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Petrography of a Sulfur Occurrence in the Castile Formation,
Southwest Texas

By

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ABSTRACT

The occurrence of native sulfur in the Castile Formation of the Delaware Basin, New Mexico and Texas, has been known for many years. Petrographic and mineralogic studies of samples from a core hole drilled through one of these occurrences document the petrologic changes during alteration and mineralization of these rocks. We conclude that sulfur mineralization resulted from alteration of anhydrite rock at the base of the Castile Formation by upward migration of petroleum-saturated brines from the Bell Canyon Formation.

INTRODUCTION

The occurrence of sulfur in the Castile Formation of southwest Texas has been known since the late 1800s. This paper is a report of a petrographic study of a sulfur occurrence found in core samples from the Duval Corporation core hole 258, SE1/4, SW1/4, Sec. 14, Public School Lands Block 110, Culberson County, Texas (fig. 1). The sulfur occurrence is in a zone of alteration near the base of the Castile Formation between the depths of 502 and 514 m.

The purpose of this study was to document the petrologic and mineralogic changes in the Castile rocks that occurred during alteration and mineralization by groundwater and sulfate-reducing bacteria. The biogenic origin of native sulfur in the Castile Formation of southwest Texas by sulfate-reducing bacteria (*Desulfovibrio desulfuricans*) was documented by Davis and Kirkland (1970).

GEOLOGIC SETTING

The Castile Formation is part of a thick sequence of marine evaporites that were deposited in the Delaware basin during Late Permian (Ochoan) time (Udden, 1924; Lang, 1935; Adams, 1944; and King, 1947). The Castile consists primarily of alternating laminae of anhydrite and calcite or dolomite with some beds of massive anhydrite and halite.

The zone of sulfur mineralization in the Duval core hole occurs near the base of the Castile Formation just above the Bell Canyon Formation (fig. 2).

PETROGRAPHY

This study is based on a petrographic examination of polished core sections, thin sections, and scanning electron micrographs of selected samples from the basal part of the Castile Formation. Mineral identification was by X-ray diffraction.

The lower part of the Castile Formation is composed primarily of interlaminated couplets of light-gray anhydrite and light-brown, organic-rich carbonate (fig. 3), but there are a few beds of nodular, light-gray anhydrite, and thin beds of pale yellow-brown limestone. The anhydrite crystals in the laminated rock are blocky, subhedral to euhedral (typical "pile-of-bricks" texture) and range in size from 0.01 to 0.15 mm. The primary calcite in the laminated couplets is fine grained with a crystal size generally less than 0.04 mm.

The base of the Castile Formation in this core has been altered, probably by upward migration of petroleum-saturated brines from the underlying Bell Canyon Formation. The Bell Canyon Formation has been suggested by Smith (1978) as the source of the petroleum. The alteration lithologies include: rock saturated by petroleum; various stages of replacement of anhydrite by gypsum; vugs caused by bacterial destruction of gypsum; vugs filled or partially filled by calcite; and vugs partially filled by native sulfur. In general, the most severe alteration occurs closest to the contact with the Bell Canyon Formation, and the least alteration is several meters above the contact (fig. 2).

The initial indications of rock alteration are elongated patches of gypsum caused by the hydration of the primary anhydrite (fig. 4A). The carbonate parts of the couplets were undisturbed by this alteration. A photomicrograph of one of these patches shows scattered remnants of crystals of anhydrite within the gypsum (fig. 4B). In figures 5A and B, the gypsification of the anhydrite parts of the couplets has progressed farther along the laminations. The calcite in the laminations is still intact. In figures 6A and B, the anhydrite is completely altered to gypsum. Note, however, that the laminations are as distinct as in the unaltered anhydrite-carbonate rock in figure 3. Minor folds of various amplitudes are common throughout the Castile Formation.

The next major step in the alteration of these rocks was the removal of gypsum with complete or partial replacement by secondary calcite. In a mechanism discussed by Davis and Kirkland (1970), sulfate-reducing bacteria, in the presence of brine, consumed the gypsum and petroleum to produce carbon dioxide and hydrogen sulfide. The carbon dioxide reacted with calcium in solution to produce secondary calcite. Oxidation of the hydrogen sulfide resulted in the precipitation of native sulfur.

Secondary calcite replaces gypsum/anhydrite of the laminated Castile in figure 7. The core sample in figure 7A looks like a typical, unaltered, laminated anhydrite/calcite rock of the Castile Formation, but in this sample the dark laminae are primary calcite of the original anhydrite/calcite couplets, and the light-colored laminae are secondary calcite that occupy the positions of the original anhydrite. The original anhydrite was hydrated to gypsum, then the gypsum was removed by bacteria, and the voids were filled with secondary calcite. The textures of the primary (depositional) and secondary replacement calcite are easily distinguished in thin section. In figure 7B, a lamina of fine-grained primary calcite is in the lower one-quarter of the photomicrograph. This contrasts sharply with the coarse-grained (0.02 - 0.3 mm) secondary calcite in the upper part of the photomicrograph. The euhedral nature of the crystals in the secondary calcite is shown in the SEM photograph (fig. 7C). This secondary calcite is similar

in appearance and origin to that of the carbonate masses that form the "limestone buttes" in the western part of the Delaware Basin (Kirkland and Evans, 1976).

Secondary calcite replaced anhydrite in nodular as well as laminated anhydrite/calcite rock. In figure 8A, the nodular texture is preserved in rock that is now completely calcite. The photomicrograph of figure 8B shows that the anhydrite from the nodules was removed and the voids were later filled by inward growth of secondary calcite crystals.

Native sulfur, resulting from the oxidation of hydrogen sulfide, was deposited in voids left by the bacterial removal of gypsum (fig. 9). In figure 9A, the rock contains laminations of primary calcite with native sulfur filling some of the voids. Figure 9B is a photomicrograph of the same rock. The anhydrite was apparently converted to gypsum before the bacterial reduction occurred. The alteration sequence in this core hole appears to start with hydration of anhydrite to form gypsum. The secondary products (calcite and sulfur) appear to be associated only with gypsum and not anhydrite. Probably the more soluble gypsum would have made the sulfate more readily available to the bacteria.

SUMMARY

The rock alteration that resulted in sulfur mineralization at the base of the Castile Formation occurred in a series of steps:

1. Petroleum-saturated brines from the Bell Canyon Formation migrated upward and saturated the lower part of the Castile Formation.
2. Anhydrite in laminated and nodular anhydrite/calcite rock was hydrated to gypsum.
3. Sulfate-reducing bacteria (*Desulfovibrio desulfuricans*) consumed gypsum and organic matter, resulting in the production of carbon dioxide and hydrogen sulfide.
4. The carbon dioxide reacted with calcium, in solution, to produce secondary calcite.
5. Oxidation of the hydrogen sulfide produced native sulfur.

ACKNOWLEDGMENTS

We thank Marc W. Bodine, Jr., and James B. Cathcart of the U. S. Geological Survey, and Cynthia S. A. Wallace of the Pennzoil Sulphur Company for technical reviews of the manuscript. James M. Nishi assisted with the scanning electron microscope.

REFERENCES CITED

- Adams, J. E., (1944) Upper Permian Ochoa series of Delaware Basin, west Texas and southeastern New Mexico: American Association of Petroleum Geologists Bulletin, v. 28, p. 1596-1625.
- Davis, J. B., and Kirkland, D. W., (1970) Native sulfur deposition in the Castile Formation, Culberson County, Texas: Economic Geology, v. 65, no. 2, p. 107-121.
- King, R. H., (1947) Sedimentation in Permian Castile sea: American Association of Petroleum Geologists Bulletin, v. 31, p. 470-477.
- Kirkland, D. W., and Evans, R., (1976) Origin of limestone buttes, Gypsum Plain, Culberson County, Texas: American Association of Petroleum Geologists Bulletin, v. 60, no. 11, p. 2005-2018.
- Lang, W. B., (1935) Upper Permian formations of Delaware Basin of Texas and New Mexico: American Association of Petroleum Geologists Bulletin, v. 19, no. 2, p. 262-270.
- Smith, A. R., (1978) Sulfur deposits in Ochoan rocks of southeast New Mexico and west Texas, in Geology and mineral deposits of Ochoan rocks in Delaware Basin and adjacent areas: New Mexico Bureau of Mines and Mineral Resources, Circular 159, p. 71-77.
- Udden, J. A., (1924) Laminated anhydrite in Texas: Geological Society of America Bulletin, v. 35, p. 347-354.

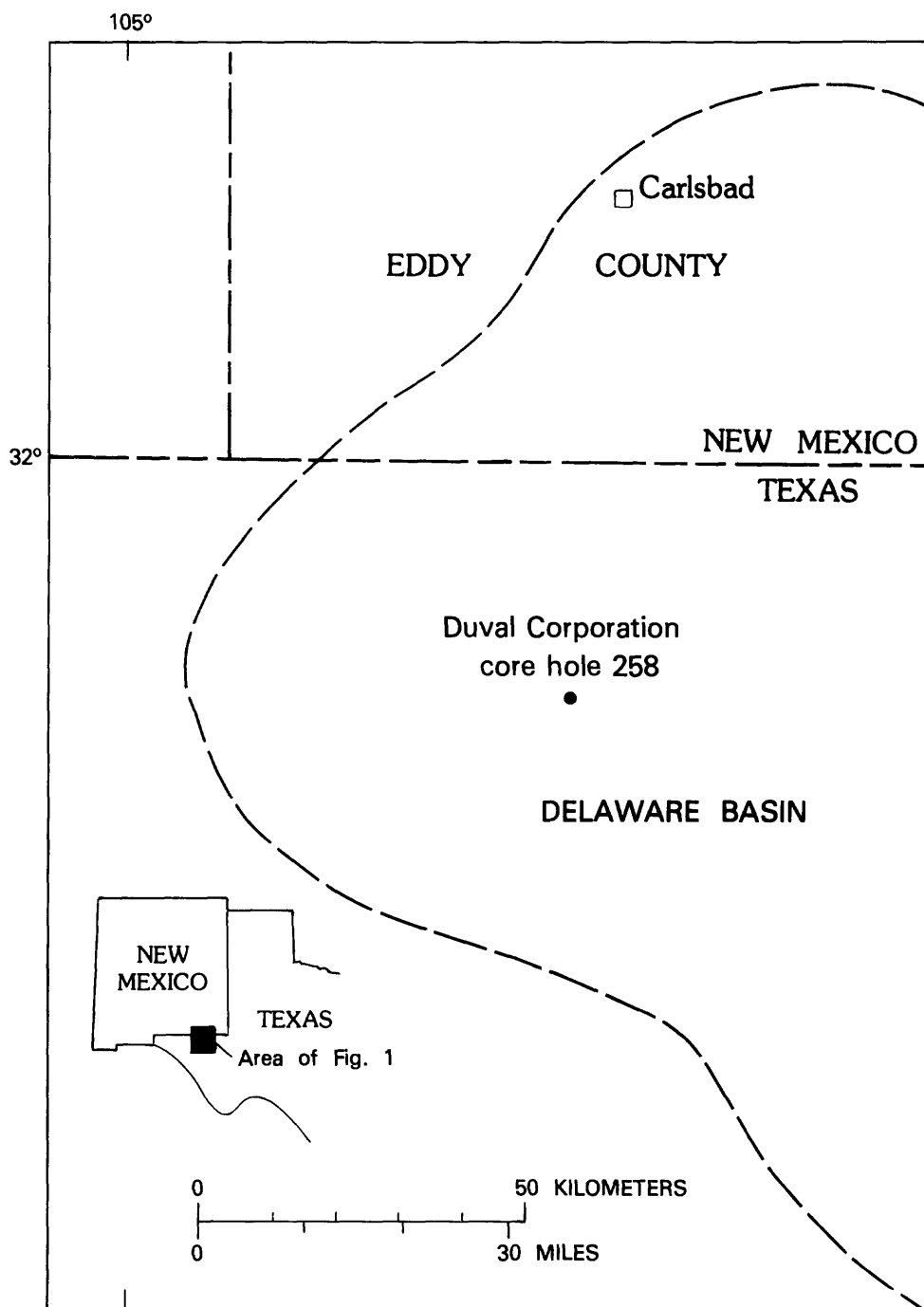


Figure 1. Index map and location of the Duval core hole 258, SE 1/4, SW 1/4, Sec. 14, Public School Lands Block 110, Culberson County, Texas. Dashed line is the western boundary of the Delaware Basin.

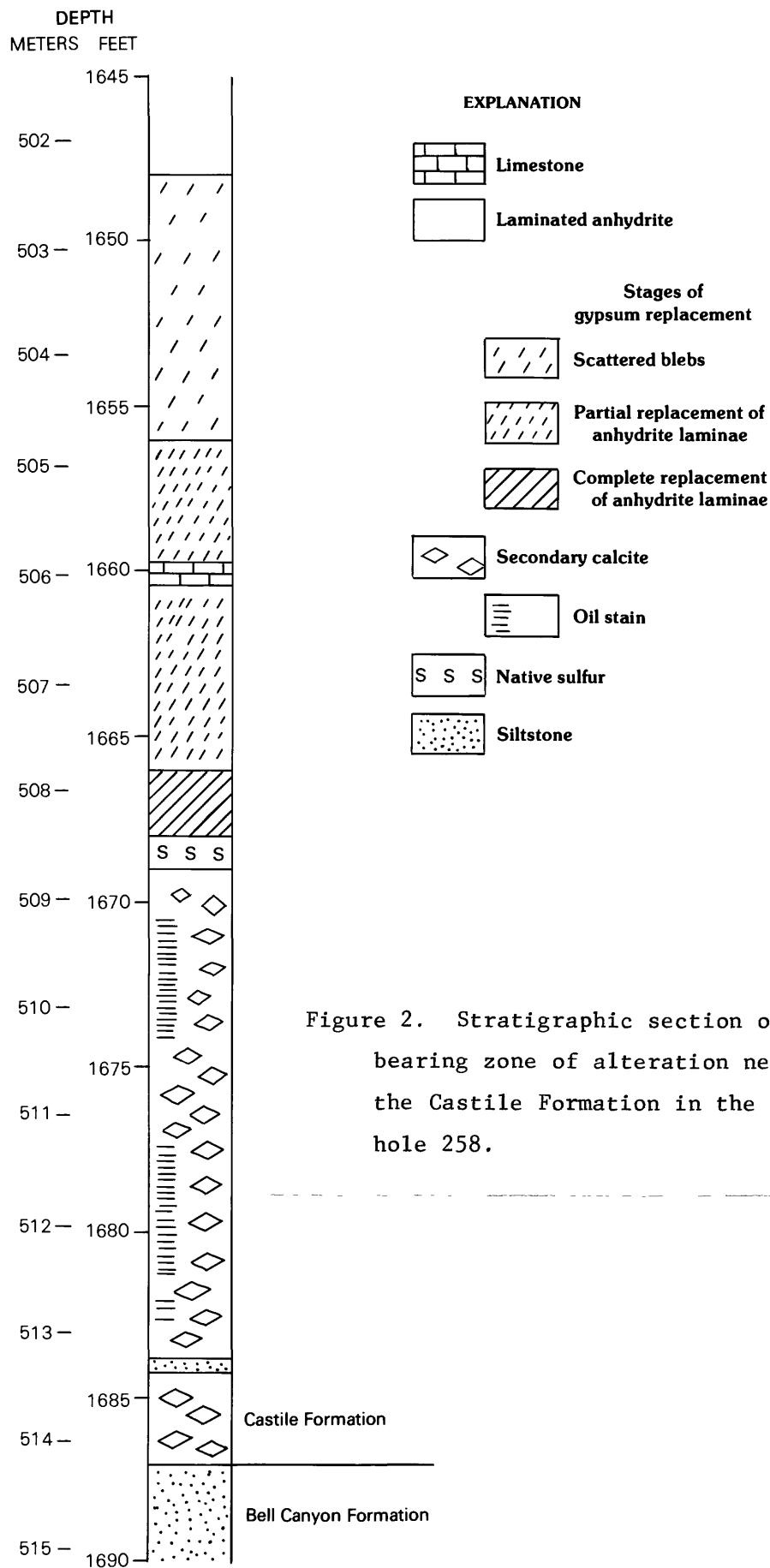


Figure 2. Stratigraphic section of the sulfur-bearing zone of alteration near the base of the Castile Formation in the Duval core hole 258.

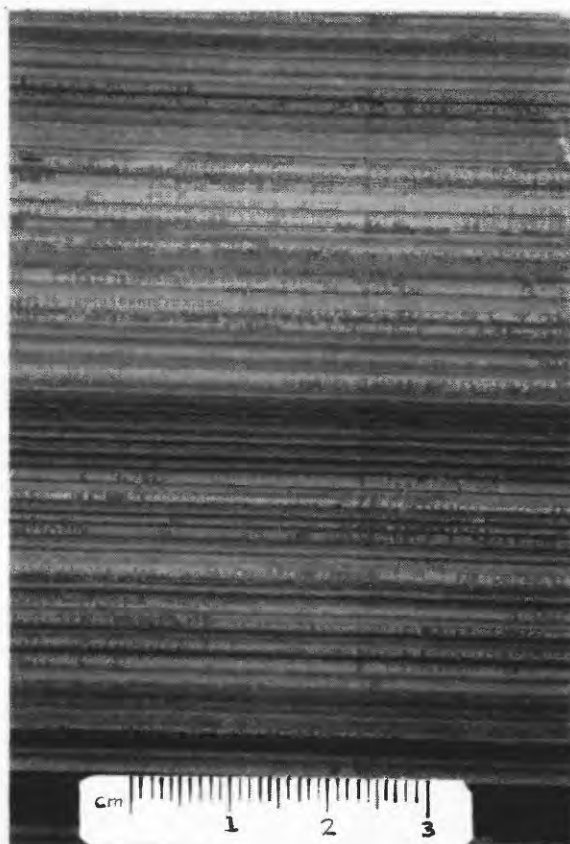


Figure 3. Polished core sample of typical interlaminated anhydrite and carbonate couplets from lower part of the Castile Formation. Light layers are anhydrite. Depth - 498.7 m.

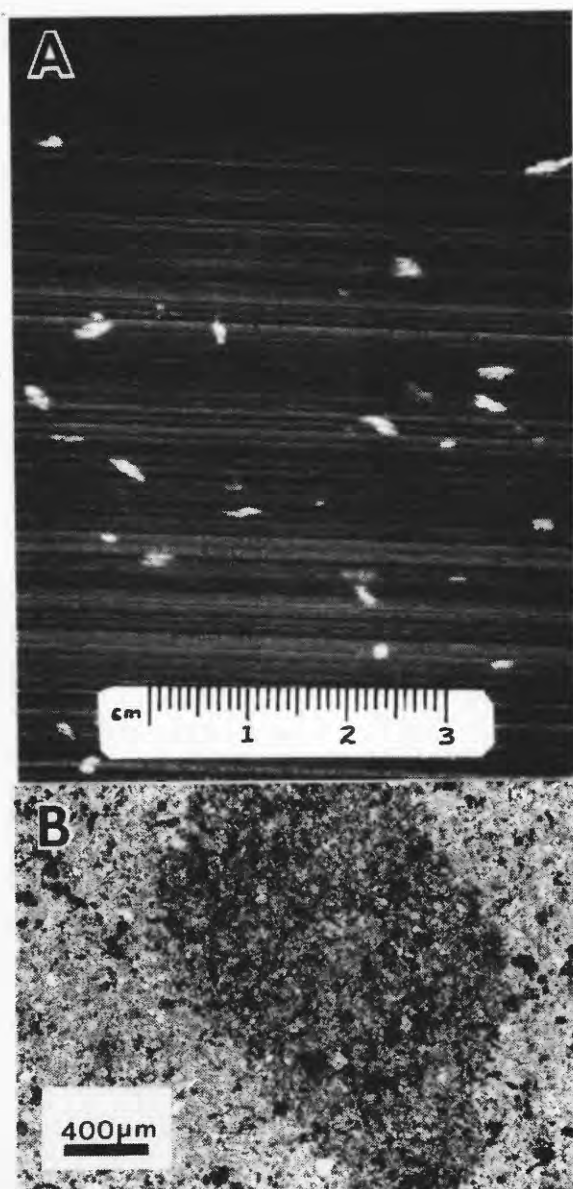


Figure 4. Widely scattered blebs of gypsum that replace anhydrite in the laminated anhydrite/calcite rock. This is the initial stage of rock alteration. Depth - 502.9 m.

- A. Polished core sample--white patches are gypsum.
- B. Photomicrograph of sample in A. Dark-gray area is gypsum with a few crystals of residual anhydrite. Light-gray area is anhydrite matrix. Crossed polarizers.

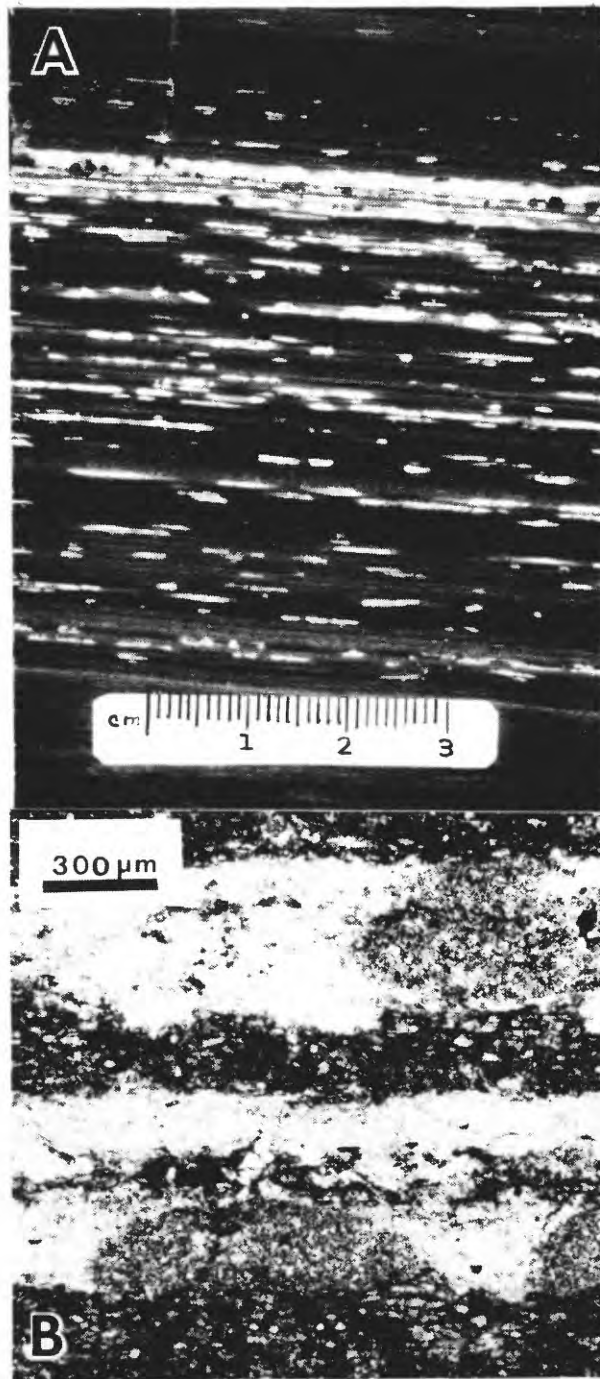


Figure 5. Partial hydration of anhydrite to gypsum along laminations. Depth - 506.4 m.

A. Polished core sample--white streaks are the gypsum alteration.

B. Photomicrograph of sample in A. Light-gray layers are the original anhydrite laminae. Medium-gray areas are gypsum. Dark-gray laminae are the original carbonate. Plain light.

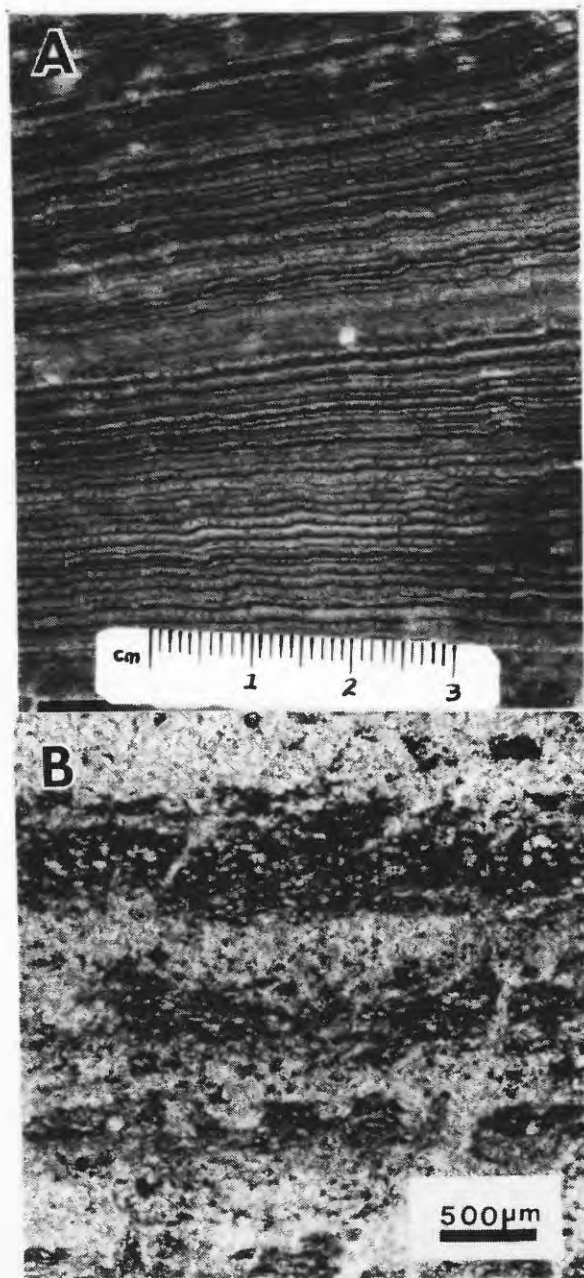


Figure 6. Complete replacement of anhydrite by gypsum. Depth - 508.3 m.

- A. Polished core sample--light layers are gypsum, dark layers are original calcite laminae.
- B. Photomicrograph of sample in A. Light layers are gypsum, dark layers are original calcite that was undisturbed by the gypsification of the anhydrite. Crossed polarizers.

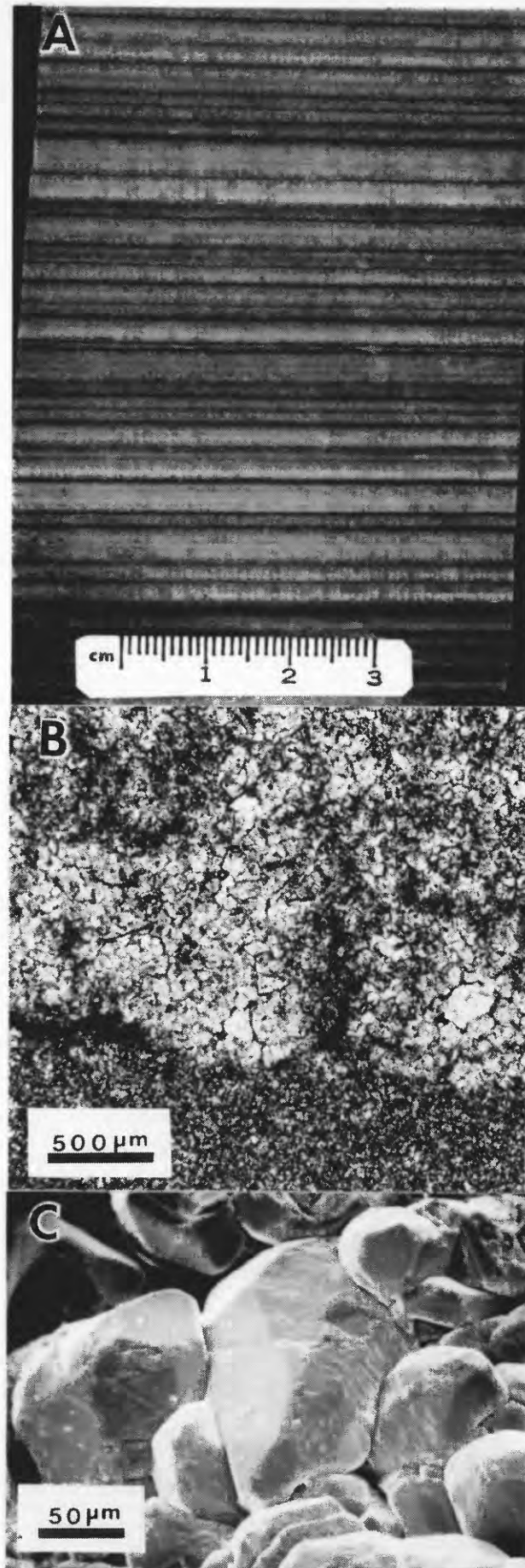


Figure 7. Laminated carbonate rock resulting from calcite replacement of anhydrite laminae in the original anhydrite/calcite rock. Prior to calcitization, the anhydrite had been replaced by gypsum. This rock still retains the original calcite laminae typical of the Castile Formation. Depth - 510.6 m.

- A. Polished core sample--dark layers are laminations of the original calcite; light layers are secondary calcite.
- B. Photomicrograph of sample in A. Lower one-quarter is the original fine-grained calcite; upper three-quarters is the coarse secondary calcite that fills the voids created by the removal of gypsum. Crossed polarizers.
- C. Scanning electron micrograph that illustrates the euhedral form of the secondary calcite.

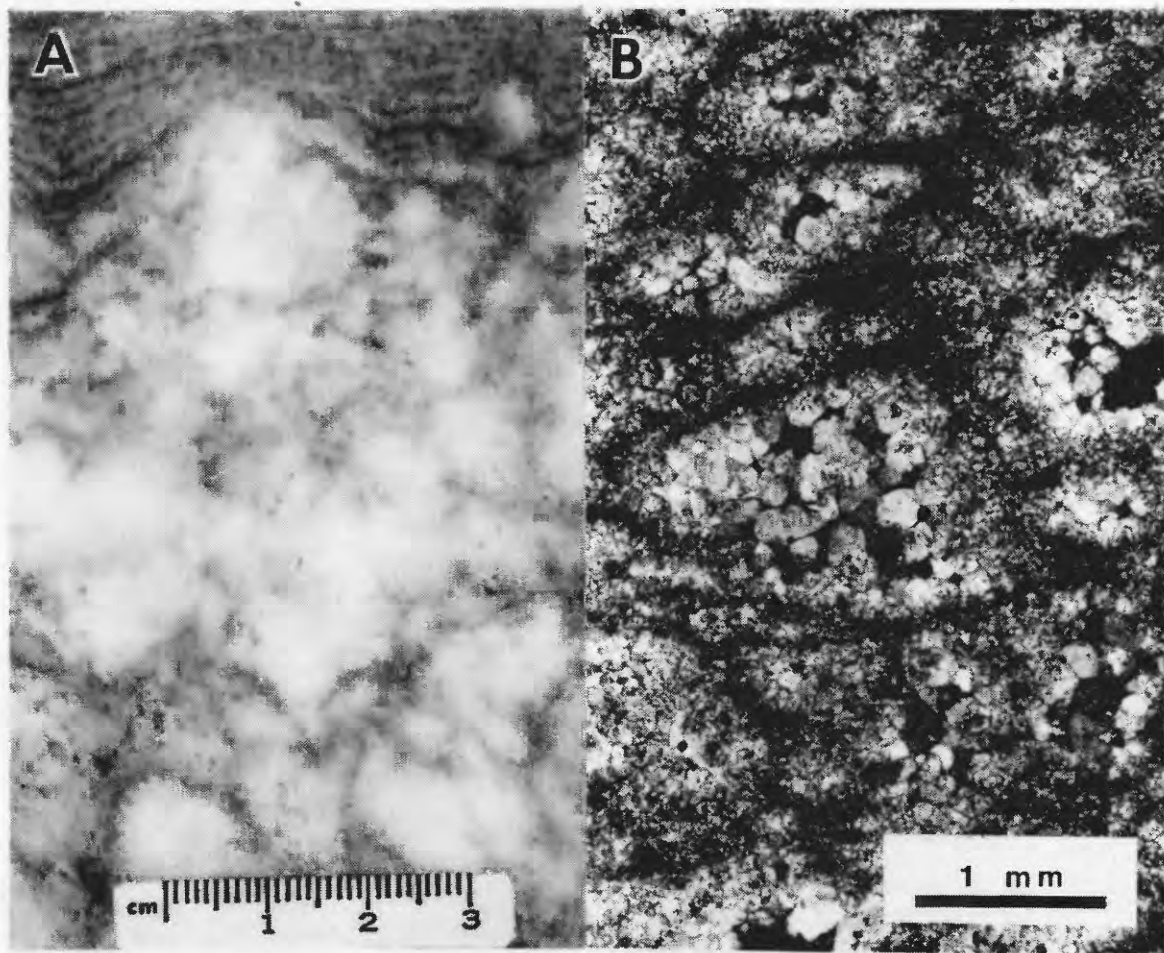


Figure 8. Calcitized rock that retains the nodular texture of the original anhydrite/calcite rock. Depth - 512.5 m.

- A. Polished core sample--light gray areas are secondary calcite that replaced anhydrite/gypsum nodules. The darker gray areas around the nodules are the original calcite.
- B. Photomicrograph of sample in A. Coarsely crystalline calcite partially to completely fills voids left by the removal of the anhydrite/gypsum nodules. Nodular shapes are surrounded by darker, original fine-grained calcite.

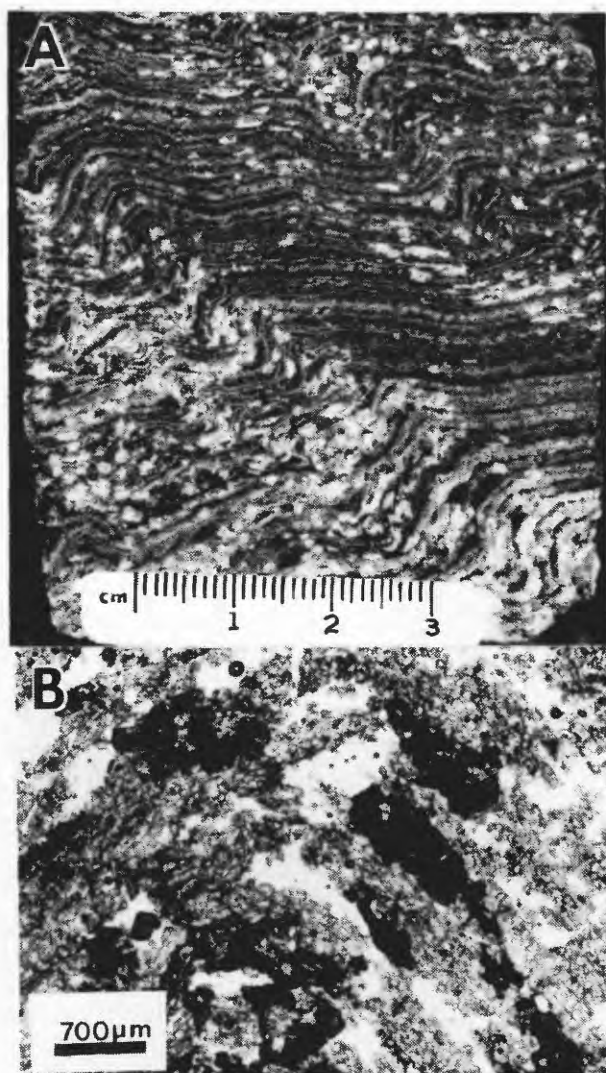


Figure 9. A framework of laminated calcite left by removal of replacement gypsum of the original anhydrite/calcite rock. Voids between the calcite laminae are partially filled by native sulfur. Depth - 508.6 m.

- A. Polished core sample--light-gray crystalline clusters are native sulfur.
- B. Photomicrograph of sample in A. Black areas are native sulfur, white areas are voids, and gray areas are calcite. Plain light.