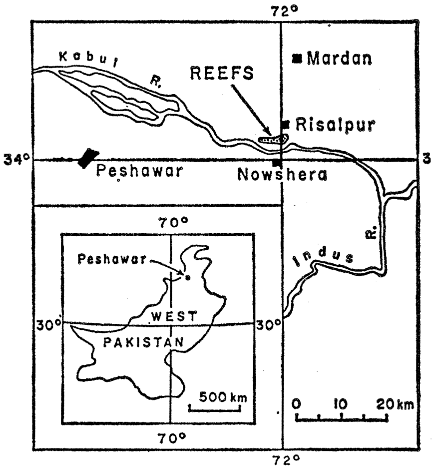

Fig. 1. Paleozoic reefs in Pakistan.

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.

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