1988

Minerology, Paragenesis and Origin of Sulfur-Bearing Mineral Phases in Caprock from Tatum Salt Dome, Mississippi

James Saunders

Recommended Citation

Saunders, James, "Minerology, Paragenesis and Origin of Sulfur-Bearing Mineral Phases in Caprock from Tatum Salt Dome, Mississippi" (1988). *Open-File Reports*. 129.
https://egrove.olemiss.edu/mmri_ofr/129

Open-File Report 88-7F

Mineralogy, Paragenesis and Origin of Sulfur-Bearing Mineral Phases in Caprock from Tatum Salt Dome, Mississippi

James A. Saunders

1988

The Mississippi Mineral Resources Institute
University, Mississippi 38677

FINAL REPORT

Mineralogy, Paragenesis and Origin of Sulfur-Bearing Mineral Phases in Caprock from Tatum Salt Dome, Mississippi

Mississippi Mineral Resources Institute Grant 88-7F
U.S. Bureau of Mines Grant G1174128

By

James A. Saunders
Dept, of Geology and Geological Engineering
University of Mississippi
University, MS 38677

ABSTRACT

Tatum salt dome was the site of two underground nuclear tests in the early 1960's. Prior to the tests, the U.S. Atomic Energy Commission drilled several core holes into the dome and the core from two of these provided the basis for this study. Approximately 100 thin and polished thin sections were prepared from caprock samples to determine the general mineralogy, stages of mineral deposition, and their relative timing to provide information on the mineral resource potential of the caprock environment at Tatum dome and potentially other domes in Mississippi. Caprock samples from Tatum dome contain anomalous amounts of the strontium minerals celestite and strontianite and minor amounts of Fe, Zn, and Pb sulfide minerals associated with bitumen. These minerals originated most likely as a result of the introduction of hot saline brines containing Sr - Pb - Zn - Fe - Ba and liquid hydrocarbons into the caprock. Sulfate from anhydrite ($CaSO_4$) in the caprock was reduced by bacteria using the liquid hydrocarbons as a nutrient source, resulting in the precipitation of the metal sulfide minerals, calcite and producing the associated solid bitumen. Decreased activity of these bacteria resulted in the precipitation of the later-stage Sr minerals. A survey of the limited descriptions of cores from other Mississippi salt domes indicate similar enrichments in Sr minerals, and that they may represent a potential mineral resource.

INTRODUCTION

Tatum dome is located in Lamar County, Mississippi at the southern edge of the Mississippi Salt Basin. The dome is somewhat unique from two standpoints: 1) it was the site of underground nuclear testing in the mid-1960's (Project Dribble); and 2) the dome caprock contains significant amounts of the strontium minerals strontianite ($SrCO_3$) and celestite ($SrSO_4$). As part of Project Dribble, the U.S. Atomic Energy Commission (AEC) drilled a series of holes into Tatum dome, two of which were cored. In addition, Freeport Sulfur Company drilled 9 holes into the Tatum caprock during 1941-1942. Only minor amounts of sulfur were encountered but celestite and "possibly barite" were recognized in core samples. The U.S. Geological Survey conducted reconnaissance geologic and mineralogic studies on the AEC core, and identified the presence of significant amounts of celestite and strontianite (Eargle, 1962a,b; Schlocker, 1963).

The AEC core is archived at the Mississippi Bureau of Geology, and provided the basis for a detailed petrographic study of the caprock. Approximately 100 polished and standard thin sections were prepared from selected samples, most of which came from the limestone caprock. Mineral identification was augmented by X-ray diffraction, selective staining, and reconnaissance geochemical analyses for a limited suite of elements.

GENERAL GEOLOGY

Tatum dome is roughly elliptical in outline (Figure 1), and is approximately 1 mile in diameter along its principal axis (U.S. Atomic Energy Commission, 1972). The top of the dome lies approximately 900 feet below ground surface, and is hosted by the Catahoula Formation of Oligocene-Miocene age (Figure 2). The Catahoula Formation is overlain by the Miocene Hattiesburg and Pascagoula Formations, the latter of which crops out in the vicinity of the dome. Drilling and seismic studies indicate that the dome has a pronounced overhang on the southwestern flank (Figure 2).

The caprock shows the stratigraphy common to many Gulf Coast salt domes, consisting of an anhydrite zone overlain successively by gypsum and limestone. The anhydrite zone at Tatum dome is approximately 500 feet thick, and is overlain by gypsum of highly variable thickness. In the two AEC core holes, this zone is 2-4 feet thick, but logs from Freeport's exploration program indicate the zone locally reaches 92 feet in thickness. The limestone portion of the caprock reaches a maximum thickness of 200 feet. The limestone caprock is extremely porous, with numerous solution cavities. This feature caused lost circulation problems in both Freeport and AEC drilling, resulting in poor core recovery. In addition, none of the thin gypsum zone was recovered in the AEC core holes.

The limestone caprock contains two distinct textural varieties. The upper portion is composed of massive to porous, commonly brecciated, light-gray limestone. The lower portion, 20-40 feet thick in the AEC core holes, is horizontally banded, with alternating layers of dark carbonaceous and fine-grained calcite and lighter bands of coarse-grained calcite or Sr minerals. It is difficult to determine the thickness of the banded zone elsewhere in the dome from the Freeport logs, as they mainly describe the limestone caprock in terms of degree of brecciation and the presence or absence of sulfur. However, this zone is apparently 105 feet thick in Freeport hole no. 6. From the Freeport logs, it is apparent that blocks of surrounding sediment were locally incorporated into the limestone caprock. In addition, Schlocker (1963) describes the presence of "sandstone breccia pieces cemented by calcite and celestite" at the base of the limestone caprock in AEC hole E-2. This observation apparently came from rotary drill cuttings, because there is no record of coring at AEC E-2.

MINERALOGY AND PARAGENESIS OF THE CAPROCK

The upper portion of the limestone caprock is typically composed of equigranular euhedral calcite rhombs generally less than 0.5 mm in diameter. Cavities of similar size are common, and some are filled with a later stage of calcite or strontianite and celestite. Rounded detrital quartz grains are present in minor amounts, and some have authigenic overgrowths around them. Carbonaceous matter is present as fracture fillings and as disseminations throughout the upper limestone portion of the caprock. This material observed in thin section may be equivalent to semi-solid hydrocarbons (”asphalt") present locally in cavities throughout the AEC caprock cores and described in the Freeport logs. In some places, carbonaceous veinlets 0.5 to 1.0 mm thick contain abundant sulfides, quartz, and albite and appear to be pressure solution features (stylolites). Disseminated sphalerite and pyrite are associated with the carbonaceous matter, as are doubly terminated quartz crystals of probable authigenic origin. The quartz crystals are generally less than 0.3 mm in length, and commonly contain inclusions of the carbonaceous matter, and more rarely, sulfides. One sample from the upper limestone zone contained 3.3 ppm U and 2100 ppm Zn (Table 1). The texture of this zone is apparently similar to what is considered ”detritus-bearing false-caprock” by Posey et al. (1987).

The banded caprock contains alternating layers 1-10 cm thick. In some places, the banded core is composed of alternating bands of dark and light calcite very similar to banded calcite caprock in other domes (cf., Posey et al., 1987) . However, the majority of the core recovered from the banded zone contains tan to yellow-brown bands of complexly intergrown celestite and strontianite (Figure 3) alternating with the dark bands. In some cases, the dark bands show evidence of dissolution and minor brecciation, and may be coated by a layer of euhedral sparry calcite. In addition, brown celestite fills cavities up to 5 cm in size, or is present in veinlets to 1 cm in width that crosscut the dark and light bands.

The dark bands contain abundant carbonaceous matter similar in appearance to that in the upper portion of the caprock. In addition, the dark bands have a distinctive texture that is consistent from band to band. The bands contain pelletai calcite grains to 3 mm in size in a matrix of much finer-grained calcite, carbonaceous matter and disseminated sulfides (<1%). Some of the pelletai calcite grains represent overgrowths on earlier rhombohedral grains of dolomite (Figure 4). However, most of these grains are relatively inclusion free. In fact, many appear to have grown at the exclusion of carbonaceous matter that commonly mantles the pelletai calcite grains. The dark bands typically contain 5-10% doubly terminated quartz crystals generally less than 0.5 mm in length. The quartz is intimately associated with the carbonaceous material and with disseminated sulfides. Inclusions of carbonaceous matter and sulfides are common, and may outline boundaries of earlier quartz grains. Pyrite is the predominant sulfide mineral, and commonly occurs as framboids with carbonaceous matter, although other habits are also present. Euhedral crystals of galena (Figure 5) and sphalerite to several mm in diameter are also present (Figure 6). Chalcopyrite is present in only trace amounts. Trace amounts of native sulfur occur in cavities in the light bands.

Fine-grained (<0.2 mm) angular plagioclase feldspar, identified as albite by Schlecker (1963) is also present in minor amounts in the dark bands. Trace amounts of albite were also found by Schlocker in both the anhydrite section and the underlying salt. This suggests that the albite accumulated and possibly was concentrated by the dissolution of anhydrite, and that the dark bands formed at the upper surface of the anhydrite section during the dissolution (Posey et al·., 1987). However, the apparent concentration of albite in the dark bands with respect to the anhydrite suggests that they did not form by a simple isovolume replacement of the anhydrite.

The lighter bands generally contain coarser-grained crystals than do the dark bands. The lighter bands are composed primarily of euhedral calcite, celestite and strontianite that were apparently precipitated in open spaces between dark bands. These bands are virtually devoid of the carbonaceous matter and disseminated sulfides found in the darker bands. Calcite may comprise all of a light-colored band, or may be present as a layer that encrusts dark bands. In addition, calcite occurs in late-stage cavities and cross-cutting veinlets commonly with celestite. Celestite and strontianite occur in complex intergrowths, where it appears that the latter has either replaced the former, or was coprecipitated with. Sub-graphic intergrowths between fine-grained strontianite and coarser-grained celestite are common. However, strontianite also forms euhedral rosettes up to 1 cm in diameter associated with the sub-graphic intergrowths. These were apparently precipitated in open spaces, because some of the rosettes project into cavities that were later filled with celestite (Figure 7). At least some of the strontianite formed by the replacement of calcite, for in places coarse-grained strontianite has replaced the dark bands, leaving a sub-horizontal trail of carbonaceous material and quartz. Barite and/or witherite may be present locally in minor amounts in the lighter bands, for one sample analyzed contained at least 1000 ppm (Table 1) . However, no Ba minerals were detected by X-ray diffraction, and it is possible that the Ba is present in celestite and/or strontianite.

The anhydrite zone is composed predominantly of massive dark-gray coarse-grained crystals that exhibit a faint sub-horizontal layering defined by faint color differences. Individual crystals occur as euhedral prisms, 1-10 mm in diameter. Locally, there appears to be a slight preferred orientation of the crystals with respect to the banding. Gypsum veins and veinlets are present throughout the anhydrite, but increase in size and frequency at the top, where they grade into the gypsum zone. Some of the gypsum veinlets contain abundant native sulfur exhibiting elongated and stringy shapes (Figure 8). Minor amounts of dolomite, calcite, and quartz associated with carbonaceous matter are also present in the anhydrite. The base of the anhydrite section is finer-grained, has a lighter color, and is more friable near the contact with the underlying salt.

Consistently observed textural relationships such as crustification, pseudomorphism, open-space filling, and cross-cutting features make it possible to establish a generalized paragenetic sequence representative of the minerals in the banded portion of the limestone caprock (Figure 9). However, not all of the phases shown in Figure 9 are present in every set of light and dark bands.

DISCUSSION AND CONCLUSIONS

The banded portion of the limestone caprock at Tatum dome is similar in many respects to that at other Gulf Coast salt domes such as Oakwood (Kreitler and Dutton, 1983), Hockley (cf., Kyle and Price, 1986), Winnfield (Ulrich et al., 1984; Posey, 1986), and Richton (Drumheller et al., 1982). The banding is interpreted to have formed by the progressive dissolution of the anhydrite, where the oldest bands overly younger bands (Kreitler and Dutton, 1983; Posey et al., 1987). The dark bands apparently precipitate from supersaturated solutions resulting from the bacterial reduction of sulfate and concomitant oxidation of hydrocarbons, producing dissolved carbonate (Posey et al., 1987). Continued dissolution of anhydrite below the horizon of a dark band created open spaces in which the coarser-grained, euhedral minerals of the lighter bands were precipitated. Interpretation of trace-element geochemical and light-stable isotopic data at Oakwood dome by Kreitler and Dutton (1983) lead them to suggest that the lighter bands precipitated from a different fluid than did the darker bands. Posey (1986) and Posey et al. (1987) argue from isotopic data from Hockley and Winnfield domes that the lighter bands precipitated from a solution that evolved from the original one that precipitated the dark bands. In the latter interpretation, fluid mixing is important in the solution evolution.

The presence of appreciable quantities of the Sr minerals celestite and strontianite in the light-colored bands at Tatum dome is anomalous in comparison to other domes. However, a trend of Sr enrichment of the light bands with respect to the dark bands has been observed at Spindletop (Feely and Kulp, 1957) and Oakwood (Kreitler and Dutton, 1983). However, the Sr content of both types of bands is less than that for the underlying anhydrite, which contains 800-1200 ppm Sr at Oakwood and Spindletop. At Tatum dome, the anhydrite contains 400-800 ppm Sr (Schlocker, 1963; Russell, 1985).

Based on the mineralogy and textural features of the banded caprock, a few observations concerning the nature of the solutions involved can be made. The solutions were probably always undersaturated with respect to anhydrite, or at least never precipitated anhydrite. The precipitation of several stages of calcite, and the partial dissolution of one, suggest that saturation with respect to calcite fluctuated with time. In addition, the differences in texture and composition of the light and dark bands suggest that either the solution composition changed, or the conditions governing mineral precipitation changed.

The general mechanism by which limestone caprock forms by the replacement of anhydrite is fairly well established. Freely and Kulp (1957) showed that the following reaction takes place during this process:

$$CaSO_4 + CH_4 = CaCO_3 + H_2S + H_20$$

where hydrocarbons are used as as nutrient source for the bacterial reduction of anhydrite sulfate to produce calcite. Liquid hydrocarbon was probably the nutrient source at Tatum dome due to the presence of bitumen that is associated with calcite. A chromatographic analysis of this bitumen (Figure 10) shows that it is depleted in the lighter alkanes (C10-C20) relative to the isoprenoids phytane and pristane. This signature probably represents the result of limited aerobic or anaerobic biodegradation of liquid hydrocarbons (Roger Sassen, personal communications, 1988).

The production of sulfide sulfur by the bacterial reduction process caused the precipitation of the Fe - Pb - Zn suflides in the dark calcite bands at Tatum dome. The general fine-grained texture of the dark bands suggests that the precipitation of the sulfides and calcite was quite rapid. The partial dissolution of the dark calcite bands and the precipitation of the coarser Sr minerals and lighter calcite at Tatum dome imply a significant change in the solutions that previously precipitated the dark bands. The precipitation of abundant celestite and the lack of sulfides and carbonaceous matter indicate a more oxidizing environment during the precipitation of the light-colored bands. Perhaps the activity of sulfate-reducing bacteria decreased at this time due to the consumption of a finite source of the lighter hydrocarbons. If so, the lighter bands represent the changeover of mineral precipitation by organic processes to simple inorganic processes. In the latter case, the continued dissolution of anhydrite releases Ca^{2+} to solution and precipitates calcite by the common ion effect, although an external source of dissolved carbonate might be required. Precipitation of calcite and the associated minerals under these conditions is likely to be slower than during the formation of the dark bands. This might explain the increased grain size of the lighter bands over the dark bands. Sulfate released by anhydrite dissolution could also cause the solutions to become saturated with respect to celestite by the same process.

The precipitation of abundant strontium minerals at Tatum dome requires some special circumstances, for other domes contain only minor amounts of these minerals. Schlocker (1963) proposed that the dissolution of anhydrite released Sr and caused the precipitation of celestite and strontianite. Because the Sr content of anhydrite is similar to other domes, simple mass balance considerations require that large volumes of anhydrite would have to be dissolved to account for the amount of Sr. Although there is some evidence for the concentration of detritus from the anhydrite in the dark bands, it is difficult to envision a process that would concentrate the required amount of Sr at the expense of Ca in the caprock solutions.

An alternative explanation involves the introduction of Sr into the caprock by the deep basinal brines interpreted to have been responsible for precipitating the dark bands containing Fe-Pb-Zn sulfides. Na-Ca-Cl brines produced from oil fields in Mississippi contain up to 3000 ppm Sr, in addition to significant amounts of Pb and Zn (Carpenter et al., 1974). Sr from these brines, in combination withthat from anhydrite dissolution, probably was required for the formation of the Sr mineralization at Tatum dome. In addition, the apparent reduction in the activity of the sulfate-reducing bacteria after the precipitation of the dark bands would move the solutions toward celestite saturation by increasing sulfate activity.

It is apparent from the caprock mineralogy at Tatum dome, which includes minerals with sulfur in three (3) different oxidation states, that the geochemical processes responsible for caprock formation were complex. The relative abundance and paragenesis of the minerals indicates that sulfate reducing bacteria were only periodically active, and that external sources of Sr and other trace metals were required to produce the observed mineralogy. Deep basin brines, moving up along the sides of the dome, probably provided these constituents. In all probability, these brines were also important in the dissolution of anhydrite at the crest of the dome.

REFERENCES

Carpenter, A.B., Trout, M.L., and Pickett, E.E., 1974. Preliminary report on the origin and chemical evolution of lead and zinc-rich oil field brines in central Mississippi. Econ. Geol., 69, 1191-1206.

Drumheller, J.D., Fuerst, S.I., Cavan, B.P., and Saunders, J.A., 1982. Petrographic and geochemical characteristics of the Richton salt core, ONWI-277. Prepared by Law Engineering Testing Co. for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 94 pp.

Eargle, D.H., 1962a. Geology of the core hole WP-1, Tatum dome, Lamar County, Mississippi. Unpub. U.S. Geol. Surv. Tech. Letter (Dribble 15).

Eargle, D.H., 1962b. Geology of the core hole WP-4, Tatum dome, Lamar County, Mississippi. Unpub. U.S. Geol. Surv. Tech. Letter (Dribble 19).

Feely, H., and Kulp, J., 1957. Origin of Gulf Coast salt dome sulfur deposits. Am. Assoc. Petr. Geol. Bull.., 83: 3551-3574.

Kreitler, C.W., and Dutton, S.P., 1983. Origin and diagenesis of cap rock, Gyp Hill and Oakwood salt domes, Texas. Univ. Texas (Austin) Bur. Econ. Geol., Rept, of Invest. 131, 58 pp.

Kyle, J.R., and Price, P.E., 1986. Metallic sulfide mineralization in salt dome cap rocks, Gulf Coast, U.S.A. Trans. Inst. Min. Metall., 95: B6-B16.

Posey, H.H., 1986. Regional characteristics of strontium, carbon, and oxygen isotopes in salt dome cap rocks of the western Gulf Coast. Unpub. Ph.D. dissertation, Univ. North Carolina (Chapel Hill), 258 p.

Posey, H.H., Price, P.E., and Kyle, J.R., 1987. Mixed carbon sources for calcite cap rocks of Gulf Coast salt domes. In: I. Lerche and J.J. O'Brien (Editors), Dynamical Geology of Salt Domes and Related Structures. Academic Press, Austin, pp. 593-630.

Schlocker, J., 1963, Petrology and mineralogy of Tatum salt dome, Lamar County, Mississippi. Unpub. U.S. Geol. Surv. Tech. Letter (Dribble 28), 95 p.

Ulrich, M.R., Kyle, J.R., and Price, P.E., 1984. Metallic sulfide deposits in the Winnfield salt dome, Louisiana: evidence for episodic introduction of metalliferous brines during cap rock formation. Trans. Gulf Coast Assoc. Geol. Soc., 34: 435-442.

U.S. Atomic Energy Commission, 1972. Tatum dome test site, Lamar County, Mississippi: status report on decommissioning, June 30, 1972, NVO-117, 64 pp.

Table 1.

Geochemical Analyses of Limestone Caprock Samples, Tatum Dome

Sample

	1-980	1-984	1-1000	1-004.5	1-1006	1-1020	1-1028	1-1042	4-988	4-1018
Ca %	42	42	24	10	26	13	19	23	36	14
Fe %	0.12	0.12	0.14	0.07	0.10	0.08	0.06	0.13	0.06	0.08
Na %	< 0.05	<0.05	0.13	0.08	0.11	<0.05	0.07	0.17	0.10	0.05
Ba ppm	<200	<200	1600	4600	3200	500	4700	1600	200	18,000
Cr ppm	40	70	40	40	20	30	40	30	30	40
As ppm	4	5	< 2	<2	<2	<2	<2	<2	< 2	<2
Sb ppm	0.8	0.9	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
U ppm	<0.5	0.6	3.3	0.8	0.8	0.8	0.5	0.5	0.5	0.7
Zn ppm	600	2100	<200	<200	< 200	< 200	<200	< 200	<200	<200
Ag ppm	<5	<5	<5	<5	<5	<5	<5	<5	< 5	<5
Au ppb	<5	<5	<5	<5	<5	<5	< 5	<5	< 5	< 5

Note: All values determined by instrumental neutron activation by Nuclear Activation Services Hamilton Ontario. Ni, Co, Mo and Se were all below detection limits of 200, 5, 20 and 20 ppm, respectively. Samples are from coreholes WP-1 and WP-4,

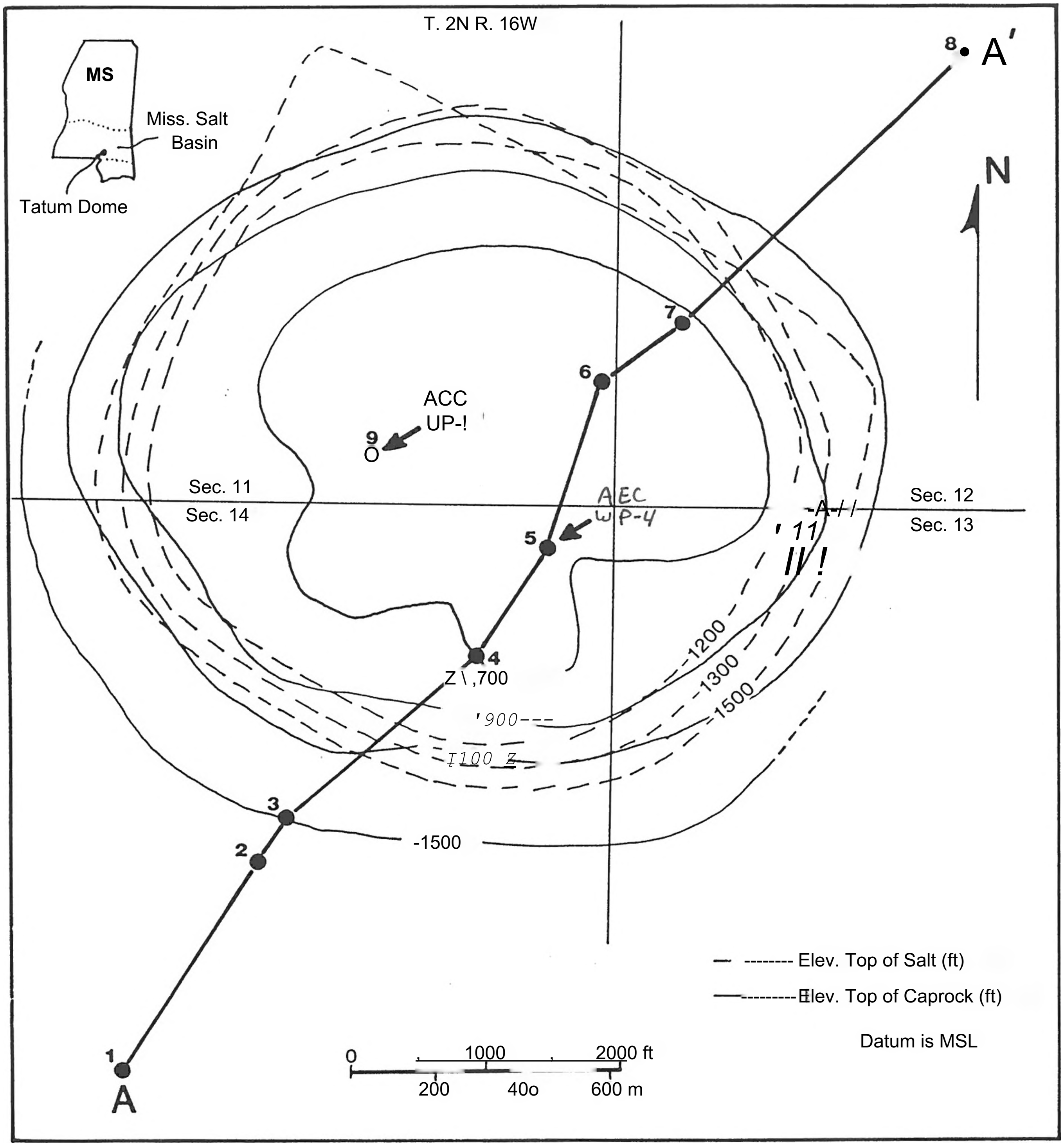

Figure 1. Contour map showing configuration of the top of salt and top of caprock, Tatum dome. Location of the geologic cross section (Figure 2) is also shown.

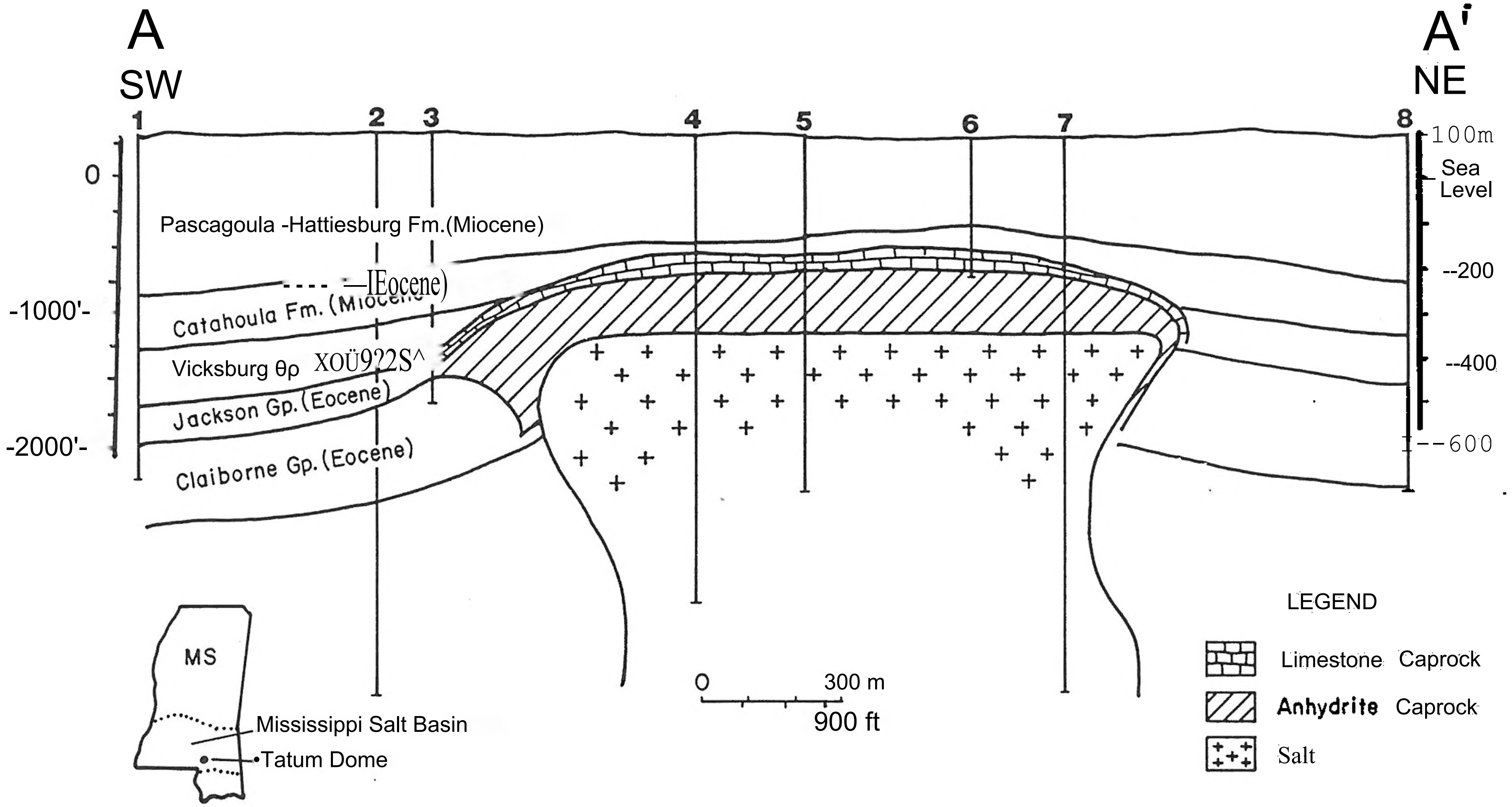

Figure 2. Diagrammatic geologic cross section through Tatum dome. Modified from U.S. Atomic Energy Commission (1972).

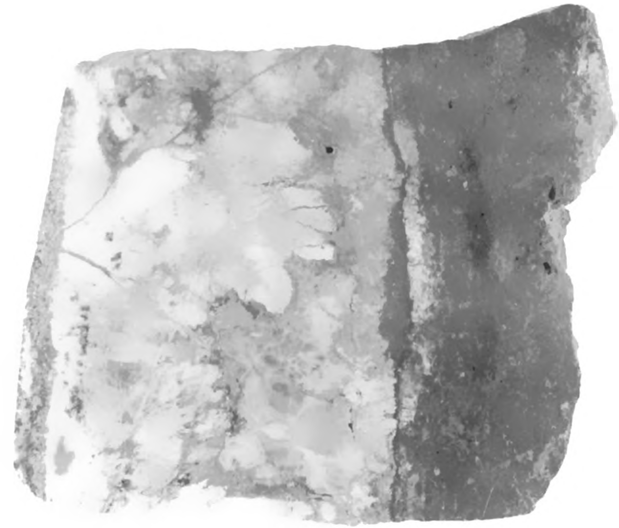

Figure 3. Core sample showing a dark calcite band and a lighter band of strontium minerals, from the banded limestone zone.

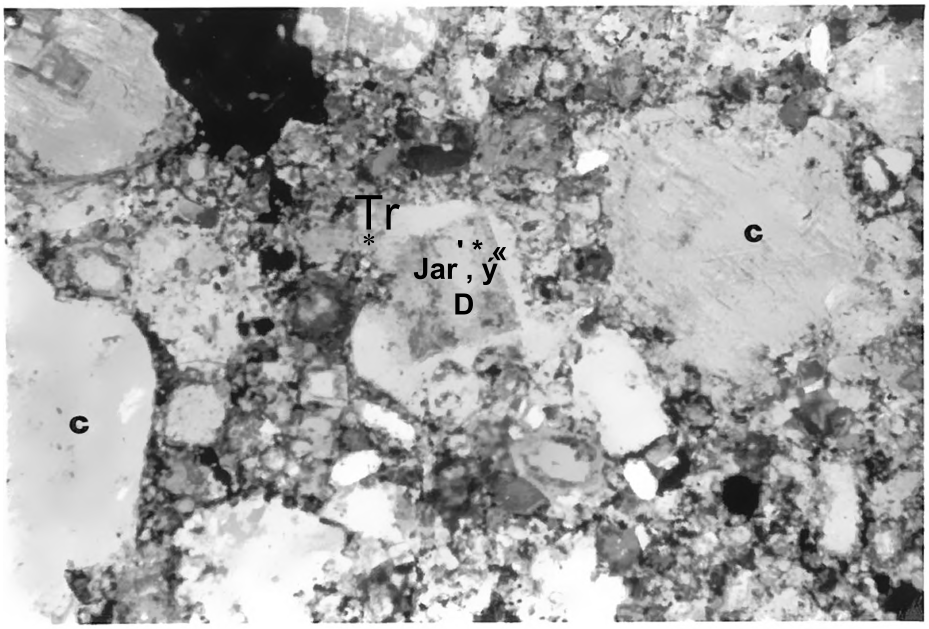

Figure 4. Photomicrograph of peletal calcite (c) from a dark calcite band. Dolomite (d) forms the nucleus of one grain in center of the photograph. Field of view is 0.16 mm.

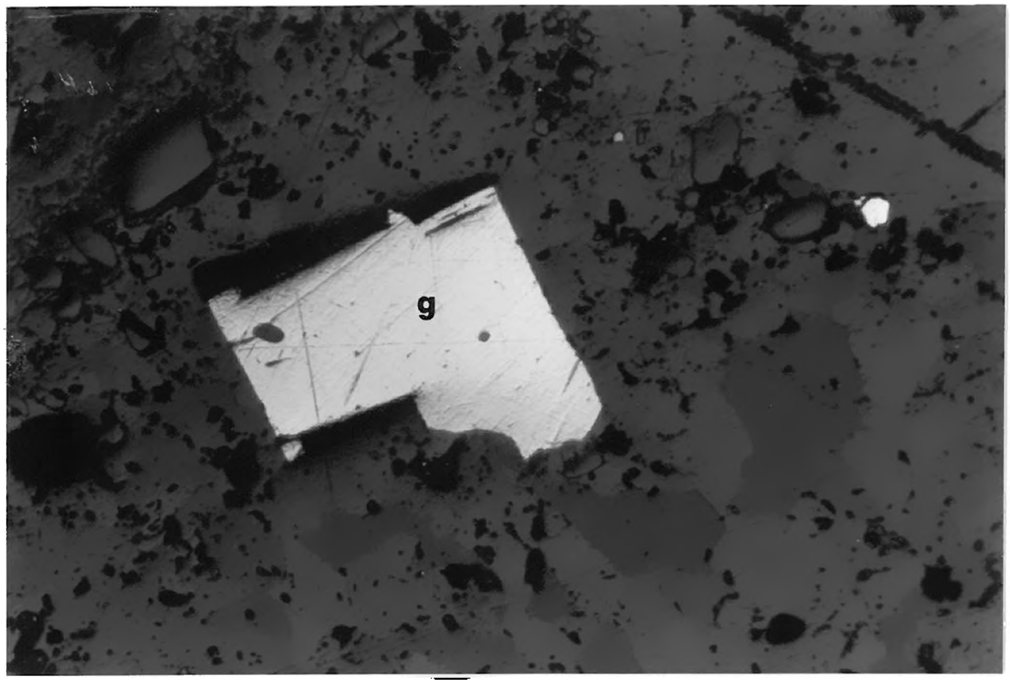

Figure 5. Photomicrograph of a galena (g) crystal in a dark calcite band. Reflected light, field of view is 0.64 mm.

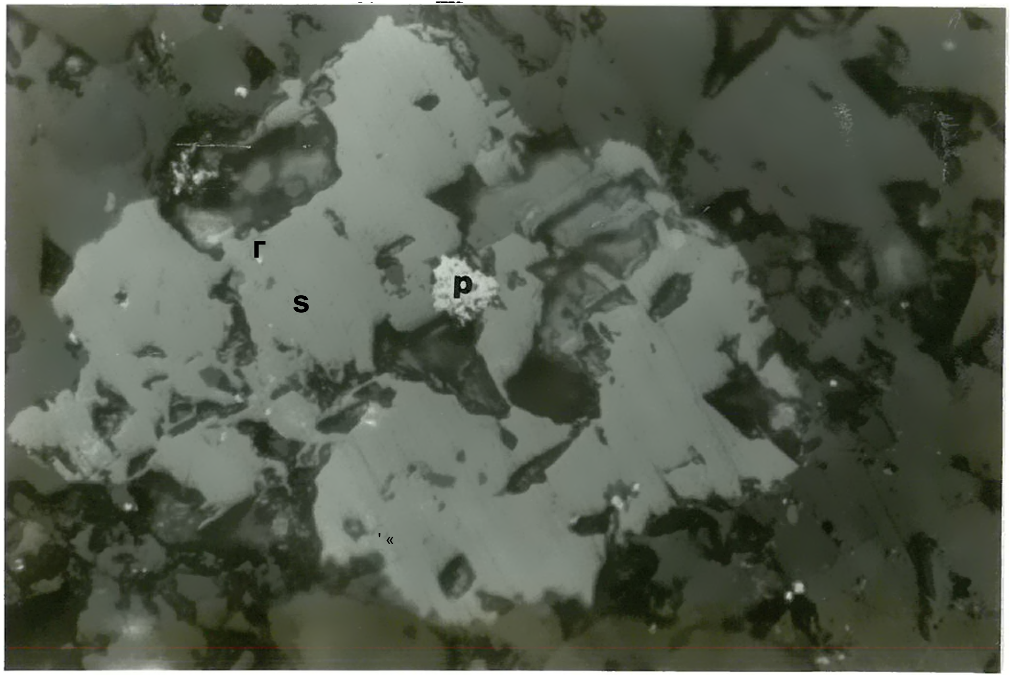

Figure 6. Photomicrpgraph of sphalerite (s) intergrown with pyrite (p). Reflected light, field of view is 0.16 mm.

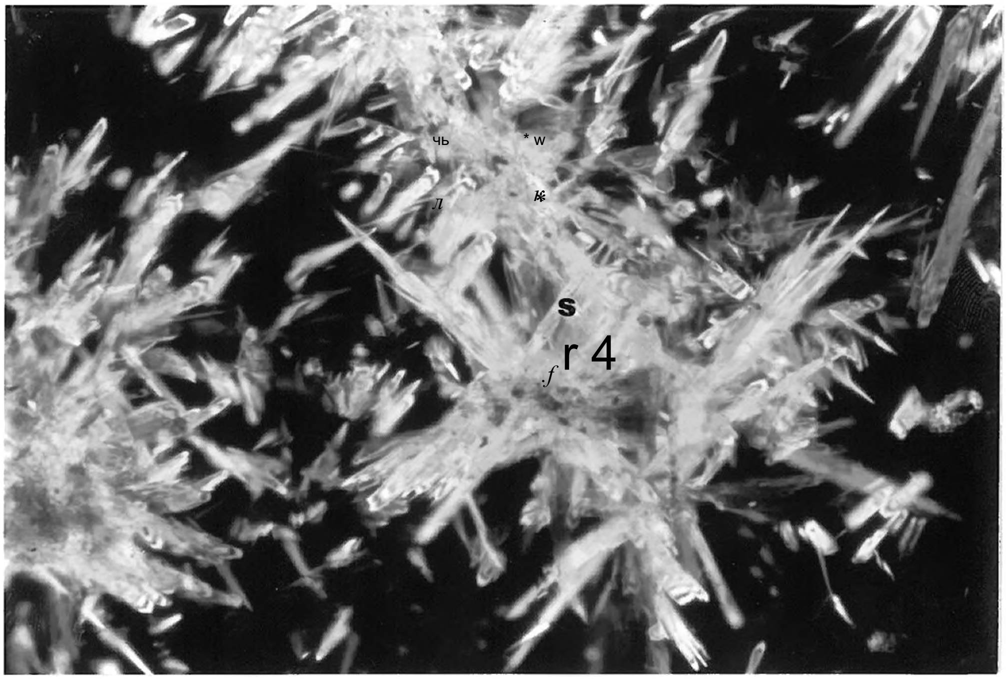

Figure 7. Photomicrograph of strontianite rosette (s) in celestite (dark). Field of view is 0.64 mm.

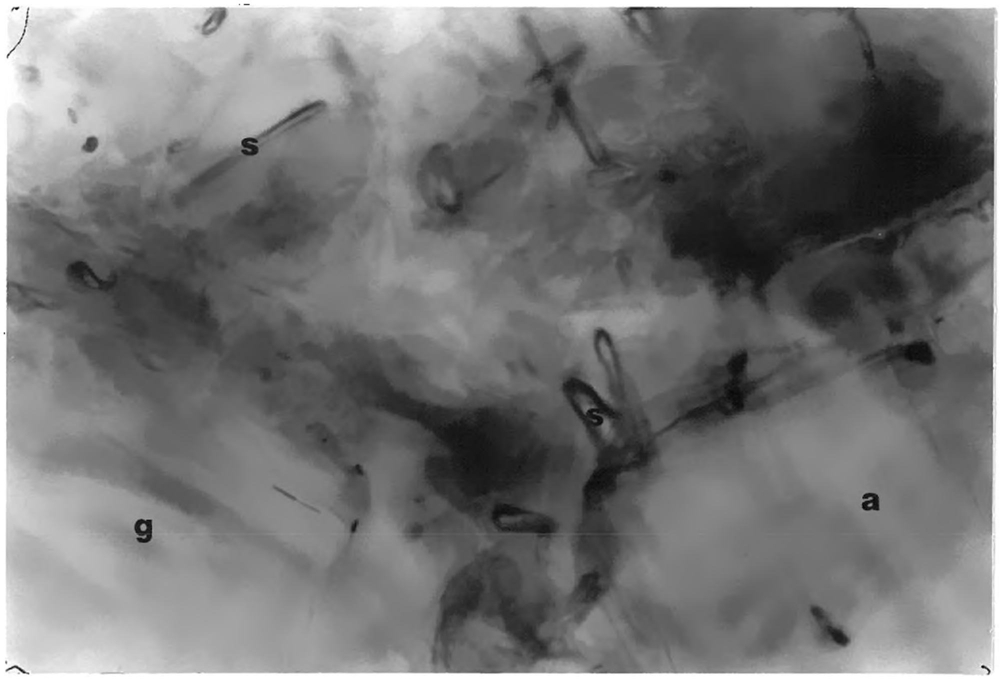

Figure 8. Photomicrograph of stringy sulfur (s) in a gypsum (g) veinlet that crosscuts anhydrite (a). Field of view is 0.16 mm.

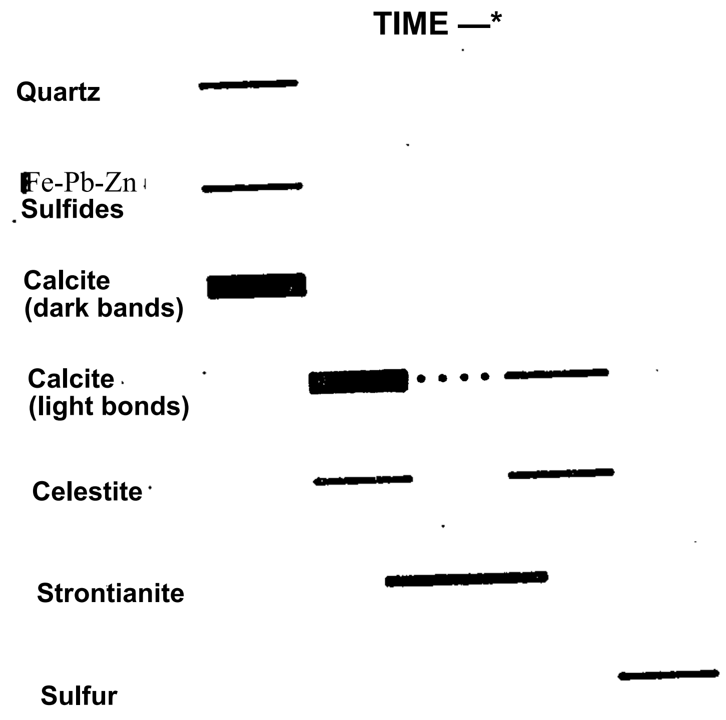

Figure 9. Paragenesis of minerals in limestone caprock at Tatum dome.

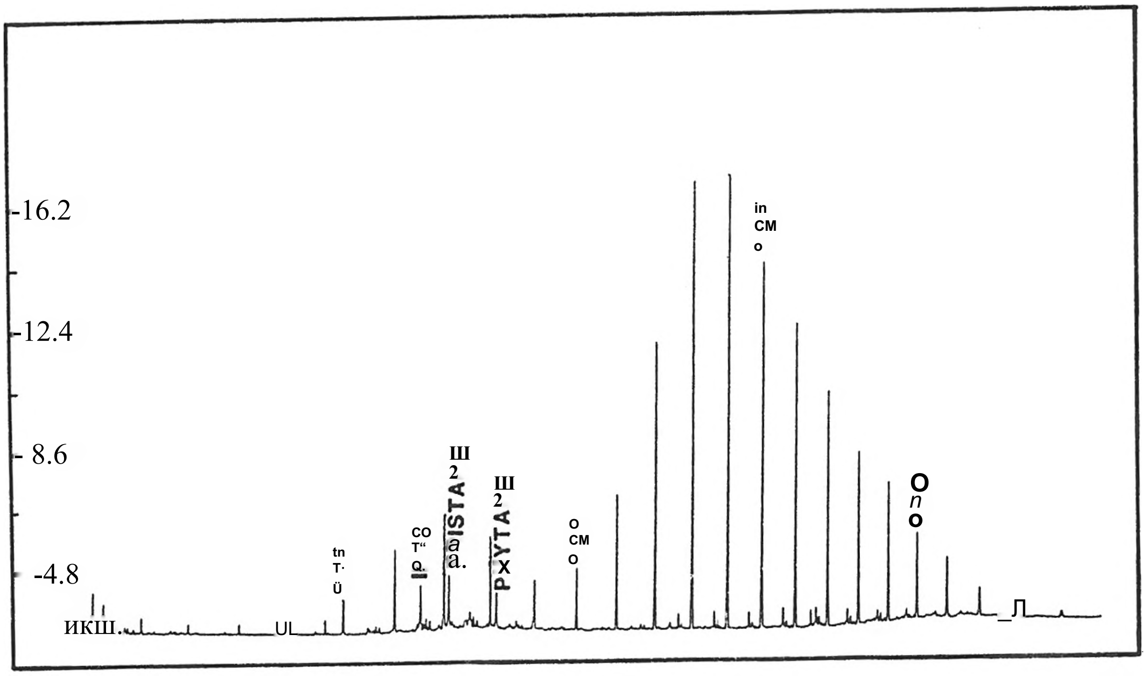

Figure 10. Chromatographic signature of the Cp+/abated hydrocarbons from limestone caprock at Tatum dome. Analysis by Core Labs, Dallas, Texas