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# Use of sulfates to identify weathered coal

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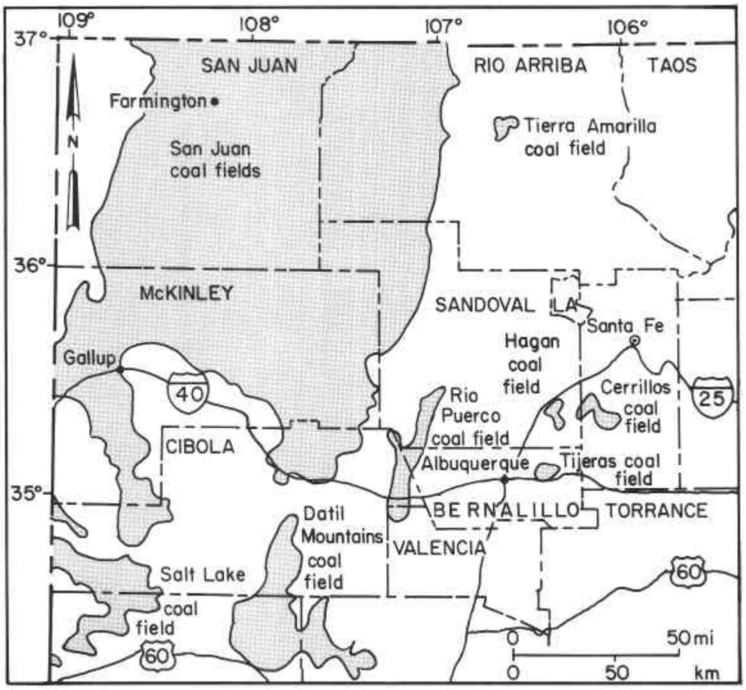

FIGURE 1—Location of Salt Lake coal field, Catron and Cibola Counties, New Mexico (from Kottlowski et al., 1985).

## Introduction

The advantages of using fresh core or channel samples over highly weathered and oxidized outcrop samples in evaluating quality of coal in an area are well established. In obtaining coal cores, an arbitrary depth is set, above which coals are assumed to be oxidized, and all coals below this depth are unoxidized. The data presented here will demonstrate that obtaining a fresh core sample does not ensure that an unoxidized sample will be obtained. How can an investigator differentiate between oxidized and fresh coals if the cores do not always accurately represent the true quality of the coal? Is there a minimum depth below which fresh coals can always be retrieved? What are the effects on the combustion qualities of coal with depth and oxidation? How does the lithology of the overburden affect the depth of oxidation of coal in a particular area?

For the past 7 years (1979–1986), New Mexico Bureau of Mines and Mineral Resources (NMBMMR) staff has been conducting a geologic investigation in the Salt Lake coal field (Fig. 1), which includes mapping and drilling, as part of an overall evaluation of coal quality and resources (Anderson, 1981; Anderson and Frost, 1982; Campbell, 1981; Roybal and Campbell, 1981; Campbell and Roybal, 1982). The work was done in cooperation with the U.S. Geological Survey (McLellan et al., 1984). Sixty coal core samples were collected during the course of this study. Twenty-two combustion and chemical analyses including eight major-oxide analyses were run on each of the samples shortly after collection. By using this entire population of samples as representative of the coals of the Salt Lake coal field the mean and standard deviation values were obtained (Table 1, group A). Calculation of rank based on these analyses results in a moist, mineral-matter-free (mmf) heating value of 10,988 Btu/lb, which in-

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TABLE 1—Analyses of Salt Lake coals based on sulfate content (as-received basis); S.D. = standard deviation.

| | Group A—all coals | | | Group B—coals with sulfates | | | Group C—coals without sulfates | | |
|---|---|---|---|---|---|---|---|---|---|
| Parameters | Number of samples | Mean | S.D. | Number of samples | Mean | S.D. | Number of samples | Mean | S.D. |
| Equilibrium moisture | 60 | 14.66 | 2.80 | 26 | 16.18 | 3.63 | 34 | 13.58 | 1.21 |
| Moisture | 60 | 15.48 | 2.94 | 26 | 16.96 | 3.68 | 34 | 14.37 | 1.55 |
| Ash | 60 | 17.91 | 4.63 | 26 | 18.56 | 5.21 | 34 | 17.50 | 4.29 |
| Volatile matter | 60 | 29.94 | 1.78 | 26 | 29.37 | 1.86 | 34 | 30.33 | 1.66 |
| Fixed carbon | 60 | 36.69 | 3.24 | 26 | 35.11 | 3.16 | 34 | 37.80 | 2.90 |
| Btu | 60 | 8,856 | 1,000 | 26 | 8,191 | 1,049 | 34 | 9,329 | 646 |
| mmf Btu | 60 | 10,988 | 1,023 | 26 | 10,249 | 1,302 | 34 | 11,513 | 312 |
| Sulfur | 60 | .62 | .20 | 26 | .61 | .19 | 34 | .60 | .16 |
| Carbon | 43 | 50.99 | 4.82 | 18 | 47.98 | 4.93 | 24 | 53.13 | 3.51 |
| Hydrogen | 43 | 3.74 | .47 | 18 | 3.41 | .54 | 24 | 3.98 | .20 |
| Nitrogen | 43 | .97 | .08 | 18 | .98 | .08 | 24 | .97 | .08 |
| Oxygen | 43 | 10.29 | 1.83 | 18 | 11.47 | 2.29 | 24 | 9.44 | .61 |
| Sulfide | 60 | .16 | .13 | 26 | .12 | .14 | 34 | .17 | .10 |
| Sulfate | 18 | .03 | .07 | 18 | .09 | .07 | 34 | 0.00 | 0.00 |
| Organic sulfur | 60 | .43 | .13 | 26 | .40 | .13 | 34 | .43 | .11 |
| $SiO_2$ | 60 | 55.22 | 6.79 | 26 | 53.59 | 6.79 | 34 | 56.82 | 6.49 |
| $Fe_3O_4$ | 60 | 3.80 | .92 | 26 | 3.66 | .79 | 34 | 3.74 | .75 |
| $Al_2O_3$ | 60 | 27.50 | 5.46 | 26 | 27.66 | 4.60 | 34 | 27.40 | 6.11 |
| $TiO_2$ | 60 | 1.43 | .30 | 26 | 1.43 | .29 | 34 | 1.43 | .31 |
| CaO | 60 | 4.23 | 1.42 | 26 | 3.87 | 1.25 | 34 | 4.49 | 1.51 |
| MgO | 60 | .63 | .17 | 26 | .71 | .21 | 34 | .58 | .11 |
| $Na_2O$ | 60 | .71 | 1.78 | 26 | .37 | .22 | 34 | .51 | .37 |
| $K_2O$ | 60 | .29 | .24 | 26 | .33 | .27 | 34 | .25 | .19 |

dicates a rank of subbituminous C for the coals in this area. In calculating resources, the U.S. Geological Survey (Wood et al., 1983) has specified that coal of this rank have a minimum thickness of 2.5 ft in order to be considered a resource.

Sulfates were detected in many of the cores. In the Salt Lake coal field samples, sulfate values near the surface are highest. Figure 2 shows the variation of sulfate-bearing coals with depth; 16 of the 26 sulfate-bearing coals sampled occurred within 60 ft of the surface. Twenty coal samples were taken within 60 ft of the surface; 16 of these have sulfates. Of the remaining 40 coal samples (deeper than 60 ft), nine demonstrated sulfate development (Fig. 2). Sulfate-bearing coals in this field occur to a maximum depth of 180 ft. One exceptional case, however, showed 0.03% sulfate at 180 ft. This core was taken near the edge of a 150-ft mesa escarpment. Other deep sulfate-bearing coals are located below thick alluvium with less than 60 ft of undisturbed sediments overlying the coal, or they are located a short distance from outcropping coal. Those coals that are shallower than 60 ft and do not have any sulfates have a greater percentage of nonporous materials (claystones and mudstones) acting as an impermeable barrier.

Additional differences are illustrated by dividing this group of data into two separate populations, based on the presence or absence of sulfates. The samples in group B (with sulfates) show notably poorer values in combustion analyses than those in group C (without sulfates; Table 1).

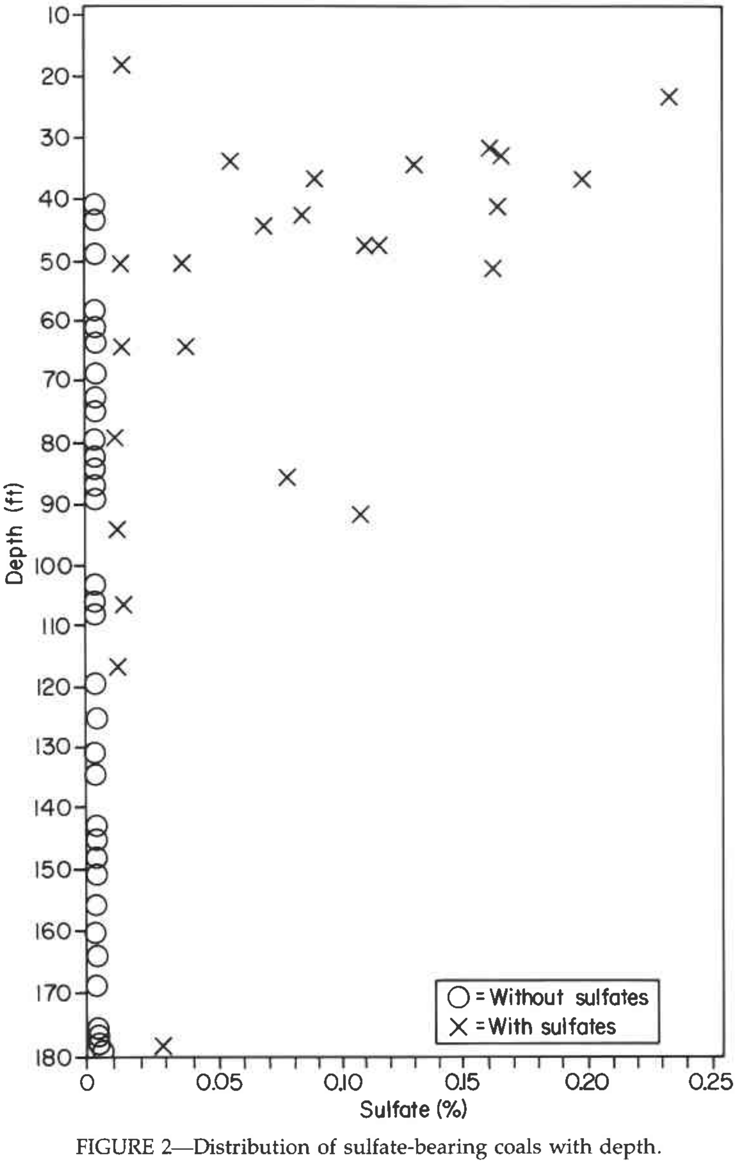

FIGURE 2—Distribution of sulfate-bearing coals with depth.

### Proximate analyses

Comparing the proximate analyses of the two groups of data shows the sulfate-bearing coals to be considerably degraded. The parameters that show no significant change are the ash and volatile-matter content. A t-test for the volatile-matter populations shows a significant difference between sulfate- and nonsulfate-bearing coals. The absolute difference is 0.96%, which is greater than ASTM (1983) standards for repeatability (0.7%), but less than the 1.00% reproducibility limit for bituminous coals. Because this difference is detectable within a laboratory but not detectable between laboratories, it is not considered significant for purposes of this paper.

The moisture content of the sulfate-bearing population is considerably higher than in the nonsulfate-bearing population. Figure 3 shows the change in moisture with depth, with a marked change in the moisture content of the coals at 50–60 ft. Above 50 ft the mean moisture content becomes significantly higher (see Table 1, groups B and C). The range of moisture content is much greater for those coals containing sulfates (12.06–23.41%) than for coals without sulfates (17.84–11.09%). There are two anomalously high moisture values below 60 ft that are in sulfate-bearing coals. One coal is at a depth of 180 ft, but the hole is located on top of a 150-ft mesa, 300 feet from the escarpment edge. Because the sample was downdip from the escarpment, the effective cover thickness is only 30 ft. The second sample was taken at a depth of 70 ft, with 40 ft of alluvium

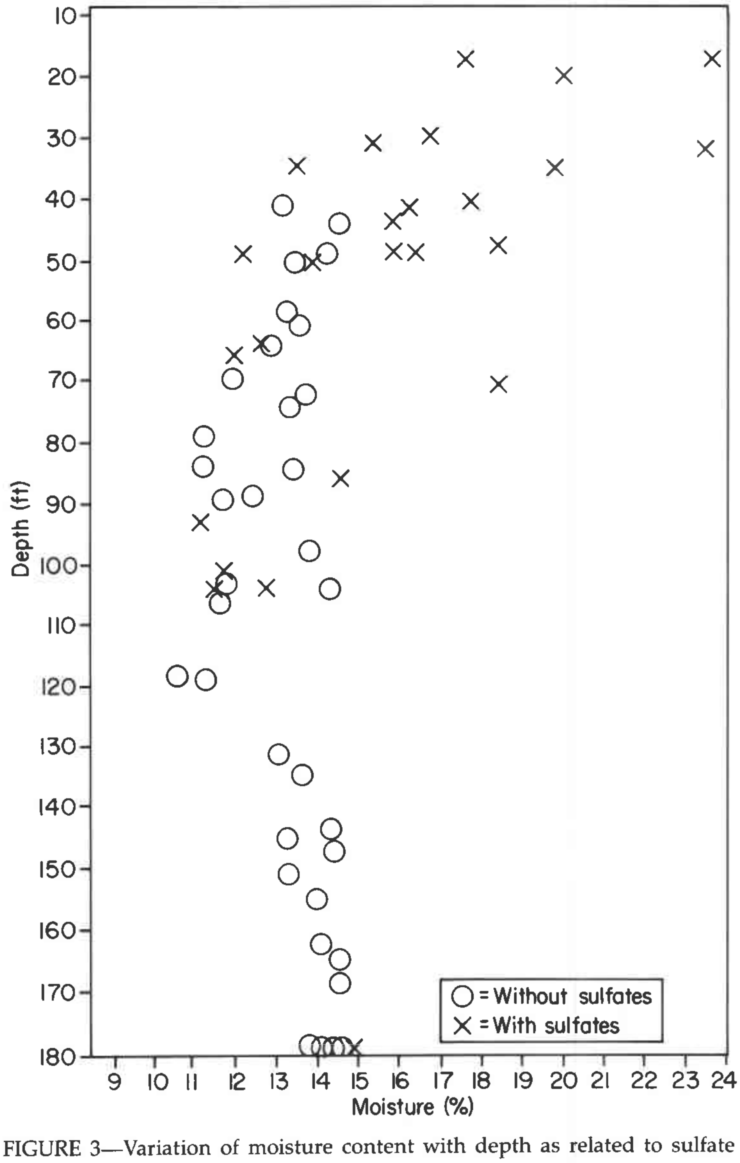

FIGURE 3—Variation of moisture content with depth as related to sulfate content.

overlying it. In this case, the effective overburden thickness is only 30 ft.

The last parameter of the proximate analysis is fixed carbon. The sulfate-bearing population has a mean value of 35.11 ± -3.16%, while the nonsulfate-bearing group has a mean of 37.80 ± -2.90%. This difference remains significant, even when compared on a dry basis. The depth at which the fixed carbon values undergo this change is 50–60 ft. The population that contains the sulfates also has a slightly lower range in fixed carbon values (40.12–29.80%) than does the nonsulfate-bearing population (42.50–28.94%). A range of values are expected because the fixed carbon is achieved by difference.

### Heating value

The average as-received Btu values for those coals with sulfates are significantly lower (8,191 Btu/lb) than those samples showing no sulfates (9,329 Btu/lb). The difference of 1,138 Btu/lb between these two populations is considered significant. This may appear to be due to the increase in the mean moisture content of 2.59% for the sulfate-bearing coals. The dry heating value for coals without sulfates averages 10,799 Btu/lb; for coals with sulfates it is 9,772 Btu/lb, resulting in a difference of 1,027 Btu/lb. There is approximately a 1,000-Btu/lb difference regardless of whether the coals are compared on an as-received or dry basis. Figure 4 shows the moist, mineral-matter-free heating values plotted against depth. At about 50 ft there is a marked change in slope. The coals above 50 ft have a much wider range in values and show a lower heating value. Nearly all these shallow coals have sulfates. Coals deeper than 50 ft show a very reduced range in both as-received and dry heating values. The nonsulfate-bearing population has an average moist, mineral-matter-free Btu of 11,513 Btu/lb, indicating a rank of high volatile C bituminous for the Salt Lake coals. The sulfate-bearing population has an average moist, mineral-matter-free heating value of 12,049 Btu/lb, indicating an average rank of subbituminous C. The range in moist, mineral-matter-free heating value is much narrower in the nonsulfate-bearing coals (12,213–11,113 Btu/lb) than in the oxidized sulfate-bearing coals (12,087–7,790 Btu/lb).

### Ultimate analyses

The ultimate analyses also show differences depending on whether or not sulfates are present. Both the carbon and hydrogen contents of the coals are significantly reduced in those coals containing sulfates (see Table 1, groups B and C). These two elements are the major contributors to the heating value of coals. Thus, a reduction in the amount of these two elements, especially carbon, will result in a reduction of the heating value. Finally, oxygen affects the heating value of coal negatively. The oxygen content is greater in coals that have sulfates (11.47%) than in those without sulfates (9.44%). An increase in the oxygen content is accompanied by a lower heating value of the coal. There is no change in the amount of nitrogen or sulfur present for either the sulfate- or nonsulfate-bearing coals. The depth at which most of these parameters change is 50–60 ft. The range in value increases dramatically for those coals within 50 ft of the surface.

The total sulfur content remains constant between the two populations (Table 1, groups B and C). A difference occurs when the sulfur forms are compared. No significant change occurs in the organic sulfur values when sulfate- and nonsulfate-bearing populations are compared. Sulfide sulfur is significantly reduced in the sulfate-bearing coals. This indicates that only the sulfide sulfur is being oxidized to sulfate, with both jarosite and gypsum occurring.

### Effects on major elements

Eight major elements ($SiO_2$, $Al_2O_3$, $Fe_3O_4$ $TiO_2$, CaO, MgO, $Na_2O$, $K_2O$) were analyzed using the high-temperature ash. The means and standard deviations of these elements for all samples are given in Table 1 (group A). Calcium and sodium values are both lower when sulfates are present; neither calcium nor sodium is strongly associated with either the organic or mineral portion of the coal. When coals are subject to oxidation the organic bonds between calcium and sodium are broken, and they recombine with the released sulfur to form gypsum and thenardite. No thenardite was detected in the coals, but this mineral, as well as some of the gypsum, might have been removed from the coal by ground water. Potassium and magnesium values, however, show an increase with the development of sulfate.

### Resource evaluation

The variability of the oxidized (sulfate-bearing) coals is much greater than that for nonsulfate-bearing coals. It is therefore easier to predict coal quality parameters in the nonsulfate-bearing coals. The difference in rank determination based on the presence or absence of oxidized coals could lead to significant discrepancies in coal-resource figures. A population weighted in sulfate-bearing, essentially shallow (<60 ft) coals will show a rank of subbituminous B. According to U.S. Geological Survey guidelines, coals of this rank have a minimum thickness for resource calculation of 2.5 ft. However, if drilling extended well past the 60-ft depth, the coal rank would be high volatile C bituminous. This rank coal has a minimum resource thickness of 1.2 ft; the difference could affect the measured resource of an area by a minimum of .29 million tons per drill site. Using the presence or absence of sulfates in the cores, one can calculate how much of the resource in an area is oxidized and of lower quality and how many tons are present as fresh coal. Campbell and Roybal (1982)

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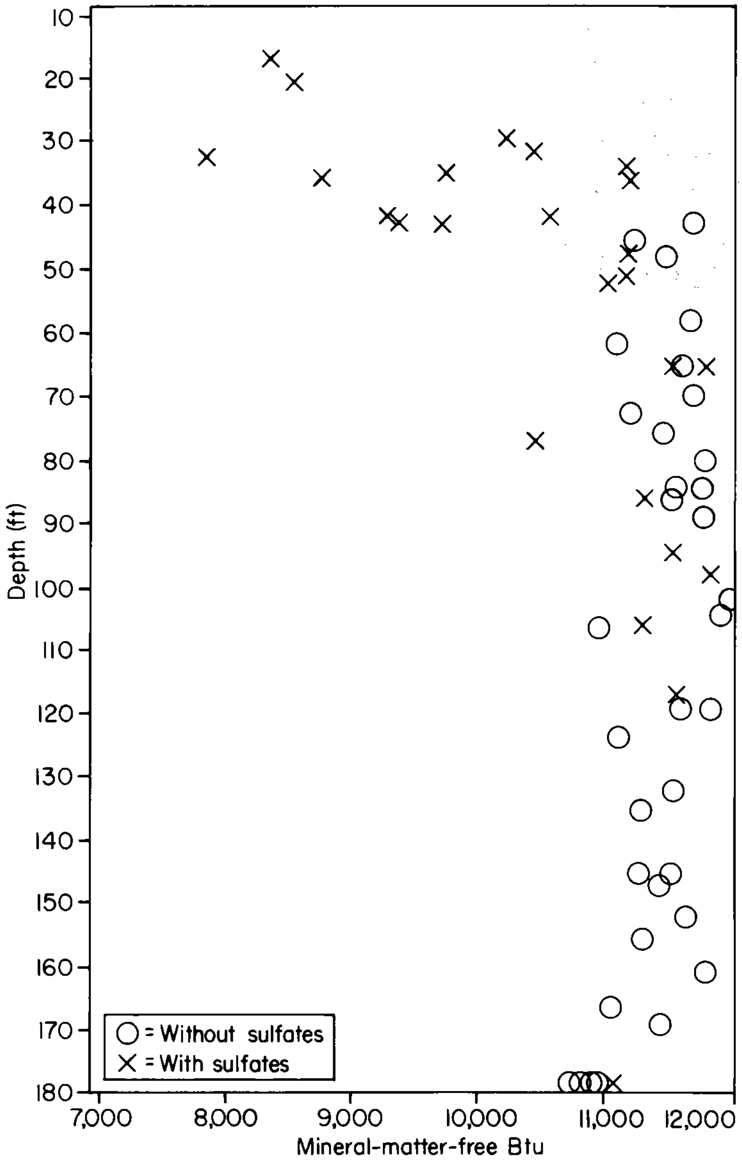

FIGURE 4—Variation of moist, mineral-matter-free coal with depth as related to sulfate content.

estimated a reserve base for the Salt Lake coal field of 347 million tons within 250 ft of the surface. Using sulfates as a factor, this reserve base can be recalculated as approximately 69 million tons of oxidized, lower rank coal and 278 million tons of unoxidized reserve base.

## Conclusions

The formation of sulfates is due to an increase in the amount of oxygen-rich surface water reaching the coal. The oxygen then reacts with the sulfides, pyrite, and marcasite to form sulfates. Although the maximum depth at which sulfate is found is 180 ft, most of the sulfates are found within 50–60 ft of the surface. Coals containing sulfates that are deeper than this 50–60-ft interval are overlain by greater amounts of porous sandstones or alluvium. In either case, surface moisture, carrying oxygen, penetrated deeper than coals not overlain by the same thicknesses of these porous lithologies. Conversely, several coals that have no sulfate development, yet are within 50–60 ft of the surface, are overlain by impermeable materials such as mudstone and claystone. In this case, the impermeable nature of the overburden prevents oxygen-bearing water from reaching the coal. The shallowest coal in which no sulfate development occurs is 40 ft.

When analyzing the combustion characteristics and estimating the resources of a coal-bearing area, attention should be paid to the distribution of sulfate values in the coals. Coals in the Salt Lake coal field within 40 ft of the surface have sulfates, high moisture, low Btu, and increased oxygen values. The range of values for those parameters is much greater than for deeper coals. In the Salt Lake coal field all coals within 40 ft of the surface can be considered oxidized. None of these features is desirable for a steam coal. These data, if figured with the rest of the analyses, will tend to bias the coal negatively. Likewise, excluding these data from an area-wide appraisal would bias the results positively. Reporting both sets of data and noting the maximum, minimum, and average depths of oxidation will allow a better assessment of area coals.

ACKNOWLEDGMENTS—I wish to thank Lynn Brandvold and William Stone for helpful comments and Orin Anderson, Louie Martinez, and Ralph Wilcox for reviewing a version of this paper.

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## Review

**Precambrian and Paleozoic algal carbonates, west Texas–southern New Mexico**, by *Donald F. Toomey* and *Jack A. Babcock*, August 1983: Colorado School of Mines, Professional Contributions No. 11, 345 pp., 53 figs., 97 plates. $25.00

This book was published as the field guide for the 3rd International Symposium on Fossil Algae. It covers selected localities of Late Precambrian, Ordovician, Pennsylvanian, and Permian algal carbonates in westernmost Texas and south-central and southeastern New Mexico and is a significant contribution to knowledge of fossil algae and algal carbonate rocks. Many of the Paleozoic carbonate rocks of this region owe their origin directly to marine algae, and, most important, they continue into the subsurface as economically productive petroleum reservoirs.

Seventeen areas were selected as field localities. Beginning with the phylloid algal mound complexes of Late Pennsylvanian age in the Hueco Mountains, the localities visited include: Early Ordovician algal-sponge bioherms and stromatolites in the southern Franklin Mountains; Late Precambrian stromatolites and varied carbonate structures in the northern Franklin Mountains; Late Pennsylvanian phylloid algal mound complexes and Early Permian algal bioherms, miniherms, and biostromes in the Sacramento Mountains; and the world-famous Permian reef complexes of the Guadalupe Mountains, where the algal-rich microfacies of these reefs are emphasized.

Each road log begins with a description of the general stratigraphy and geology of the mountain ranges and areas visited; then each stop that was made is explained in detail. Pertinent descriptions and comments on carbonate-rock and algal morphology are interspersed throughout the text. Visits to the gypsum sand dunes of White Sands National Monument and magnificent Carlsbad Caverns are also included.

The maps and sketches, along with outcrop photographs, show the detailed local and regional relationships of the algal-bearing carbonate rocks. The carbonate petrography as well as the algal descriptions and identifications are well illustrated by numerous photomicrographs.

Many field guides are of use mainly during the field trip when the trip leaders and other experts are present. This guidebook is actually a text. The descriptions of each site, along with sketches and photographs, allow anyone to utilize the book to revisit the outcrops and see the significant features of algal carbonates in the rocks.

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