

OKLAHOMA GEOLOGICAL SURVEY  
CARL C. BRANSON, *Director*

BULLETIN 92

BORATE MINERALS IN PERMIAN GYPSUM OF  
WEST-CENTRAL OKLAHOMA

*by*

W. E. HAM, C. J. MANKIN, AND J. A. SCHLEICHER

The University of Oklahoma  
Norman  
1961

## CONTENTS

ABSTRACT	5
INTRODUCTION	7
Previous and present investigations	8
Acknowledgments	8
Geologic setting	9
BORATE MINERALS IN WEST-CENTRAL OKLAHOMA	11
Probertite	14
Chemical composition	23
X-ray diffractograms	23
Ulexite	26
Occurrence	27
Blaine gypsum	30
Core holes in Cloud Chief gypsum	31
Chemical composition	33
X-ray diffractograms	34
Priceite	36
Other minerals	38
Economic possibilities of the borate minerals	41
ORIGIN AND SOURCE OF THE BORATE MINERALS	43
Borates in bedded marine evaporites	43
Inder district, Russia	45
Zechstein of northern Germany	47
England and New Mexico	48
Nova Scotia	48
Comparison of major features	48
Oklahoma	50
Boron in anhydrite and gypsum from Oklahoma	54
Comparison with the Zechstein of Germany	58
Genetic relations of borate minerals to anhydrite	59
Laboratory investigations of the nature of boron in anhydrite	61
Tests for inclusions of borate minerals	61
Water-soluble boron in anhydrite	62
X-ray diffraction data	63
Laboratory precipitation of boron-containing anhydrite	64
Summary	64
EMISSON SPECTROGRAPHIC DETERMINATION OF BORON IN GYPSUM AND ANHYDRITE	67
Preparation of samples	68
Preparation of standards and analytical curves	68
Technique and equipment	68
REFERENCES	71
INDEX	73

## ILLUSTRATIONS

### PLATES

- |      |   |           |
|------|---|-----------|
| I.   | Isobar map of basal anhydrite of Cloud Chief formation in the Weatherford District                  | In pocket |
| II.  | Geologic sections through Cloud Chief evaporites in the Weatherford district                        | In pocket |
| III. | Photomicrographs of probertite, celestite, and anhydrite from Nescatunga member of Blaine Formation | Page 39   |

### FIGURES

- |     | Page  |    |
|-----|---|----|
| 1.  | Geologic map and cross section of Custer and Blaine Counties, Oklahoma, showing regional occurrences of borate minerals | 10 |
| 2.  | Diagram showing occurrences of probertite and ulexite in Cloud Chief gypsum   | 12 |
| 3.  | Diagram showing occurrences of probertite and priceite in Nescatunga gypsum in quarries of Blaine County, Oklahoma      | 15 |
| 4.  | Diagram showing occurrence of probertite and ulexite at locality 3  | 16 |
| 5.  | Photograph of probertite nodules on bedding surface of gypsum at locality 2   | 17 |
| 6.  | Photograph of probertite nodules from locality 1  | 19 |
| 7.  | Photograph of probertite nodule from locality 1   | 19 |
| 8.  | Photograph of probertite nodule that has replaced Cloud Chief gypsum  | 20 |
| 9.  | Photograph of probertite nodule that occurs along solution-enlarged bedding surface                                     | 21 |
| 10. | X-ray diffractograms of probertite from Oklahoma and California   | 25 |
| 11. | Photograph of large nodule of ulexite from locality 3   | 27 |
| 12. | Photographs of a discoidal ulexite nodule from locality 3   | 29 |
| 13. | Photograph showing ulexite occurring as fibrous tufts in Cloud Chief gypsum   | 32 |

14. X-ray diffractograms of ulexite from Oklahoma, Nova Scotia, and California	35
15. X-ray diffractograms of priceite from Oklahoma and California	37
16. Distribution of borate minerals in bedded marine evaporites of the world	44
17. Photograph of probertite nodule in gypsum that is altering from anhydrite	52
18. Summary diagram of boron content in analyzed samples of gypsum and anhydrite from Blaine and Cloud Chief formations	55
19. Diagrams showing boron content in selected cores of gypsum and anhydrite from Blaine and Cloud Chief formations	56
20. Photograph illustrating partial and complete solution of probertite nodules in gypsum	60

## TABLES

1. Chemical analyses of probertite from Oklahoma and California	22
2. Chemical analyses of ulexite from Oklahoma and California	33
3. Chemical analyses of priceite from Oklahoma and California	36
4. Principal occurrences of borate minerals in bedded marine evaporites	46
5. Boron in Permian shales of western Oklahoma	53
6. Boron content of Permian gypsum and anhydrite in western Oklahoma	In pocket
7. Insoluble residues from Oklahoma anhydrite	62
8. Loss of $B_2O_3$ from Oklahoma anhydrite by water leaching	63

# BORATE MINERALS IN PERMIAN GYPSUM OF WEST-CENTRAL OKLAHOMA

W. E. HAM, C. J. MANKIN, AND J. A. SCHLEICHER

## ABSTRACT

The borate minerals probertite, ulexite, and priceite occur as replacement nodules in massive gypsum beds of the Blaine formation (Middle Permian) and the Cloud Chief formation (Late Permian) in three districts of Custer and Blaine Counties in west-central Oklahoma. The strata of the region are nearly horizontal and are unbroken by faults. From the nature of the associated rocks and the lack of igneous intrusions, flows, or evidence of hydrothermal activity, it is inferred that the borate minerals are related in origin to the Permian seas from which the sulfate evaporites were precipitated. Geochemical investigations indicate that borates probably are present in Permian gypsum over a region covering at least 20,000 square miles in western Oklahoma.

Probertite ( $\text{NaCaB}_5\text{O}_{10} \cdot 5\text{H}_2\text{O}$ ) is the dominant or exclusive borate mineral at most localities, whereas ulexite ( $\text{NaCaB}_5\text{O}_{10} \cdot 8\text{H}_2\text{O}$ ) and priceite ( $\text{Ca}_2\text{B}_{10}\text{O}_{16} \cdot 7\text{H}_2\text{O}$ ) are of rare occurrence. This is the first record of probertite outside the desert deposits of southern California and Nevada, and it is the only described area in the world in which probertite is the chief borate mineral. Absent in Oklahoma are the magnesium borates and potassium salts that are typical of the bedded Permian evaporites in Germany, Russia, England, and New Mexico. Sea-water evaporation during Middle and Late Permian time in Oklahoma was confined mainly to the sulfate stage, and never reached the stage of precipitation of potassium and magnesium salts. Geologically similar are the occurrences of calcium-boron minerals in Mississippian gypsum and anhydrite of Nova Scotia.

In Oklahoma the greatest observed concentration of probertite nodules, along selected bedding surfaces, is 10 percent by area; but channel samples of probertite-gypsum rock have a maximum content of only 0.16 percent  $\text{B}_2\text{O}_3$ , which is much too low for an ore deposit.

Owing to the solution of borate minerals by acidic ground waters and their absence in the upper 15 to 35 feet of the gypsum beds, future explorations must be carried out by drilling.

The borate minerals invariably occur in gypsum near beds or lenses of boron-containing anhydrite. Borate minerals and gypsum alike occur in direct relation to present topography, and both have been derived by weathering of anhydrite during a Pleistocene-Recent cycle of erosion.

Celestite likewise is formed in gypsum as a reorganization product of strontium-containing anhydrite.

Emission spectographic determination of boron in 150 samples of Permian rocks from western Oklahoma shows an average  $B_2O_3$  content of 232 ppm in anhydrite and 43 ppm in gypsum, indicating that nearly 200 ppm  $B_2O_3$  was in solution during the process of gypsum formation. This boron is precipitated as replacement nodules of Na-Ca borates in gypsum near the anhydrite-gypsum interface. Sodium cations are contributed by the solution of small amounts of rock salt contained in the anhydrite beds.

Boron was originally derived from the Permian seas. The average content of 232 ppm  $B_2O_3$  in western Oklahoma anhydrite compares with observed values of 129 to 283 ppm  $B_2O_3$  in pools of modern sea water where sulfates have been precipitated. An isobar map of Cloud Chief anhydrite shows the greatest values ( $> 250$  ppm  $B_2O_3$ ) to be in the eastern part of the Weatherford area, nearest the reconstructed shore line where concentration through evaporation during Permian time probably was at a maximum.

The form of the primary sulfate precipitate, the original mode of occurrence of boron in this precipitate, and the nature of boron in anhydrite are not certainly known. The anhydrite is believed to have been formed by reorganization during burial of boron-containing gypsum sediment. Concerning the nature of boron in anhydrite, experimental data show that boron uptake in anhydrite can be induced through laboratory precipitation, and our investigations of boron-rich natural anhydrite similarly indicate that at least 350 ppm  $B_2O_3$  participates in some structural way within the anhydrite lattice.

## INTRODUCTION

The largest deposits of borate minerals known throughout the world are associated with nonmarine sediments of Late Tertiary age or occur in modern playa lakes in arid regions. They generally occur in regions of volcanic activity and are associated with extrusive igneous rocks.

The deposits in southern California and Nevada are the world's largest, and they are closely related in origin to deposits that have been worked in South America, Turkey, and Tibet. Magmatic solutions and emanations accompanying the extrusion of volcanic rocks are generally believed to be the source of the boron; and this genetic concept is greatly strengthened by the occurrence of boron-rich fumaroles and hot springs. Probably the most famous are the active fumaroles of Tuscany, Italy, where the boron content is so high that boric acid is recovered and sold as a commercial product. Borax also is deposited from hot springs in Kashmir, India, and from mud volcanoes on the Kerch Peninsula between the Black Sea and the Sea of Azov (Grabau, 1920, p. 337-339).

In contrast are the sporadic and generally small occurrences of borate minerals in marine evaporites. Doubtless the best known and perhaps the most abundant borate mineral of this type is boracite in the Permian Zechstein at Stassfurt and elsewhere in Germany. Of equal importance, however, is the occurrence of calcium borates in Mississippian anhydrite and gypsum of Nova Scotia (Schaller, W. T., letter of July 21, 1958), and the occurrence of magnesium and calcium borates in Permian evaporites of the Inder district in Russia (Godlevsky, 1937).

The Oklahoma borate minerals occur in undisturbed beds of Permian gypsum that are interstratified with fossiliferous dolomite, anhydrite, and reddish-brown shale (Ham, 1960), and they are clearly derived from marine deposits of a desiccating epicontinental sea.

*Previous and present investigations.*—The present work had its beginning in an investigation by extensive coring in Permian gypsum and anhydrite of the Cloud Chief formation in the Weatherford-Clinton district (Ham and Curtis, 1958). Probertite in well-crystallized nodules was found in some of the gypsum cores, establishing the first occurrence of this mineral in the United States outside California and Nevada (Ham, Curtis, and Schleicher, 1958).

In 1959 Ham and Schleicher were shown a white nodule 4.5 inches in diameter that had been taken earlier from the United States Gypsum Company's quarries at Southard, Blaine County. Laboratory study of this nodule proved it to be ulexite. Ham and Mankin then investigated gypsum and anhydrite quarries in Blaine County, as well as critical outcrops, and re-examined the probertite-bearing cores from the Weatherford area. Approximately 50 X-ray diffractograms, made by Mankin, and two chemical analyses, made by Schleicher, established that: (1) probertite and ulexite occur in gypsum of the Cloud Chief formation, and (2) probertite, ulexite, and priceite occur in the Nescatunga gypsum member of the Blaine formation. The borate-containing gypsum beds of the Blaine and Cloud Chief formations are separated by 600 feet of red shales and sandstones, and they occur in two areas 30 miles apart.

An abstract of the results of the foregoing investigations has been published (Ham, Mankin, and Schleicher, 1960).

*Acknowledgments.*—The interest, assistance, and encouragement of the Southard staff of the United States Gypsum Company at Southard is gratefully acknowledged. W. I. Blosser, works manager, permitted an unrestricted examination of the quarries; D. F. Underwood, quarry superintendent, showed the writers the precise area from which the original ulexite nodules were quarried; and W. D. Reynolds, quality superintendent, provided from a carefully kept collection the first specimens of ulexite and priceite investigated from Oklahoma.

R. O. Fay accompanied the writers on one trip to Blaine County and supplied measured-section data from his extensive studies in that area.

Dr. Waldemar T. Schaller of the U. S. Geological Survey,



Washington, D. C., has kindly given us specimens of borate minerals from California and Nova Scotia. He also has helpfully discussed with us some of the major problems dealing with the occurrence of borate minerals in Oklahoma.

*Geologic setting.*—All the borate minerals known in western Oklahoma are in massive gypsum beds of Middle and Late Permian age. The gypsum occurs in a sequence of Early, Middle, and Late Permian red clastic sediments 3,000 feet thick (Green, 1936), which crop out over much of western Oklahoma and underlie an area of 30,000 square miles. Reddish-brown and maroon shales predominate, but sandstone and siltstones in various shades of red are common as well. These strata locally contain vertebrate fossils, plant spores and pollen, shark teeth, insects, and mollusks, thus indicating near-shore marine and littoral sedimentary environments. Within the outcropping strata are two sequences of marine evaporites, each locally thick and each characterized by gypsum and anhydrite.

The earlier evaporites comprise the Blaine formation. It ranges in thickness from 100 to 250 feet and consists of cyclically interstratified dolomite, gypsum, and shale. Gypsum occurs as beds 10 to 50 feet thick and locally makes up 75 percent of the formation. At the base of each gypsum bed, with few exceptions, is a thin bed of dolomite. These dolomites are fossiliferous, containing 14 described species of pelecypods, 14 species of cephalopods, and other marine fossils that indicate Late Leonardian or Middle Permian age (Clifton, 1942). The Blaine formation is widely distributed in western Oklahoma and is extensively worked for gypsum in Blaine County. The formation in most parts of Blaine County is 100 feet thick and consists of shale with four gypsum members. The gypsum members are, in ascending order, the Medicine Lodge, "Alabaster," Nescatunga, and Shimer (Fay, 1958). These members range in thickness from 2 to 18 feet and have an aggregate thickness of 40 feet, thus making up approximately 40 percent of the formation.

Five hundred to six hundred feet stratigraphically above the Blaine is the Cloud Chief formation, in the lower part of which is the thickest body of sulfate evaporites known on the outcrop in the Permian of western Oklahoma. Drilling in the Weatherford-

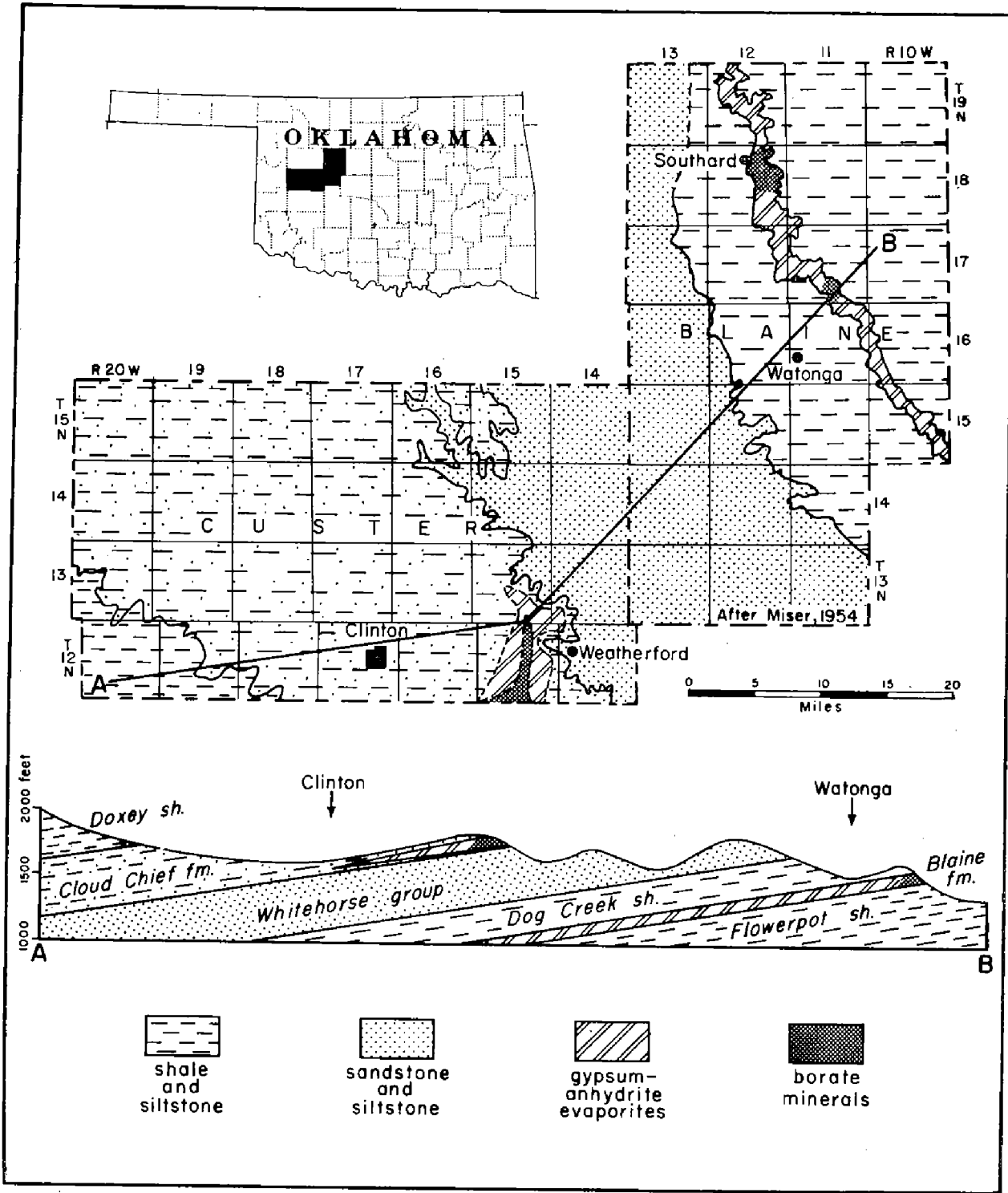


FIGURE 1. Generalized geologic map and cross section of Permian rocks in Custer and Blaine Counties, Oklahoma, showing regional occurrences of borate minerals. Dip is southwestward, approximately 30 feet per mile. Borate minerals in Southard district are in quarries of United States Gypsum Co.; those near Watonga are in quarry of Universal Atlas Co.; and those near Weatherford are in subsurface parts of the Cloud Chief formation.

Clinton district of Custer County has shown as much as 120 feet of massive gypsum and anhydrite, and thicknesses of 60 feet or more are common (Ham and Curtis, 1958). As no fossils have been recognized in the Cloud Chief formation, its age assignment to the Upper Permian (Ochoan) is based on interregional stratigraphic correlation (Dunbar et al., 1960).

### BORATE MINERALS IN WEST-CENTRAL OKLAHOMA

Borate minerals occur in the Blaine and Cloud Chief formations. At the present time they are known from three districts in Custer and Blaine Counties of west-central Oklahoma (fig. 1), where numerous cores and extensive quarries are available for study. The recorded occurrences are in cores of the Cloud Chief gypsum in the Weatherford area; in the Nescatunga gypsum of the Blaine formation at the Universal Atlas quarry, six miles northeast of Watonga; and in the Nescatunga gypsum in four quarries of the United States Gypsum Company at Southard. Other areas have been examined for borate minerals without success, but geochemical investigations made for this report indicate that borates probably are present in gypsum of the Cloud Chief and Blaine formations over a region covering at least 20,000 square miles in western Oklahoma.

In west-central Oklahoma the Permian strata dip southwestward approximately 30 feet per mile and are unbroken by faults. Drilling for oil in this region to depths as great as 24,000 feet, and to formations as old as Ordovician, has as yet revealed no extrusive or intrusive igneous rock. Evidence for hydrothermal activity also is lacking, and accordingly the inference is clear that the borate minerals have not been introduced from a subterranean or volcanic source but, as shown in a later chapter, are related in origin to the Permian sea from which the sulfate evaporites were precipitated.

The three borate minerals known from Oklahoma are probertite, ulexite, and priceite. Probertite ( $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$ ) is the dominant or exclusive borate at most localities, whereas ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ) and priceite ( $\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$ ) are of rare oc-

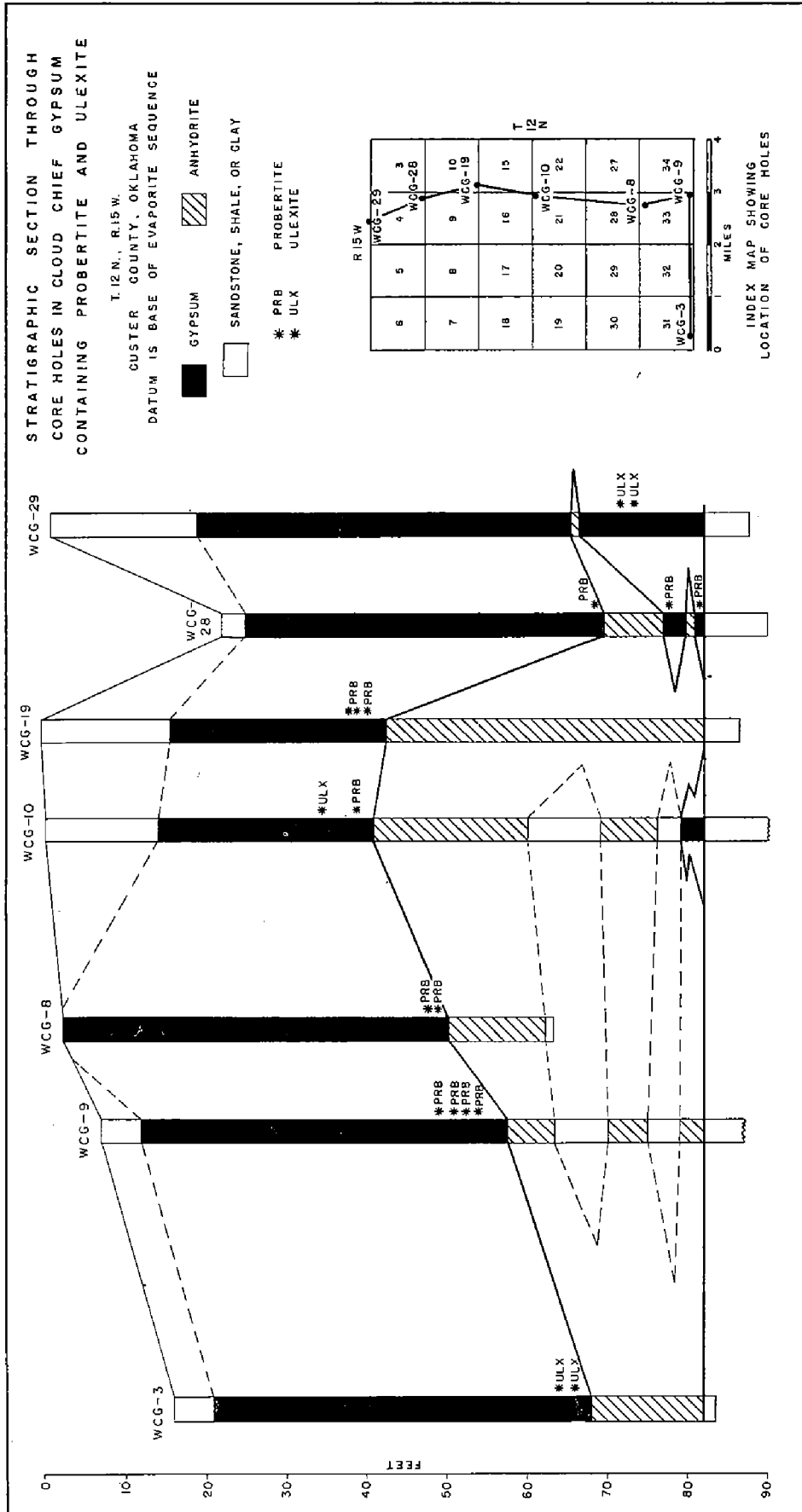


FIGURE 2. Diagram showing occurrences of probertite and ulexite in Cloud Chief gypsum. Cores from additional holes drilled in this area contain no borate minerals.

currence. Probertite and ulexite differ only in the percentage of combined water, and the percentage of  $B_2O_3$  in probertite is almost identical to that of priceite. In  $B_2O_3$  content the three minerals range approximately from 43 to 50 percent, and all are closely related in chemical composition and origin.

The borate minerals occur as small replacement nodules in massive gypsum, generally concentrated along crudely defined bedding surfaces. The pattern of distribution is precisely the same in all localities, for, although restricted in their occurrence to gypsum, the borates invariably are near beds or residual lenses of anhydrite that are now being altered to gypsum. In cores of Cloud Chief evaporites near Weatherford (fig. 2), probertite and ulexite are arranged like a halo around a lens of anhydrite at least six miles long and three miles wide, occurring there in gypsum above and below the anhydrite at a depth range of 34.5 to 72.6 feet. A part of the ulexite has the form and habit of probertite, and doubtless is a pseudomorph of it. In the quarries in the Nescatunga gypsum of Blaine County, probertite is the dominant mineral and generally occurs in the first five feet of gypsum lying directly upon massive anhydrite (figs. 3, 4). At one quarry, where the anhydrite has the form of a thin bedlike lens in gypsum (fig. 3C), probertite nodules are concentrated mostly in the first 18 inches of gypsum below the anhydrite. A few nodules of ulexite, three to five inches in diameter, and widely distributed smaller nodules of priceite are locally present in these gypsum beds.

The greatest concentration of probertite nodules along selected bedding surfaces is about 10 percent by area. Channel samples of the gypsum-probertite rock contain a maximum of only 0.16 percent  $B_2O_3$ , and thus show no probability that the deposits will be a commercial source of boron compounds.

The borate nodules are definitely of epigenetic origin. They occur as a replacement of gypsum, and the gypsum itself is being formed by hydration of anhydrite during the present cycle of weathering and erosion. The anhydrite contains substantial amounts of boron and halite and is the probable source of the essential constituents of the borate minerals. Strontium-bearing anhydrite likewise is the probable source of celestite that occurs in all the gypsum beds of the Blaine formation.

## PROBERTITE

The hydrous sodium-calcium borate mineral probertite ( $\text{NaCa B}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$ ) was described independently and almost simultaneously in 1929 by Eakle and by Schaller from the Kramer district, Kern County, California, where it occurs as rosettes of radiating thin prismatic crystals associated in clay with kernite and borax. Schaller (1930, p. 139f) gave a full description of the mineral and named it kramerite, but the short description by Eakle (1929, p. 427) was published at a slightly earlier date and the name he proposed has been adopted. The mineral has since been found in the Ryan or Death Valley district, Inyo County, California, associated with colemanite and ulexite (Foshag, 1931) and from Lang, Los Angeles County, where it is altered in part to ulexite (Murdoch, 1945).

In the California mining districts probertite occurs with other borate minerals in bedded deposits of Tertiary (Pliocene?) age that are believed to be of playa or lacustrine origin. Probertite probably occurs in other borate deposits of similar origin throughout the world, but its first occurrence in Permian marine gypsum was described from the Cloud Chief formation in the Weatherford area of western Oklahoma (Ham, Curtis, and Schleicher, 1958).

Additional investigations in Oklahoma since 1958 have shown that probertite also is common as small nodules in the Nescatunga gypsum member of the Blaine formation, in outcropping beds that are extensively worked for gypsum in Blaine County, about 35 miles northeast of the Weatherford area.

In Blaine County the probertite-containing marine evaporite beds are 600 feet stratigraphically below the Cloud Chief gypsum at Weatherford; and, although the two deposits are thus unrelated in time, it is clear that probertite in each of them has been formed by the same processes.

In Oklahoma probertite has been found at ten localities in three districts, in massive gypsum beds of the Blaine and Cloud Chief formations of Blaine and Custer Counties. It was discovered in core holes drilled for gypsum in the Weatherford-Clinton dis-

trict (fig. 2). Later it was found in four quarries of the U. S. Gypsum Company at Southard and at the quarry of the Universal Atlas Cement Company northeast of Watonga (fig. 1). In each of the three districts, probertite has the same habit and mode of occurrence, as small white nodules in rock gypsum, generally distributed

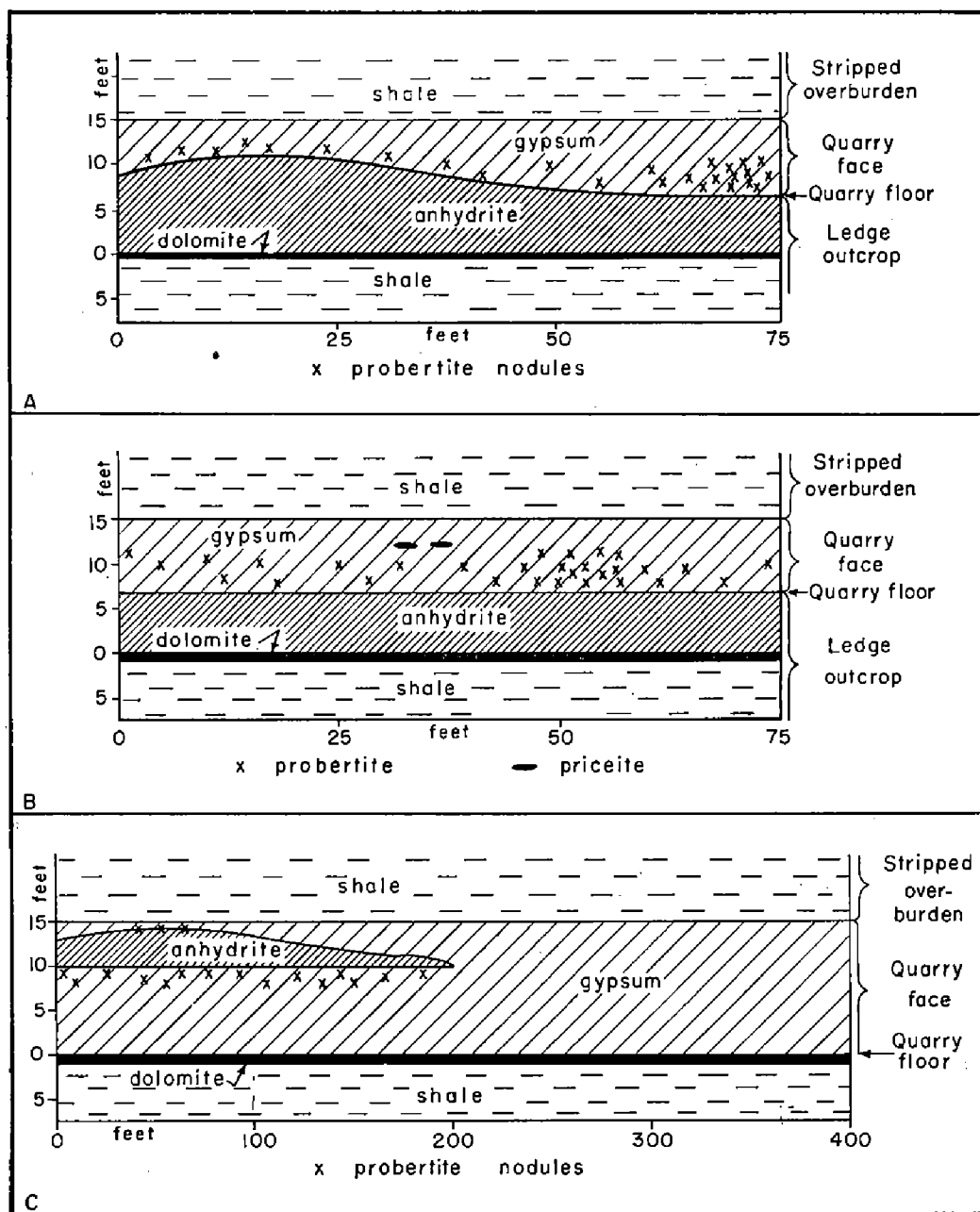


FIGURE 3. Occurrences of probertite and priceite in Nescatunga gypsum in quarries of Blaine County, Oklahoma.

- A. U. S. Gypsum Co., Southard, SW $\frac{1}{4}$  SW $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 11, T. 18 N., R. 12 W., locality 2.
- B. U. S. Gypsum Co., NW $\frac{1}{4}$  SE $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 11, T. 18 N., R. 12 W., locality 1.
- C. Universal Atlas Co., C W $\frac{1}{2}$  sec. 27, T. 17 N., R. 11 W.

along crudely defined bedding surfaces (figs. 5, 6, 9), but in places occurring as isolated nodules without regard to bedding (fig. 8). The nodules are subspherical to slightly flattened, ranging in diameter from 1 mm to a maximum of 15 mm (about 0.6 inch) and averaging 4 mm. They occur as two varieties: (a) porcelaneous nodules characterized by a botryoidal surface of warty protuberances, the nodule being composed of closely compacted and slightly curved fibers (figs. 8, 17), and (b) loosely coherent silky aggregates of randomly oriented fibrous tufts (fig. 7). Some nodules show in thin section that the individual fibers are hair-like crystals 0.5 to 1 mm long and 0.1 mm wide, arranged in subparallel bundles or slightly divergent clusters of straight needles (pl. III A, B). In other thin sections the needles are only 0.1 to 0.2 mm long and are arranged in feathery curved bundles.

Judging from published accounts and from an examination of specimens from California, the nodular habit and occurrence as extremely fine-grained fibers distinguishes the Oklahoma probertite from that in other areas. The California probertite is described as “. . . prismatic columnar, radiating from sharp centers and appearing as rosettes up to 3 centimeters in diameter” (Eakle, 1929, p.

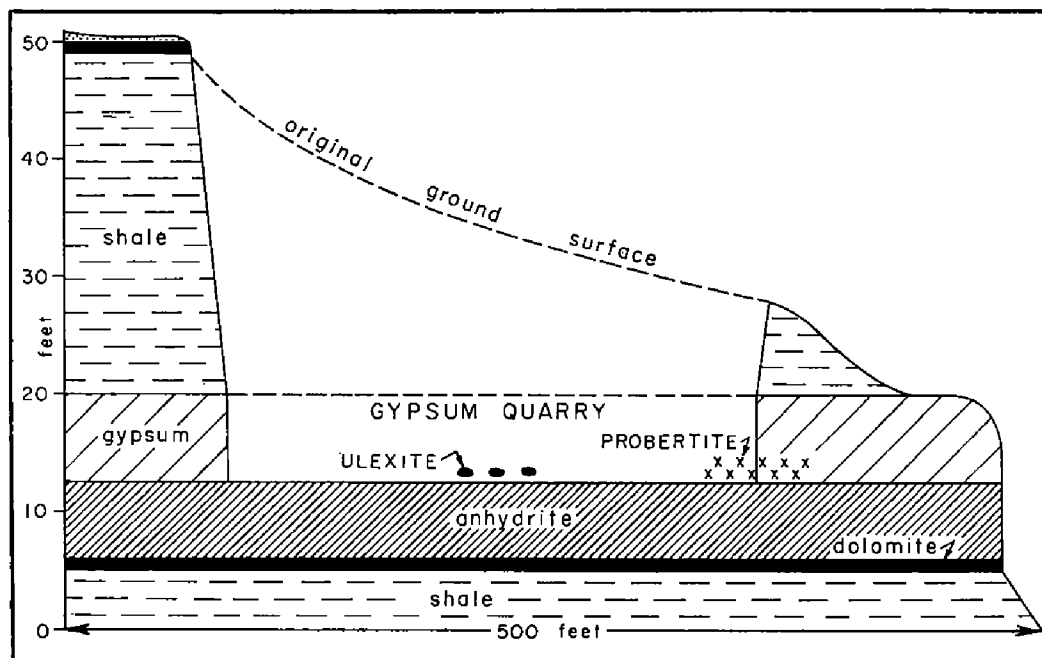


FIGURE 4. Probertite and ulexite in Nescatunga member of Blaine formation, quarry of U. S. Gypsum Co.,  $S\frac{1}{2}$   $SW\frac{1}{4}$   $SE\frac{1}{4}$  sec. 3, T. 18 N., R. 12 W., Blaine County, locality 3.



427); as “. . . prismatic crystals, usually forming spherulites but also more rarely existing as single crystals or groups of prisms in more or less parallel position, or radiating groups that do not form complete spherulites. . . . The longest crystal measured [was] 23 millimeters . . .” (Schaller, 1929, p. 139); as “. . . long, satiny, divergent needles or laths, some of the needles being as long as 30 centimeters. . . [and] as fibrous, closely reticulated aggregates with a silky to greasy luster. . .” (Foshag, 1931, p. 338); and as “. . . lenticular aggregates of groups composed of slender radiating prisms up to 15 x 0.5 mm in dimensions, these groups themselves being more or less flattened” (Murdoch, 1945, p. 719).

Another outstanding difference is the relative abundance of probertite as compared with the associated borate minerals. In California deposits, the most abundant minerals are kernite, borax, colemanite, or ulexite, but in the three districts of western Oklahoma

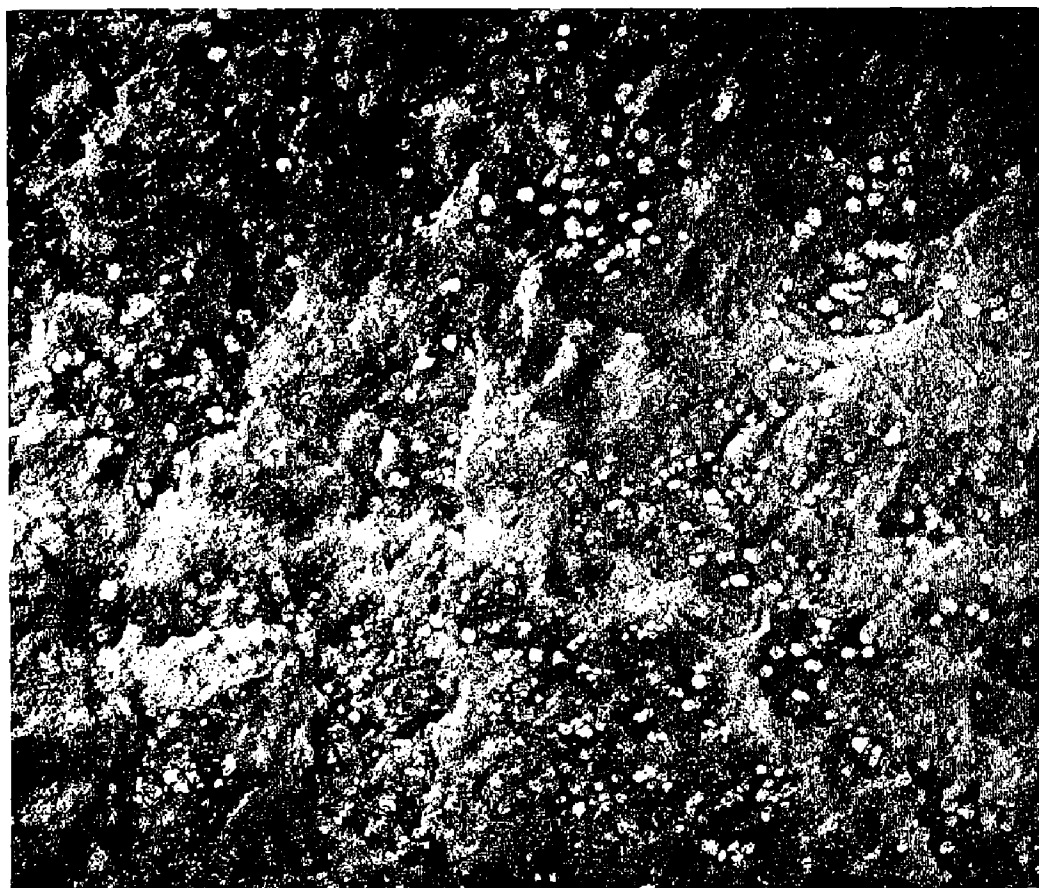


FIGURE 5. White nodules of probertite on bedding surface of fine-grained rock gypsum, Nescatunga member of Blaine formation. Quarry of U. S. Gypsum Co., locality 2, SW $\frac{1}{4}$  SW $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 11, T. 18 N., R. 12 W. The probertite nodules are 2 to 3 mm in diameter, x0.5.

probertite is the dominant borate mineral. It is the only borate mineral observed in the quarry of the Universal Atlas Cement Company, occurring there as nodules covering as much as five percent of selected bedding surfaces. It occurs to the exclusion of other borates in two quarries of the U. S. Gypsum Company, and in two other quarries of the same company it makes up at least 98 percent of the total amount of borate minerals present. Typical occurrences are illustrated in figures 5 and 6, in which the maximum concentration of probertite nodules along bedding surfaces, by area, is approximately 10 percent. In the seven borate-containing cores of Cloud Chief gypsum near Weatherford (fig. 2) probertite occurs in five holes and is the exclusive borate mineral in four of them.

Extensive investigations and the collection of numerous specimens from the gypsum quarries in Blaine County show that probertite occurs only in the Nescatunga gypsum member of the Blaine formation, and only in those parts of the gypsum that are at or near a contact with rock anhydrite. The occurrence of probertite within this selective range, however, is erratic and unpredictable, and ranges widely in concentration.

The distribution is illustrated in the four principal quarries that have been worked in the high-purity Nescatunga gypsum by the U. S. Gypsum Company over an area of two square miles at Southard. At locality 1 (fig. 3B), a quarry in eight feet of gypsum that covers about one acre, probertite occurs in the first five feet of gypsum directly above the anhydrite floor and is so abundant that every block from these gypsum layers contains, along certain bedding surfaces, two to ten percent of probertite. It is present in all parts of the quarry. In a companion quarry about 1,000 feet away, in the same ledge, probertite is so scarce that it can be found only by diligent inspection. At still a third quarry nearby (locality 2, fig. 3A), probertite in the west quarry wall is especially abundant, but along the south wall it decreases notably toward the east. About 20 acres of the same gypsum bed was quarried half a mile to the north by the company in 1950-1953 (locality 3, fig. 4); and here, in one part of the quarry wall, as much as five percent probertite was found in the basal 18 inches of the gypsum directly

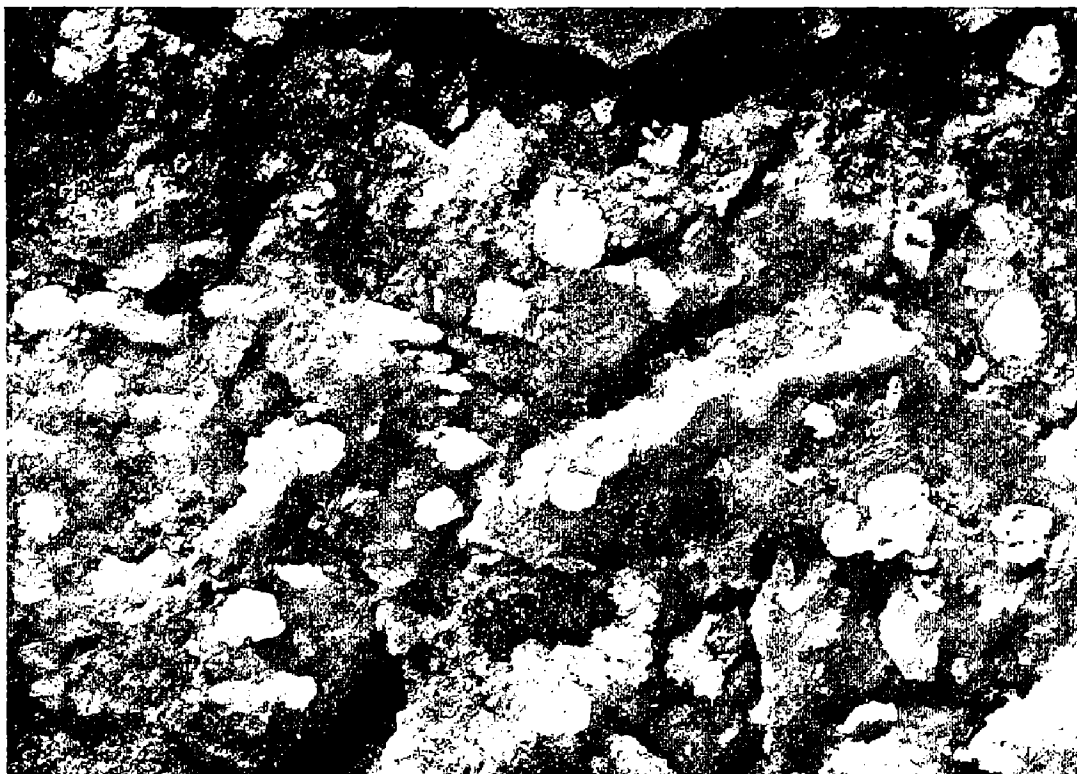


FIGURE 6. Probertite (white) occurring as nodular tufts of silky fibers along irregular bedding surface of fine-grained selenitic gypsum. Nescatunga member of Blaine formation, U. S. Gypsum Co., locality 1, NW $\frac{1}{4}$  SE $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 11, T. 18 N., R. 12 W., Blaine County. The nodules are 3 to 5 mm in diameter.

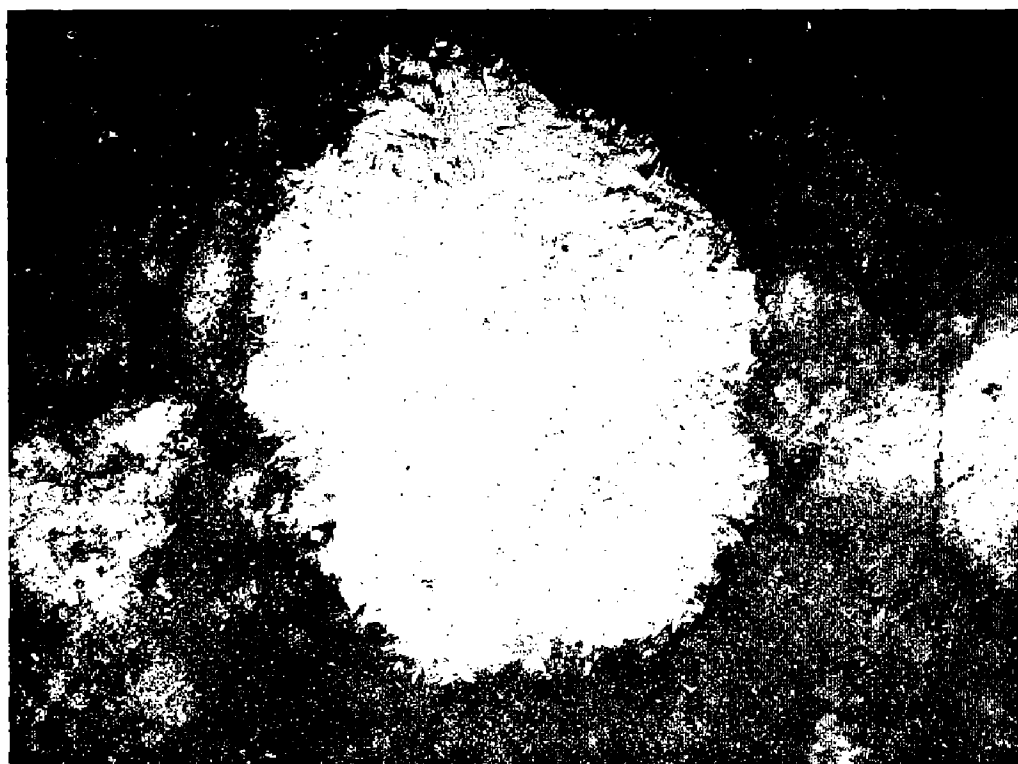


FIGURE 7. Probertite nodule about 0.5 inch (11 x 15 mm) in diameter, one of the largest observed in west-central Oklahoma, x4.5. It consists of aggregated curved silky fibers and occurs on bedding surface of Nescatunga gypsum, U. S. Gypsum Co., locality 1.

above the anhydrite floor. Elsewhere at this quarry the walls are barren, although the former existence of probertite is shown by small subspherical cavities in the gypsum from which probertite has been leached by ground waters. At each of the remaining quarries probertite is absent, with the exception of a few millimeter-sized concretions at the interfingering anhydrite-gypsum contact.

Similar cavities were noted in the Nescatunga gypsum at the quarry of Walton and Son, in the SE $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 35, T. 19 N., R. 12 W. It is inferred that probertite has been present in this gypsum bed but has been dissolved by acidic ground waters.

At the quarry in Nescatunga gypsum of the Universal Atlas Cement Company (fig. 3C), probertite is abundant as a halo around residual anhydrite lenses, but where anhydrite is absent the gypsum walls, fifteen feet high and fully exposed for examination, contain no borate minerals.

The subsurface distribution of probertite is entirely similar to that of the outcrop. In cores from the Cloud Chief gypsum of Custer County there is a clearly defined restriction of probertite

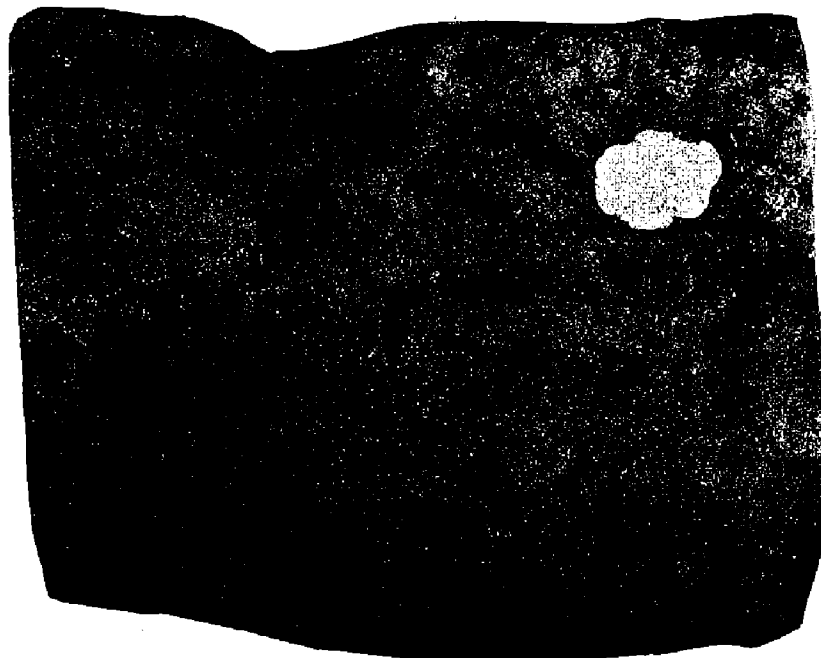


FIGURE 8. Typical probertite nodule (white) that has replaced Cloud Chief gypsum, x1.4, core hole WCG-8, depth 46.25 feet, NE $\frac{1}{4}$  NW $\frac{1}{4}$  NE $\frac{1}{2}$  sec. 33, T. 12 N., R. 15 W., Custer County, Oklahoma.

to that part of the gypsum which is 10 feet or less from an anhydrite contact (fig. 2). Cores or cuttings were obtained from 25 holes drilled about one mile apart over an area of 30 square miles (Ham and Curtis, 1958, pl. 1), and probertite or ulexite was found in seven of the 16 holes that were cored. The remaining holes were drilled in the same beds of gypsum, yet no borate minerals were found in them.

At no place in Oklahoma does probertite occur in contact with other borate minerals. Although ulexite, priceite, and probertite locally are present in the same thick gypsum bed, ulexite is separated either vertically or horizontally from probertite, and the single occurrence of priceite observed in the field was a concentration of small nodules in gypsum that is barren of other borate minerals and is slightly above the zone of probertite (fig. 3B). Similarly, it was found in the cores (fig. 2) that probertite occurs by itself in four holes and that ulexite alone occurs in two holes. Only in core hole WCG-10 are both minerals present, and in it they are separated by four feet of barren gypsum.



FIGURE 9. Probertite nodule occurring along solution-enlarged bedding surface of Cloud Chief gypsum,  $\times 1.5$ , core hole WCG-19, depth 38.1 feet, SW $\frac{1}{4}$  SW $\frac{1}{4}$  SW $\frac{1}{4}$  sec. 10, T. 12 N., R. 15 W., Custer County.

TABLE 1.—CHEMICAL ANALYSES OF PROBERTITE FROM OKLAHOMA AND CALIFORNIA

	<i>Southard, Oklahoma</i> <sup>1</sup>				<i>Weatherford, Oklahoma</i> <sup>2</sup>	<i>Kramer (Boron), California</i> <sup>3</sup>	<i>Ryan, California</i> <sup>4</sup>	<i>Theoretical proberite, NaCaB<sub>5</sub>O<sub>7</sub>·5H<sub>2</sub>O</i>
	<i>Original analysis</i>	<i>Recalculated, deleting gypsum</i>	<i>Recalculated to 100%</i>					
Na <sub>2</sub> O	7.32	7.32	8.20	9.28	8.49	9.00	8.83	
CaO	16.63	13.34	14.95	15.66	15.39	15.88	15.98	
B <sub>2</sub> O <sub>3</sub>	44.90	44.90	50.32	49.51	50.25	49.10	49.56	
H <sub>2</sub> O	25.78	23.67	26.53	25.55	25.87	25.64	25.63	
Insol.	0.54	....	....	....	....	0.20	....	
R <sub>2</sub> O <sub>3</sub>	....	....	....	....	....	0.38	....	
MgO	....	....	....	....	....	0.06	....	
SO <sub>3</sub>	4.70	....	....	....	....	....	....	
Total	99.87	89.23	100.00	100.00	100.00	100.26	100.00	

<sup>1</sup> J. A. Schleicher, analyst. Selected nodular tufts in Nescatunga member of Blaine formation, quarry of U. S. Gypsum Co., locality I, NW<sup>1</sup>/<sub>4</sub> SE<sup>1</sup>/<sub>4</sub> NW<sup>1</sup>/<sub>4</sub> sec. 18, T. 18 N., R. 12 W., Southard, Blaine County. Na<sub>2</sub>O includes 0.30 K<sub>2</sub>O.

<sup>2</sup> J. A. Schleicher, analyst. Composite samples of nodules from Cloud Chief gypsum, core hole WCG-9, depth 41.9-47.0 feet, SE<sup>1</sup>/<sub>4</sub> SE<sup>1</sup>/<sub>4</sub> SE<sup>1</sup>/<sub>4</sub> sec. 33, T. 12 N., R. 15 W., Custer County. Analysis reduced to 100 percent, as sample is admixed with gypsum (Ham et al., 1958, p. 27).

<sup>3</sup> W. T. Schaller, analyst. Average of three samples, reduced to 100% (Schaller, 1929, p. 144).

<sup>4</sup> W. F. Foshag, analyst. (Foshag, 1931, p. 339).

*Chemical composition.*—Chemical analyses of probertite from two widely separated localities in west-central Oklahoma, one from shallow cores in the Cloud Chief gypsum and the other from outcrops of the Blaine gypsum, are given in table 1 and compared with analyses of specimens from California. Each of the samples from Oklahoma was admixed with fine-grained gypsum that could not be removed, and the analyses have been recast on a gypsum-free basis. By this means it is shown that the Weatherford sample has almost exact correspondence with the chemical formula required for pure probertite,  $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$ , whereas the Southard sample has slight but nonessential deficiencies in sodium and calcium. Considering the minor substitutions that take place within the mineral itself, the two analyses from Oklahoma and the two from California are fully satisfactory and are well within the limits of analytical error.

The content of  $\text{B}_2\text{O}_3$  in probertite is nearly 50 percent, and accordingly it has been mined in California, along with other borate minerals, as a commercial source of boron compounds. Probertite does not occur as the dominant mineral in any of the California deposits, however, and its production is considered incidental to large-scale mining of borax, kernite, or colemanite.

*X-ray diffractograms.\**— X-ray diffractograms of probertite from the three districts of western Oklahoma are illustrated in figure 10 and compared with diffractograms of probertite from California. The diffractograms shown in figures 10a and 10b are of samples that were chemically analyzed. The exceptionally sharp peak at

---

\* A Norelco X-ray source unit equipped with the Norelco (modified Brown) recorder was used. The minerals were ground in an agate mortar and powder-packed into a slotted aluminum holder, or into the depression of a standard petrographic glass slide, devised for holding small samples. X-ray diffractograms were obtained by using nickel-filtered copper radiation ( $K\alpha$ ) at a setting of 35 kilovolts and 18 milliamps. The recorder was operated at a constant multiplier value of one, at time constant of four seconds, and a scale factor that produced maximum chart resolution. The diffraction goniometer was operated from low to high angle at one degree  $2\theta$  per minute with a chart speed of two degrees per inch. Film camera patterns were not obtained because the diffraction traces were sufficiently accurate to allow positive mineral identification.

9.1 Å is especially noteworthy in the identification of probertite by X-ray diffraction methods, and the principal confirming peaks are at 6.55 Å and 2.90 Å. In the samples of figures 10a and 10c, the peak at 7.56 Å is caused by the presence of admixed gypsum.

About fifty diffractograms were made from selected nodules and from composite samples of nodules, taken from every locality where borate minerals were found. The close resemblance in habit between ulexite and probertite from Oklahoma makes identification in the field uncertain, and leads to inaccurate determinations. It was originally believed that all the nodules from the cores at Weatherford were probertite, but it is now known that nearly one-third of them are ulexite. In the course of examining the quarries it was at first believed that ulexite was probably of common occurrence, just as it is in the cores at Weatherford and in the California deposits. With progress of work in the quarries, however, it began to appear that probertite was overwhelmingly predominant and that ulexite was absent from most localities. Being contrary to the expected relations, the concept of probertite dominance was repeatedly checked and finally confirmed by numerous X-ray diffractograms. In this way we also were able to determine that other borate minerals, such as colemanite, kernite, or borax, are not present in the Oklahoma deposits.

---

#### EXPLANATION OF FIGURE 10

- a. From Cloud Chief gypsum, core hole WCG-9, depth 42.0 feet, SE $\frac{1}{4}$  SE $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 33, T. 12 N., R. 15 W., Custer County, Oklahoma.
- b. From Nescatunga gypsum member of Blaine formation, quarry of U. S. Gypsum Co., Southard. Locality 1, NW $\frac{1}{4}$  SE $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 11, T. 18 N., R. 12 W., Blaine County, Oklahoma.
- c. From Nescatunga gypsum member of Blaine formation, quarry of Universal Atlas Co., C W $\frac{1}{2}$  sec. 27, T. 17 N., R. 11 W., Blaine County, Oklahoma.
- d. Schaller Gulch, Monte Blanco, Furnace Creek Wash area, Death Valley region, California. Specimen given by W. T. Schaller.



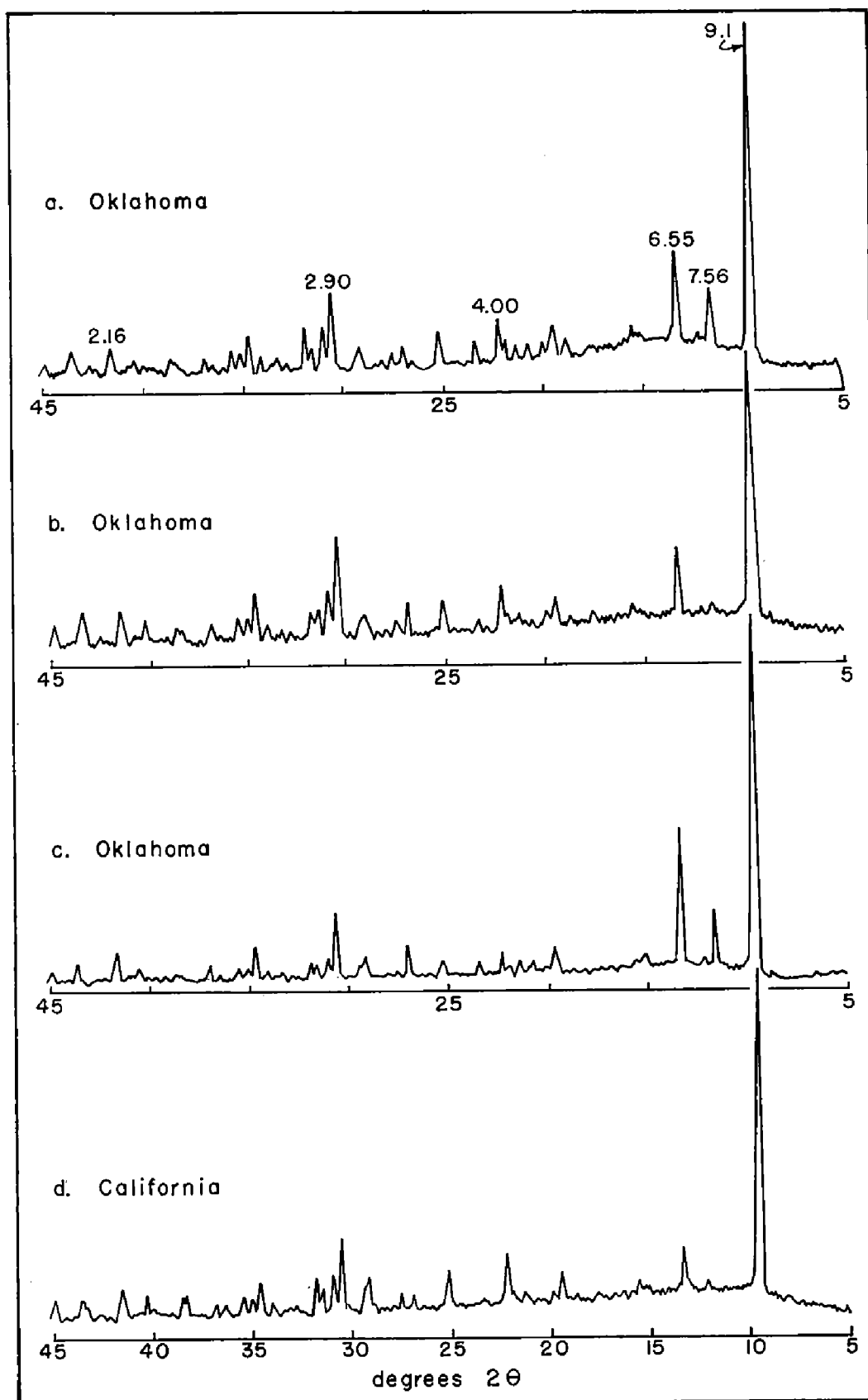


FIGURE 10. X-ray diffractograms of probernite from Oklahoma and California.  $\text{CuK}\alpha^1$ , Ni-filtered.

## ULEXITE

Ulexite is one of the common borate minerals in the world, occurring in recent playa deposits and in Tertiary bedded deposits of California, Nevada, Argentina, Chile, Peru, and Turkey (Smith, 1960, p. 107-114). It also occurs as nodules in gypsum of Mississippian age at Windsor and Dingwall, Nova Scotia (Goodman, 1952, p. 15, 43), and as a replacement of gypsum in the Inder borate district of Russia (Godlevsky, 1937). The Oklahoma occurrence of ulexite most closely resembles that of Nova Scotia, but is completely unlike that of the bedded deposits or playas.

Like probertite, ulexite is a hydrous sodium-calcium borate ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ). In containing eight molecules or 35.5 percent of water it is a mineral of high hydration and therefore is an expectable primary mineral in the borate playas (Muessig, 1958, p. 1619).

In bedded or older deposits, the chemically similar probertite and ulexite ordinarily do not occur together in the same specimen, and accordingly their time relations can not be directly inferred. Schaller (1929, p. 139) converted ulexite into probertite by heating powdered ulexite in a sealed tube with a saturated solution of sodium chloride in a steam bath for one week; and Foshag (1931, p. 341) suggested that at Ryan, California, the ". . . probertite is a recrystallization of ulexite, the formation of the lower hydrate being favored by the pressure of the superincumbent load of sediments and lavas or by the pressure induced by earth movements." On the other hand, ulexite pseudomorphs after probertite were found both at Lang and at Kramer by Murdoch (1945), who concluded that the ulexite in those localities had been formed by the hydration of probertite.

Ulexite does not occur directly with probertite at any of the Oklahoma localities. Some of the nodules are three to five inches in diameter, or occur as encrusting fibers, and neither of these is at all similar in habit to the typical occurrence of probertite. Three small nodules of ulexite in core holes WCG-10 and WCG-29, however, have the external form and size of probertite nodules and are suggestive of a pseudomorphic origin. From field relations in Oklahoma it is believed that probertite is the originally formed

mineral, remaining without change until it is dissolved by shallow ground waters. Locally probertite is pseudomorphically replaced by ulexite, but in general the solutions containing dissolved probertite are ponded or otherwise concentrated and the much rarer ulexite is deposited, mainly in the form of large nodules.

*Occurrence.*—Ulexite was first identified in Oklahoma from nodules collected at a quarry of the U. S. Gypsum Company near Southard, Blaine County. White cauliflower-like nodules, three to five inches in maximum diameter, were given to the writers by Mr. W. Dale Reynolds during a visit to the gypsum plant in 1959.

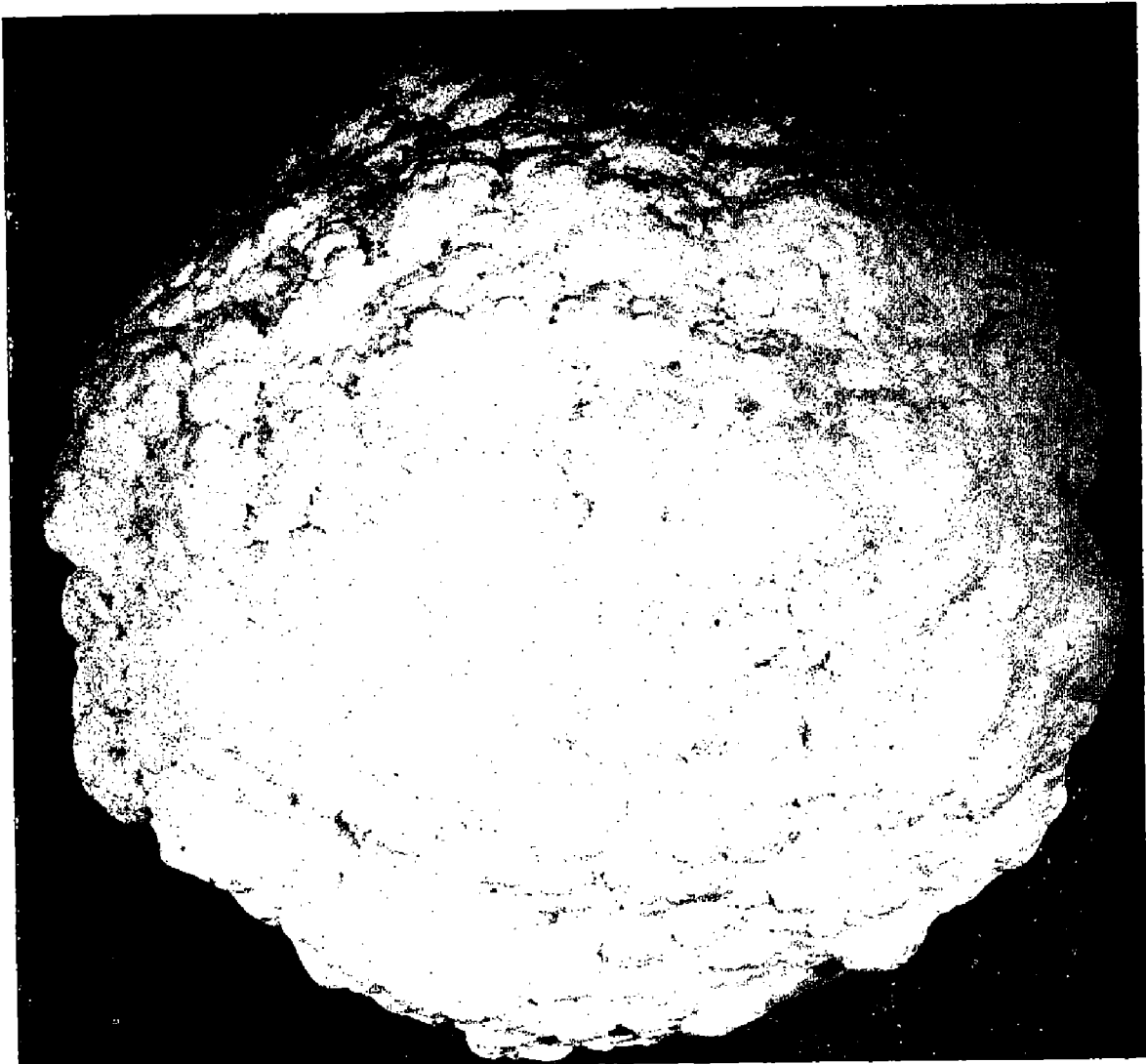


FIGURE 11. Ulexite from the Nescatunga gypsum, quarry of U. S. Gypsum Co., locality 3, S $\frac{1}{2}$  SW $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 3, T. 18 N., R. 12 W., Blaine County, Oklahoma. This cauliflower-shaped nodule is 4.75 inches (12 cm) in maximum diameter and is the largest specimen of borate mineral known in Oklahoma.

One of the nodules was almost entirely embedded in fine-grained gypsum, and all were stated to have been found in the quarrying of the Nescatunga gypsum during the period 1950-1953. Upon laboratory examination by X-ray, chemical, and immersion oil methods, the nodules were shown to be ulexite, and a search for borate minerals in the gypsum quarries of Blaine County was begun.

Carefully examined were 10 quarry openings in the Shimer and Nescatunga gypsum members of the Blaine formation, covering an area of three square miles in the Southard area on property of the U. S. Gypsum Company; four quarries in the Nescatunga and Medicine Lodge gypsum members of the Blaine formation at Gyp Siding, one mile north of Southard, covering approximately half a square mile on property worked by S. A. Walton and Son; and the large quarry in Nescatunga gypsum 10 miles southeast of Southard that is worked by Universal Atlas Cement Company. Probertite was discovered to be of common occurrence in the Nescatunga gypsum at many of these localities, but no additional ulexite was found.

A further examination was then made of the cores from the Cloud Chief gypsum near Weatherford, in which probertite had been previously reported (Ham, Curtis, and Schleicher, 1958). Ulexite was positively identified as the sole borate mineral in two of the core holes, and it was further identified along with probertite from a third core hole.

The certain knowledge that ulexite occurs in Permian gypsum of western Oklahoma has led us to accept without reservation the reported location of the ulexite nodules from the central part of the large quarry in the Nescatunga gypsum at Southard, and it is here designated as locality 3. As no ulexite could be found in the gypsum walls around the edges of the quarry, it is presumed that all the ulexite and all the gypsum containing it have been removed by quarrying. The following descriptions are based on the four specimens obtained from this locality, together with five specimens from the core holes at Weatherford (fig. 13).

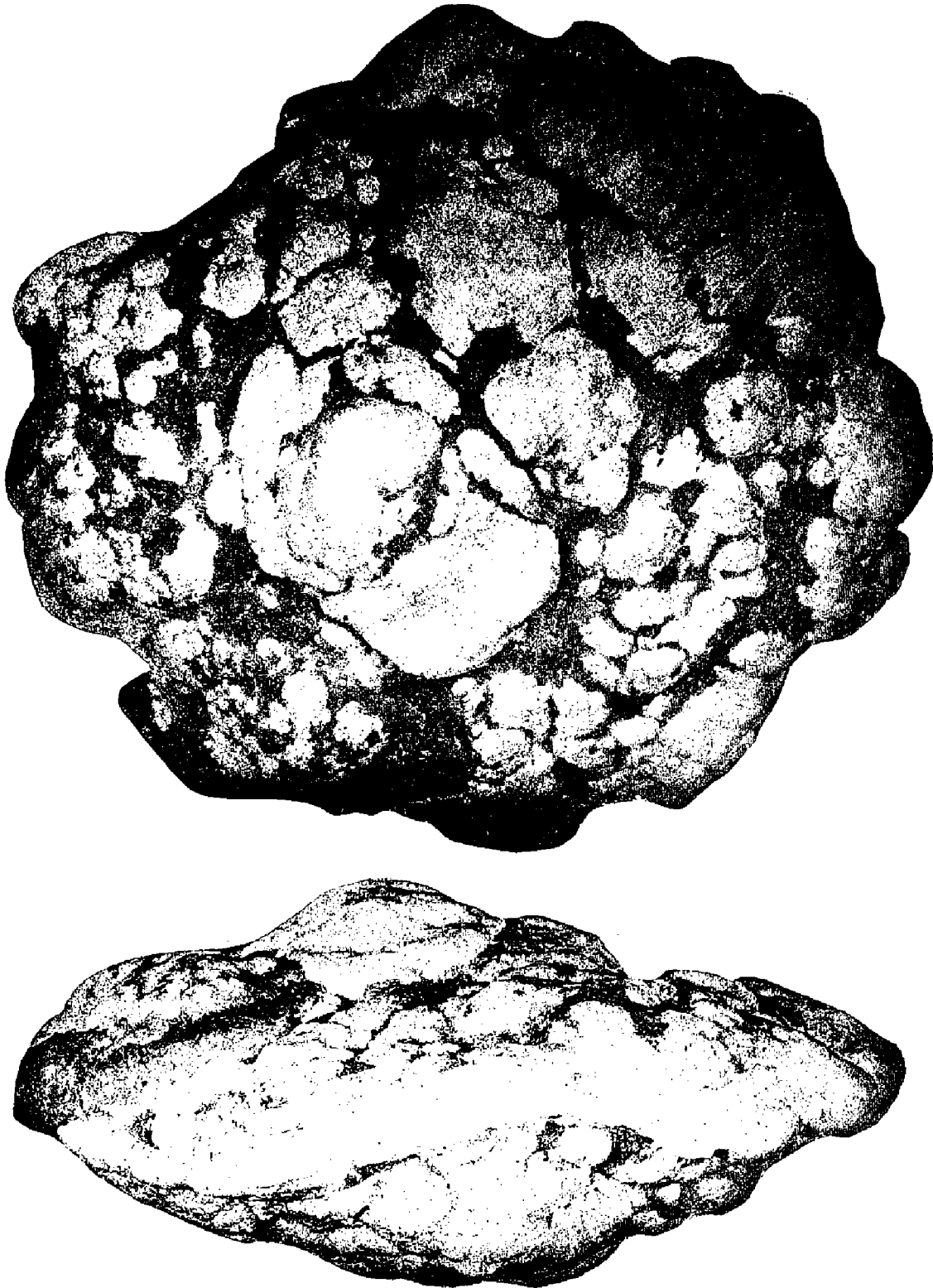


FIGURE 12. Ulexite from the Nescatunga gypsum, U. S. Gypsum Co., locality 3. Top view (above) and side view (below) showing irregular surface and discoidal form. Dark gray is matrix of fine-grained gypsum. Specimen is 3 inches (7.7 cm) long.

*Blaine gypsum*, Locality 3. S $\frac{1}{2}$  SW $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 3, T. 18 N., R. 12 W., quarry of U. S. Gypsum Company east edge of Southard, Blaine County. The quarried stone is high-purity Nescatunga gypsum, eight feet thick. Nodules of ulexite were reportedly found in the central part of the quarry near the base of the worked gypsum (fig. 4).

Specimen no. 1. This fine specimen of ulexite is an oblate spheroid measuring 4.75 by 3.25 inches (12 by 8 cm), broken free from the enclosing gypsum (fig. 11). It closely resembles in color, size, and shape a typically formed cauliflower, with an exterior surface of numerous warty bumps. The specimen is made up of silky curved fibers arranged in compact divergent bundles. A chemical analysis is given in table 12 and an X-ray diffractogram is illustrated in figure 14a.

Specimen no. 2. The nodule is 3 inches in diameter, 1.25 inches in thickness, and is characterized by a conspicuously bumpy surface (fig. 12). It is composed of divergent silky fibers as much as 0.5 inch in length. Fine-grained gypsum from the enclosing matrix adheres to the depressions of the irregular surface. Judging from the specimens examined, this is the typical form of ulexite from the Southard locality.

Specimen no. 3. The nodule is similar to specimen no. 2, measuring 3.25 by 1.5 inches and consisting of divergent and recurved bundles of silky fibers, mostly  $\frac{1}{8}$  to  $\frac{1}{4}$  inch in length. It is embedded in fine-grained compact gypsum and lies with its long dimension parallel to well-defined slightly wavy bedding surfaces. The nodule cuts across 1.5 inches of the compact gypsum without disturbing bedding, showing clearly that the ulexite is a replacement of rock gypsum.

Specimen no. 4. This specimen is an irregular nodule measuring 5 by 4 by 1.5 inches that has the typical warty exterior and composition of silky curved fibers. It is half enclosed by compact alabaster that occurs in alternating layers with coarser textured selenitic gypsum, and the nodule lies with its long dimensions in the bedding defined by these layers.

*Core holes in Cloud Chief gypsum.*—Seven of the 16 core holes drilled to evaluate gypsum resources of the Cloud Chief formation in southeastern Custer County near Weatherford (Ham and Curtis, 1958) contain probertite or ulexite. Although probertite is the dominant mineral, ulexite occurs in massive grayish-pink gypsum in core holes WCG-3, WCG-10, and WCG-29 (fig. 2; pls. I, II).

CORE HOLE WCG-3. SW $\frac{1}{4}$  SE $\frac{1}{4}$  SW $\frac{1}{4}$  sec. 31, T. 12 N., R. 15 W. The cores contain only ulexite.

Depth 47.9 feet. Ulexite occurs as a flattened compact nodule 1.25 inches in diameter and 0.25 inch thick lying on a bedding surface of gypsum and in part replacing it. The surface of the nodule is covered irregularly with small bumps, and the specimen is composed of divergent curved silky fibers. Under the petrographic microscope the fibers are seen to be polysynthetically twinned. The specimen was identified by means of an X-ray diffractogram.

Depth 50.0 feet. Ulexite, identified from an X-ray diffractogram, occurs as flattened bundles or tufts of divergent silky threads randomly disposed on a selenite-covered bedding surface of gypsum (fig. 13). The nodular form is lacking, and the occurrence suggests deposition of ulexite along an open bedding parting.

CORE HOLE WCG-10. NE $\frac{1}{4}$  NE $\frac{1}{4}$  NE $\frac{1}{4}$  sec. 21, T. 12 N., R. 15 W. The cores contain ulexite at 34.5 feet and probertite at 38.5 feet.

Depth 34.5 feet. A loosely coherent subspherical nodule of ulexite 0.25 inch in diameter replaces massive gypsum. The specimen is composed of short and slightly curved silky fibers, and does not resemble the ulexite of core hole WCG-3. It probably is a pseudomorph after probertite. No probertite remains, however, as an X-ray diffractogram of powder from the entire nodule showed only ulexite.

CORE HOLE WCG-29. SE $\frac{1}{4}$  SE $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 33, T. 13 N., R. 15 W. The cores contain only ulexite.

Depth 70.65 feet. A subspherical nodule of ulexite, 0.5 inch in diameter, is composed of loosely coherent straight short needles

in random orientation. The nodule lies directly in the plane of a steeply dipping and imperfectly formed joint surface, along which ground waters apparently have entered the gypsum rock and converted the nodule from probertite to ulexite. Identified by means of an X-ray diffractogram.

Depth 72.6 feet. A ulexite nodule, 0.25 inch in diameter, is embedded in massive pink gypsum. It consists of short straight needles arranged in subparallel bundles. The specimen was identified in immersion oils.

Both nodules are probably pseudomorphs after probertite. They have the external form and size of typical probertite nodules from the Cloud Chief gypsum, and the ulexite itself occurs in the form of short straight needles like those of probertite.

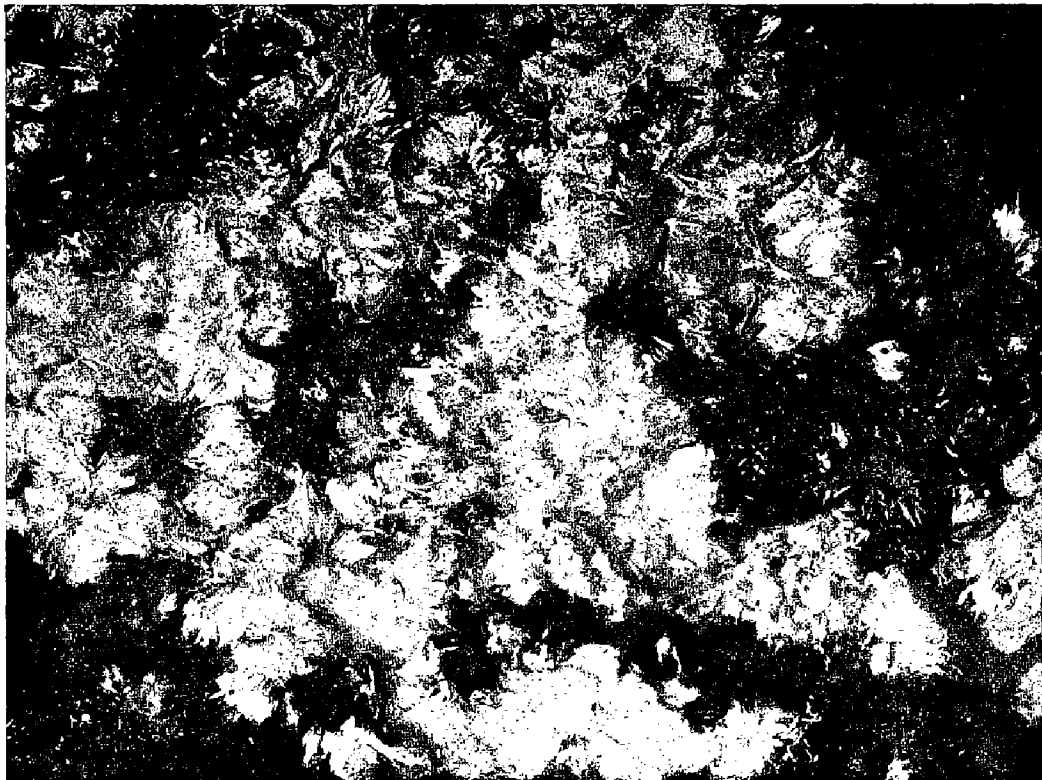


FIGURE 13. Fibrous tufts of ulexite along bedding plane in Cloud Chief gypsum, x5.5, core hole WCG-3, depth 50.0 feet, SW $\frac{1}{4}$  SE $\frac{1}{4}$  SW $\frac{1}{4}$  sec. 31, T. 12 N., R. 15 W., Custer County, Oklahoma.



*Chemical composition.*—A part of the large cauliflower-shaped ulexite nodule from Southard (locality 3, specimen no. 1, fig. 11) was analyzed chemically as shown in table 2. The small amount of admixed gypsum is reflected in the  $\text{SO}_3$  content of 2.06 percent, equivalent to a gypsum content of 4.43 percent. The specimen also contains 0.75 percent chlorine, which is equivalent to 1.24 percent NaCl. By deducting these impurities and the insoluble residue, and reducing the analysis to 100 percent, it is shown that the sample is normal ulexite corresponding closely to the theoretical formula,  $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ , and to an analyzed specimen from Kramer, California.

TABLE 2.—CHEMICAL ANALYSES OF ULEXITE FROM OKLAHOMA AND CALIFORNIA  
*Southard, Oklahoma*<sup>1</sup>

	<i>Original analysis</i>	<i>Recalculated, deleting gypsum and halite</i>	<i>Recalculated to 100%</i>	<i>Kramer California</i> <sup>2</sup>	<i>Theoretical ulexite NaCaB<sub>5</sub>O<sub>9</sub>·8H<sub>2</sub>O</i>
Na <sub>2</sub> O	7.95	7.29	7.74	7.09	7.65
CaO	13.84	12.40	13.16	14.06	13.85
B <sub>2</sub> O <sub>3</sub>	40.83	40.83	43.33	42.94	42.95
H <sub>2</sub> O	34.63	33.70	35.77	35.54	35.55
Insol.	0.07	----	----	0.10	----
MgO	nil	----	----	----	----
CO <sub>2</sub>	trc	----	----	----	----
SO <sub>3</sub>	2.06	----	----	----	----
Cl	0.75	----	----	----	----
Total	100.13	94.22	100.00	99.73	100.00

<sup>1</sup>J. A. Schleicher, analyst. Ulexite nodule 4.75 inches in diameter from Nescatunga gypsum, U. S. Gypsum Co., locality 3, S $\frac{1}{2}$  SW $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 3, T. 18 N., R. 12 W., Southard, Blaine Co., Okla. Specimen illustrated in figure 11.

<sup>2</sup>W. T. Schaller, analyst. Satin spar variety of compact ulexite (Schaller, 1929, p. 139).

The B<sub>2</sub>O<sub>3</sub> content of ulexite is approximately 43 percent and is seven percent lower than that of probertite, owing to its higher content of chemically combined water. Ulexite was an important ore in the early mining of borate minerals from California, but it has now been largely displaced by the mining of the sodium borates, kernite and borax.

*X-ray diffractograms.*—Two X-ray diffractograms of ulexite from Oklahoma are reproduced in figure 14. One, representing the typical occurrence, is made from the large nodule of silky curved fibers taken from the quarry in Nescatunga gypsum at Southard (fig. 14a), and the other is made from a nodule of short straight fibers in the Cloud Chief gypsum at Weatherford (fig. 14b).

Seven diagnostic peaks, including those at 4.15 Å, 6.06 Å, 12.3 Å, and the pair at 7.8 Å and 8.0 Å, allow positive mineralogical identification. Diffractograms of reference specimens from Nova Scotia and California are given for comparison.

---

#### EXPLANATION OF FIGURE 14

- a. From Nescatunga gypsum member of Blaine formation, quarry of U. S. Gypsum Co., Southard, Blaine County, Oklahoma, locality 3. Specimen no. 1, illustrated in figure 11.
- b. From Cloud Chief gypsum, core hole WCG-29, depth 70.65 feet, SE $\frac{1}{4}$  SE $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 33, T. 13 N., R. 15 W., Custer County, Oklahoma.
- c. Ulexite from gypsum in Windsor series, White Rock quarry, Wentworth, Hants County, Nova Scotia. Specimen given by W. T. Schaller.
- d. Pacific Coast Borax mine, Boron, Kern County, California.

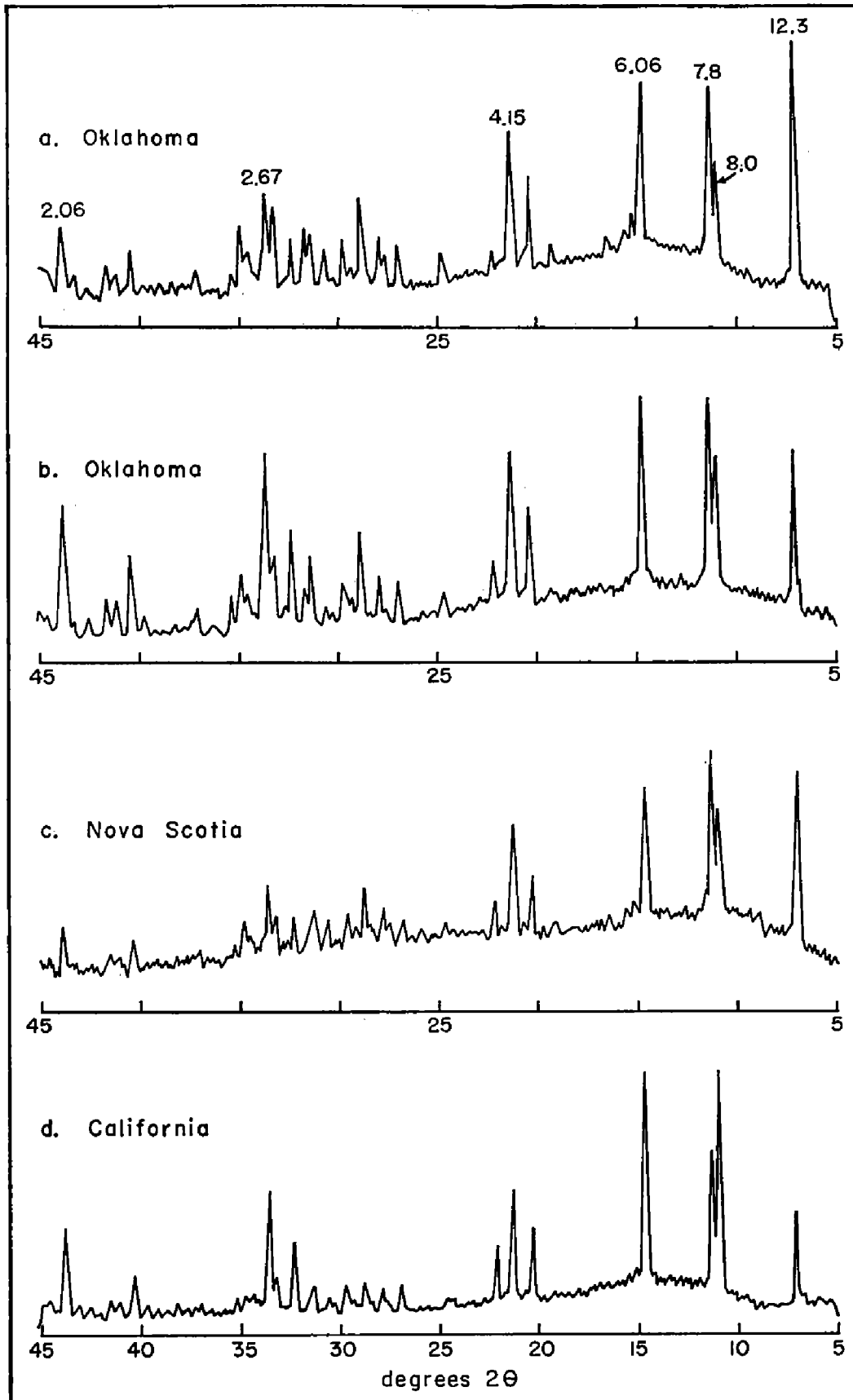


FIGURE 14. X-ray diffractograms of ulexite from Oklahoma Nova Scotia, and California.  $\text{CuK}\alpha_1$ , Ni-filtered.

## PRICEITE

Priceite is a hydrous calcium borate mineral corresponding approximately to the formula  $\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$ . The largest known deposits are in western Turkey, where they occur in gypsum of Tertiary age as fine-grained nodules and irregular masses weighing as much as one ton. Priceite also has been mined from serpentine in Curry County, Oregon, where its origin is attributed to the intrusion of a rhyolite dike (Staples, 1948); and the mineral has been described as occurring with colemanite in green shale at Furnace Creek Wash, Inyo County, California (Foshag, 1924).

TABLE 3.—CHEMICAL ANALYSES OF PRICEITE FROM OKLAHOMA AND CALIFORNIA

	<i>Southard, Oklahoma</i> <sup>1</sup>	<i>Furnace Creek Inyo Co., Calif.</i> <sup>2</sup>	<i>Theoretical priceite Ca<sub>4</sub>B<sub>10</sub>O<sub>19</sub>·7H<sub>2</sub>O</i>
CaO	32.18	32.20	32.11
B <sub>2</sub> O <sub>3</sub>	49.92	49.03	49.84
H <sub>2</sub> O	18.20	17.86	18.05
Cl	v.f.tre.	---	---
Rem	---	1.16	---
Total	100.30	100.25	100.00

<sup>1</sup> J. A. Schleicher, analyst. Chalk-like nodule 1.5 inches in diameter from Nescatunga gypsum, quarry of U. S. Gypsum Co., S $\frac{1}{2}$  SW $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 3, T. 18 N., R. 12 W., Southard, Blaine County, Oklahoma

<sup>2</sup> W. F. Foshag, analyst (Foshag, 1924, p. 11).

From the results of this investigation priceite is now known to occur as small nodules in Permian gypsum of western Oklahoma. It is the rarest of the three borate minerals of that area, occurring only at two quarries in the Nescatunga gypsum near Southard. Fine-grained chalk-like nodules from other quarries suspected in the field of being priceite were shown by X-ray examination to be thenardite, and it is concluded that priceite is of extremely uncommon occurrence.

At locality 1, NW $\frac{1}{4}$  SE $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 11, T. 18 N., R. 12 W., where probertite is abundant in the lower four or five feet of the quarried gypsum, priceite was found one foot above the probertite zone as compact chalky nodules 0.25 inch in diameter, distributed along a bedding surface of medium-crystalline selenitic gypsum (fig. 3B). They are concentrated to the extent of one nodule per

square inch of surface, and they evidently have originated by replacement of the gypsum. The mineral was identified as priceite by means of an X-ray diffractogram.

A second specimen was obtained from locality 3, S $\frac{1}{2}$  SW $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 3, T. 18 N., R. 12 W. It is a nodule of irregular shape and 1.5 inches in diameter, resembling in every superficial respect a mass of chalk, except that, when rubbed on a freshly broken surface, it has a distinct unctuous or talc-like feel. A chemical analysis of this specimen (table 3) shows that it is virtually pure priceite containing 49.92 percent B<sub>2</sub>O<sub>3</sub>, and an X-ray diffractogram reproduced in figure 15 confirms the identification. Of the seven strongest peaks, those at 3.49 Å, 3.63 Å, and 10.9 Å are the most pronounced.

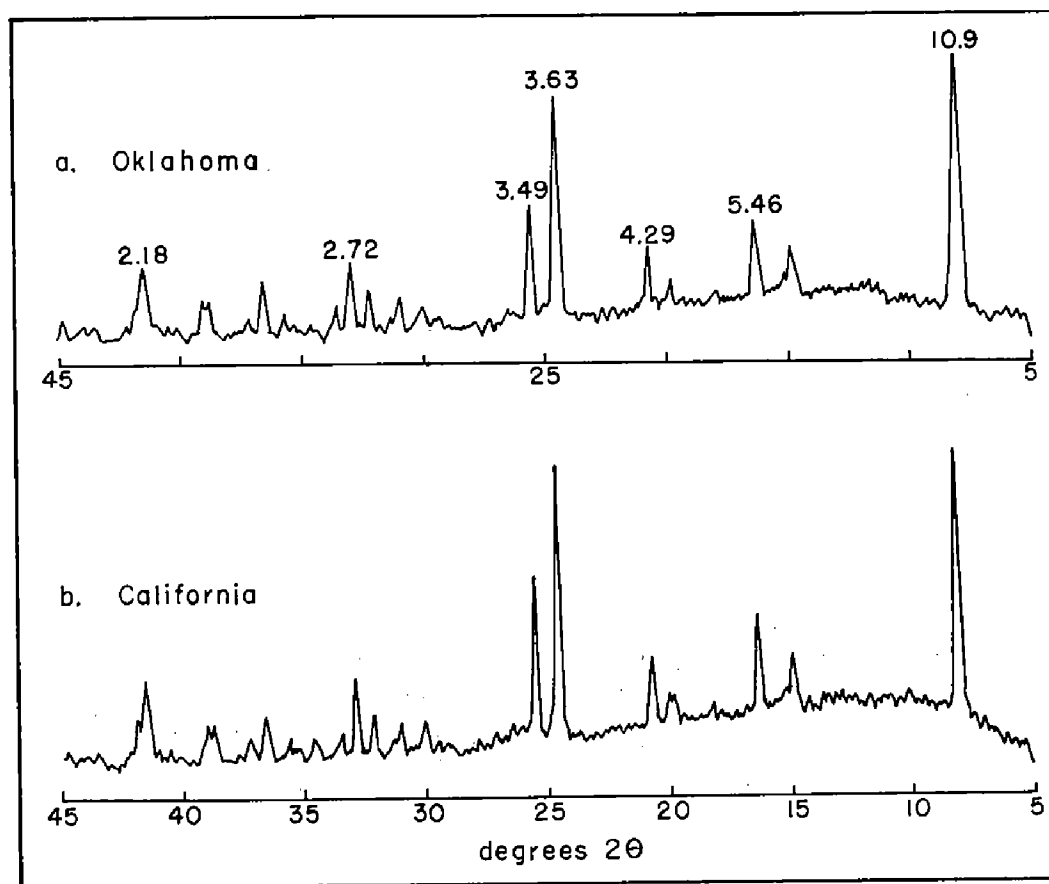


FIGURE 15. X-ray diffractograms of priceite from Oklahoma and California. CuK $\alpha_1$ , Ni-filtered.

a. From Nescatunga gypsum, U. S. Gypsum Co., locality 1, Southard, Blaine County, Oklahoma.

b. From Twenty Mule Team Canyon, Furnace Creek Wash, Death Valley region, California. Specimen from W. T. Schaller.

## OTHER MINERALS

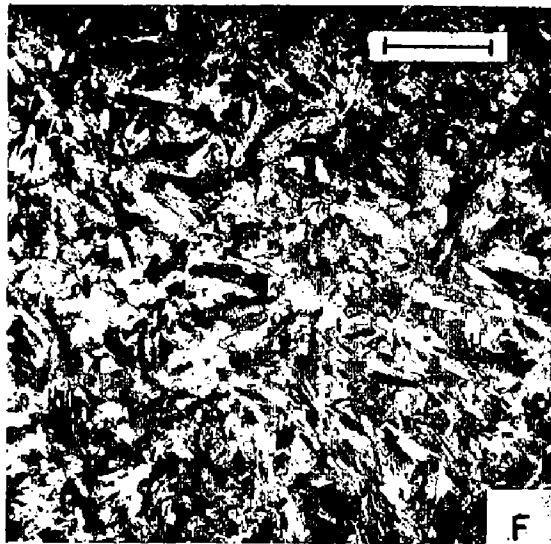
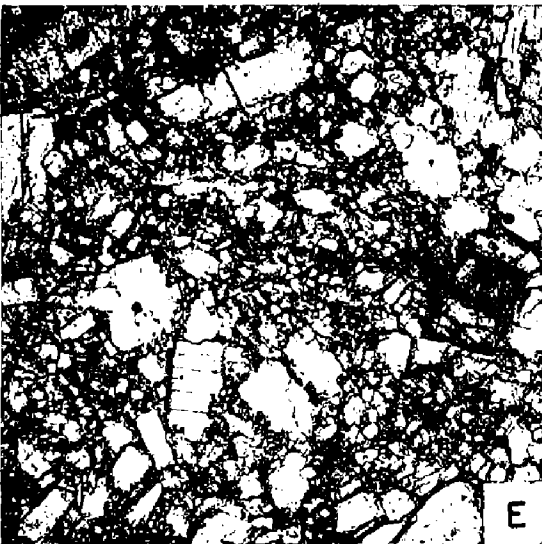
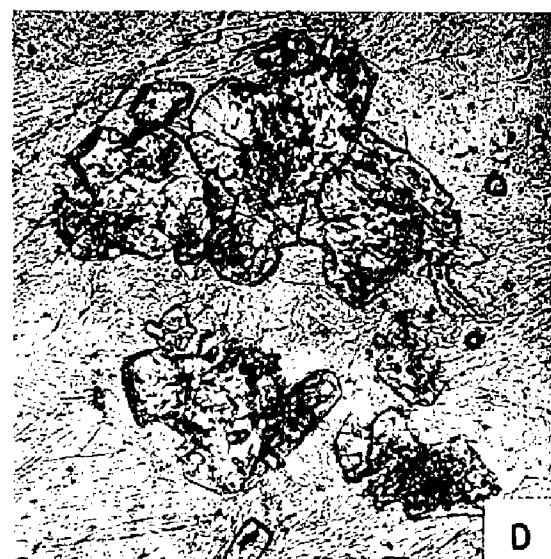
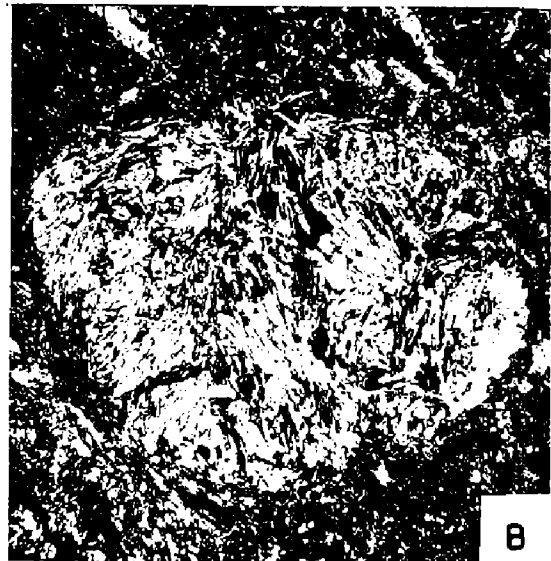
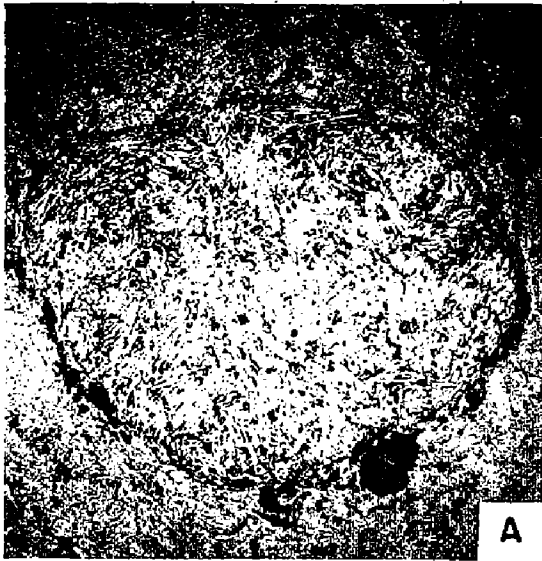
Gypsum of the Blaine formation in Blaine County is worked because of its high chemical purity, and, as shown by chemical analyses, the quarried rock ordinarily contains 96 to 98 percent theoretical gypsum. One to two percent calcium and magnesium carbonates, in the form of dolomite and/or calcite which are distributed as small grains throughout the gypsum, make up the principal impurities. A study of 16 thin sections shows that anhydrite is locally present as residual grains, this observation confirming the conclusion from the study of field relationships that the gypsum originated through hydration of anhydrite.

Thenardite,  $\text{NaSO}_4$ , occurs in small amounts with the borate minerals in quarries of the Nescatunga gypsum and is also found without borates in the Shimer gypsum. It was identified by means of X-ray diffractograms at numerous localities in the Southard area. The nodules are fine grained and superficially resemble priceite. The typical occurrence is as discoidal white nodules half an inch in diameter lying randomly in the plane of bedding, the nodules replacing gypsum on either side of the bedding surface along which ground waters have percolated. In a few places thenardite occurs in the form of bedding encrustation, as much as

## EXPLANATION OF PLATE III

Photomicrographs of probertite, celestite, and anhydrite from Nescatunga member of Blaine formation.

- A. Nodule of probertite that has replaced fine-grained gypsum. The nodule is 2.6 mm in long dimension. Universal Atlas quarry. Plain light, thin section 974.
- B. Same as A, crossed nicols. Probertite occurs as bundles of straight fibers.
- C. Celestite rosette of clustered blades, some of which are euhedral, in fine-grained gypsum. Maximum dimension of rosette is 0.12 mm. Dark areas are reorganized aggregates of clay. The rosette is shown as a dark grain just below bottom of probertite nodule in the lower part of figure A. Plain light.
- D. Celestite grains in recrystallized gypsum, upper part of Nescatunga member, quarry of U. S. Gypsum Co. The cluster in upper part of photograph is 0.4 mm long. Plain light, thin section 964.
- E. Anhydrite rock at base of Nescatunga gypsum, quarry of U. S. Gypsum Co. Fine-grained early anhydrite occurs with later blocky crystals of anhydrite. Dolomite rhombohedron of high relief at right is 0.45 mm long. Plain light, thin section 966.
- F. Recrystallized coarse-textured anhydrite from abandoned quarry, SW $\frac{1}{4}$  NE $\frac{1}{4}$  sec. 26, T. 19 N., R. 12 W. The bar scale is 1.0 mm. Crossed nicols, thin section 831.



0.2 inch (5 mm) thick, that covers the gypsum completely over an area 10 inches square. It also occurs as nodular encrustations on the walls of vertical joints in the gypsum. In the Oklahoma quarries thenardite does not occur in anhydrite, its greatest concentration being in gypsum near a contact with an anhydrite lens or bed. It is an epigenetic mineral derived by weathering of salt-bearing anhydrite.

Celestite,  $\text{SrSO}_4$ , is a common accessory mineral in rock gypsum of the Blaine formation, occurring mostly as microscopic crystals, grains, blades, and rosettes (pl. III C, D). Like the borate minerals, celestite is a replacement of gypsum and has been derived through the reorganization of anhydrite parent rock. It is randomly distributed through the gypsum as bladed crystals 20 to 50 microns long, as rosettes with a maximum dimension of 0.3 mm, or as grains 0.05 to 1.0 mm in diameter. Some of the blades have well-formed crystal faces, and locally they occur in association with thin irregular seams of clay. The maximum concentration of celestite observed in this section of gypsum is about 0.5 percent, and the common range is 0.1 to 0.2 percent.

Measurable amounts of NaCl, generally about 0.01 to 0.02 percent, are present in outcropping gypsum and anhydrite of the Blaine formation. Higher concentrations of this water-soluble salt are found in subsurface beds nearby, particularly as shown in cores of a well drilled near the southwestern corner of Blaine County, NW $\frac{1}{4}$  SE $\frac{1}{4}$  SW $\frac{1}{4}$  sec. 36, T. 14 N., R. 13 W. In this well the Nescatunga member of the Blaine formation is 9 feet thick, it was encountered at a depth of 462-471 feet, and it consists of anhydrite of which the middle four feet contain coarsely crystallized clear halite. At shallower depths and on the outcrop most of the salt is leached away by ground waters.

The presence of NaCl as an original constituent of the Blaine evaporites is believed to have an important bearing on the origin of the associated epigenetic minerals, because the sodium ion for the building of probertite, ulexite, and thenardite probably was derived from this source.

The Cloud Chief gypsum at Weatherford is a geographically and stratigraphically different evaporite deposit, but mineralogic-



ally it is quite similar to the Blaine. In the Cloud Chief the rock-forming minerals are gypsum, residual anhydrite, dolomite, calcite, and magnesite; and the average chemical composition, as determined from 48 analyses, is 91.28 percent gypsum, 1.38 percent anhydrite, 5.34 percent calcium and magnesium carbonates, and 1.55 percent silica (Ham and Curtis, 1958, p. 14). Priceite and thenardite have not been found in the Cloud Chief gypsum and, aside from locally deposited small crystals of selenite, probertite and ulexite are the principal epigenetic minerals in it.

#### ECONOMIC POSSIBILITIES OF THE BORATE MINERALS

Boron compounds have been in commercial use since the 16th century, and world production for the years 1957-1958 was 615,000 short tons of crude borates containing approximately 50 percent  $B_2O_3$ . The United States supplies 85 percent of the world production, all from bedded deposits and brines in the desert region of southern California. Turkey, Argentina, Chile, and Italy are the other important producing countries, following the United States in the order named. Russia probably also is a producer of borates but its production data are not revealed (Smith, 1960).

Approximately half the production is used in the manufacture of heat-resistant glass, insulating glass fibers, ceramic glazes, and porcelain enamels. Borax and boric acid have detergent and mild disinfectant qualities that are utilized in making soaps, detergents, and pharmaceuticals. Some of the newer applications of boron compounds are as a neutron absorber in radioactive shields; as a component of metallic alloys; as an additive in gasoline and insecticides; as a boron-hydrogen fuel, which yields nearly 50 percent more energy per pound than conventional petroleum fuels; and as a boron nitride abrasive, which has essentially the same hardness as diamond yet can withstand temperatures in excess of 3,500° F, whereas diamond burns in air at about 1,600° F (Smith, 1960, p. 116-117).

Borax is used in small amounts in the manufacture of certain gypsum products, particularly to give added strength in wallboard constructions. The Nescatunga gypsum at Southard is extensively used by the U. S. Gypsum Company in making calcined products, and the borate minerals contained in the quarried gypsum are thus

consumed to good advantage. No borax is added at this plant, as the boron is supplied by probertite that occurs naturally in the gypsum.

None of the known borate occurrences in Oklahoma, however, can be considered commercial deposits of boron compounds. Probertite is the most abundant borate, and its maximum observed concentration is 10 percent by area along selected bedding surfaces. Most of the bedding planes of the gypsum are barren, even at localities where the borate minerals are most concentrated. Two composite samples, representing four feet of probertite-containing gypsum at locality 1, near Southard, were analyzed and found to contain an average of 0.10 percent  $B_2O_3$ , or 0.20 percent probertite (lab. no. 10385). A similar sample, representing one foot of probertite-containing gypsum at the quarry of the Universal Atlas Company, was shown by analysis to contain 0.16 percent  $B_2O_3$ , or 0.32 percent probertite (lab. no. 10386).

As no richer concentrations of borate minerals were observed, it is assumed that the maximum expectable range in boron content is approximately 0.10 to 0.16 percent  $B_2O_3$ , which is much too low for an ore deposit. Moreover, there seems to be little probability that workable deposits of borate minerals in the Blaine and Cloud Chief formations of western Oklahoma will be discovered. Enough is known of the origin of the probertite to show that it is derived by slow hydration of low-boron anhydrite, and that after their formation the probertite nodules are likely to be dissolved and removed by ground waters. Under an arid climate it might be possible to build and preserve more concentrated deposits than now known, but under the rainfall of 20 inches or more per year at the present time, and probably much more during Pleistocene time, such deposits are not likely to have been formed.

## ORIGIN AND SOURCE OF THE BORATE MINERALS

When the Oklahoma occurrences of borate minerals are compared with the bedded or playa deposits, which furnish nearly all the world's supply of boron compounds, it is readily apparent that the deposits in Oklahoma are of exceptional character and require special consideration regarding their origin. The major deposits occur with nonmarine sediments of Tertiary age, generally in those desert areas of the world near continental margins where there are geologically young volcanic activity and folding accompanying mountain building. In contrast, the Oklahoma borates occur in marine evaporites of Late Paleozoic age, located on the stable craton of the continental interior where the strata are flat-lying and are unaffected by igneous activity or hydrothermal solutions. The two regional environments are so sharply different that the borate minerals in them cannot be expected to have the same genetic history.

According to Schaller (1937, p. 151), the major deposits, chiefly in California, South America, and Turkey, ". . . began to accumulate in Tertiary time and the mineral matter in them has been augmented in places by the boron-containing products from solfataras and hot springs, which represent the last stages of Tertiary and Quaternary volcanic activity." In Oklahoma and in other areas where borates are in bedded marine evaporites, the obvious source of the boron is the sea water from which the evaporites were precipitated.

### BORATES IN BEDDED MARINE EVAPORITES

Borate minerals in bedded marine evaporite series are comparatively rare, for, until the discoveries were made in Oklahoma, they were known chiefly from only three areas of the world. The principal occurrences are in the Zechstein (Upper Permian) of Germany; in the Lower Permian of the Inder district in Russia; and in the Upper Mississippian Windsor series of Nova Scotia and New Brunswick. In addition, the Permian of England contains small amounts of boracite and veatchite, and the Permian of the New Mexico-Texas area contains small white aggregates of luene-

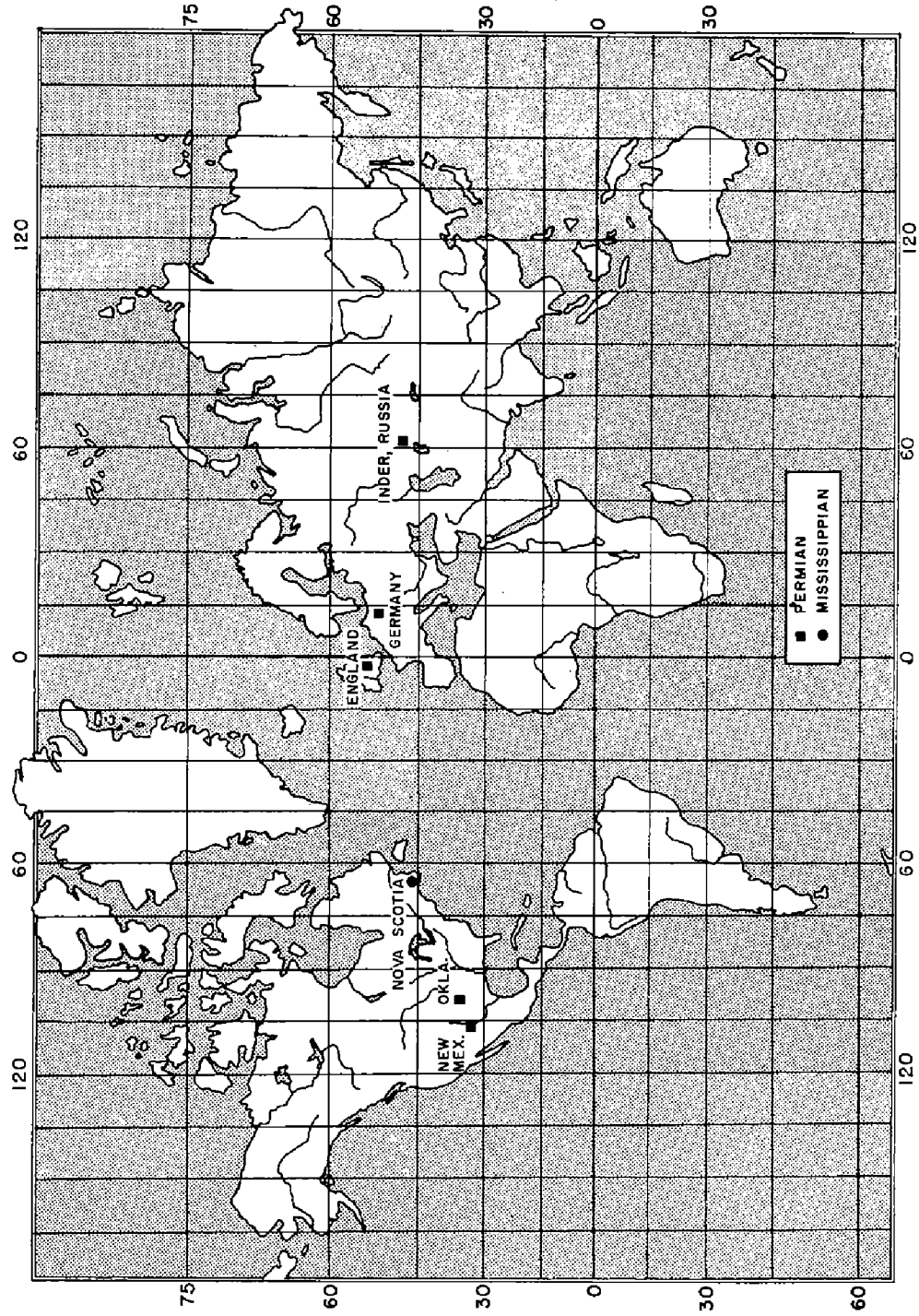


FIGURE 16. Distribution of borate minerals in bedded marine evaporites of the world.

burgite. These occurrences are summarized in table 4 and their locations are shown in figure 16.

Thick and extensively distributed marine evaporite series are known from the Precambrian, Paleozoic, Mesozoic, and Cenozoic.\* Their composite thickness is measurable in thousands of feet, and the range in age certainly exceeds 500 million years; yet, on the basis of present knowledge, borate minerals in these evaporites are believed to be almost wholly restricted to Mississippian and Permian deposits.

Even more remarkable is the abnormal concentration and vast extent of boron-rich evaporites of Permian age. One region alone extends approximately 2,500 miles from Yorkshire, England, through Germany to the Inder district in Russia; and a smaller area in the United States extends 400 miles, from west-central Oklahoma to Carlsbad, New Mexico. When compared with other periods of geologic time, it appears that the desiccating Permian seas were conspicuously rich in boron.

*Inder district, Russia.*—The greatest concentration of borates in an evaporite series is in the Inder district of southwestern Russia, about 100 miles north of the Caspian Sea. According to Godlevsky (1937), a domal uplift, covering 250 square kilometers, contains a central core of halite, sylvite, and anhydrite at least 3,000 feet thick, covered by an outcropping cap of gypsum about 150 feet thick. The evaporites are stated to be of Early Permian age. In the gypsum a karst topography has been extensively developed, and the gypsum series is of great importance because it contains large and commercially workable deposits of borate minerals. Fifty-six deposits and a reserve of 400,000 metric tons of ore containing 20 percent or more  $B_2O_3$  were known prior to 1937, at which time the Inder district was presumably the major source of boron compounds in Russia.

---

\*Precambrian of Arctic Canada; Cambrian of India; Silurian of the Great Lakes region; Devonian of the Williston basin; Mississippian of Nova Scotia, Michigan, Indiana, and Nevada; Pennsylvanian of the Paradox basin in Utah; Permian of many areas; Triassic and Jurassic of many western American states; Triassic (Keuper) of Germany; Jurassic of England and Manitoba; Cretaceous of the American Gulf Coast; Eocene of the Paris basin; Oligocene of Alsace, France.

TABLE 4.—PRINCIPAL OCCURRENCES OF BORATE MINERALS IN BEDDED  
MARINE EVAPORITES

<i>Permian (Zechstein) of Germany</i>	
Boracite <sup>1, 2</sup>	$Mg_3B_7O_{13}Cl$
Szaibelyite (ascharite) <sup>1, 2</sup>	$Mg(BO_2)(OH)$
Pinnoite <sup>1</sup>	$Mg(BO_2)_2 \cdot 3H_2O$
Hydroboracite <sup>1</sup>	$CaMgB_6O_{11} \cdot 6H_2O$
Kaliborite <sup>1</sup>	$KMg_2B_{11}O_{19} \cdot 9H_2O$
Lueneburgite <sup>1, 2</sup>	$Mg_3B_2(OH)_6(PO_4)_2 \cdot 6H_2O$
Sulfoborite <sup>1</sup>	$Mg_6H_4(BO_3)_4(SO_2)_2 \cdot 7H_2O$
Strontiohilgardite <sup>2</sup>	$(Ca, Sr)_2B_5O_8(OH)_2Cl$
Strontioginorite <sup>2</sup>	$(Ca, Sr)_2B_{14}O_{23} \cdot 8H_2O$
p-Veachite <sup>2</sup>	$SrB_6O_{10} \cdot 2H_2O$
<i>Permian of Inder district, Russia</i>	
Hydroboracite <sup>3</sup>	$CaMgB_6O_{11} \cdot 6H_2O$
Beta ascharite <sup>3</sup> (szaibelyite <sup>1</sup> )	$MgHBO_3$
Pandermite (priceite) <sup>3</sup>	$Ca_6B_{12}O_{23} \cdot 8\frac{1}{2}H_2O$
Inyoite <sup>3</sup>	$Ca_2B_6O_{11} \cdot 13H_2O$
Colemanite <sup>3</sup>	$Ca_2B_6O_{11} \cdot 5H_2O$
Ulexite <sup>3</sup>	$NaCaB_5O_9 \cdot 8H_2O$
Inderite <sup>3</sup>	$Mg_2B_6O_{11} \cdot 15H_2O$
Inderborite <sup>1</sup>	$CaMgB_6O_{11} \cdot 11H_2O$
Kurnakovite <sup>1</sup>	$Mg_2B_6O_{11} \cdot 13H_2O$
Kaliborite <sup>1</sup>	$KMg_2B_{11}O_{19} \cdot 9H_2O$
<i>Permian of England</i>	
Boracite <sup>4</sup>	$Mg_3B_7O_{13}Cl$
Veatchite <sup>5</sup>	$SrB_6O_{10} \cdot 2H_2O$
<i>Permian of New Mexico and Texas</i>	
Lueneburgite <sup>6</sup>	$Mg_3B_2(OH)_6(PO_4)_2 \cdot 6H_2O$
<i>Permian of Oklahoma (this report)</i>	
Probertite	$NaCaB_5O_9 \cdot 5H_2O$
Ulexite	$NaCaB_5O_9 \cdot 8H_2O$
Priceite	$Ca_4B_{10}O_{19} \cdot 7H_2O$
<i>Mississippian of Nova Scotia and New Brunswick</i>	
Ulexite <sup>7</sup>	$NaCaB_5O_9 \cdot 8H_2O$
Howlite <sup>7</sup>	$Ca_2SiB_5O_9(OH)_5$
Ginorite <sup>7</sup>	$Ca_2B_{14}O_{23} \cdot 8H_2O$
Danburite <sup>7</sup>	$CaB_2(SiO_4)_2$
Inyoite <sup>8</sup>	$Ca_2B_6O_{11} \cdot 13H_2O$

<sup>1</sup> Palache, Berman, and Frondel, 1951.

<sup>2</sup> Braitsch, 1960.

<sup>3</sup> Godlevsky, 1937.

<sup>4</sup> Guppy, 1944.

<sup>5</sup> Stewart, Chalmers, and Phillips, 1954.

<sup>6</sup> Schaller and Henderson, 1932.

<sup>7</sup> Schaller, 1959.

<sup>8</sup> Poitevin and Ellsworth, 1921.

The ores consist mainly of the magnesium borate beta-ascharite or szaibelyite, which is the most abundant mineral; the calcium-magnesium borate, hydroboracite; and the calcium borates, pandermite (priceite), inyoite, and colemanite. They occur as beds, lenses, or nodules within the gypsum series and are confined principally to a particular sequence of gray argillaceous gypsum rocks with interbeds of gray clay. Most of the ore deposits lie within beds of clay and have replaced the clay, but some of the borates occur also as replacement lenses in rock gypsum. Hydroboracite is the earliest-formed borate mineral, replacing gypsum and clay, but it is rarely an ore mineral as it has been replaced in turn by beta-ascharite, colemanite, inyoite, and ulexite.

Godlevsky's genetic interpretation is that primary borates of unknown composition were present with the Permian potash salts, the potassium and boron having been derived from sea water. Through leaching during formation of karst topography the boron has been transported from the potash salts into the overlying gypsum series and deposited there in the form of hydroboracite. The argillaceous sediments are regarded as boron collectors and have aided in localizing the borate deposits. No igneous rocks are known in the Inder district.

*Zechstein of northern Germany.*—The Zechstein (Upper Permian) evaporites of northern Germany contain borate minerals at many localities, chiefly in sodium and potassium salts but to some extent also in gypsum and anhydrite. Bedded or lenslike deposits are unknown, and the principal occurrence of borates is as discrete grains. Boracite in particular is widely distributed and has been recovered as a source of boron compounds. According to Braitsch (1960b) the concentration of boracite in the southern Hannover region is related to the abundance of anhydrite, ranging from 0.1 to 0.01 percent in the evaporites containing 75 percent NaCl and 24 percent anhydrite, but ranging from 0.01 to 0.001 percent in evaporites that contain carnallite, sylvite, halite, and 5 to 20 percent anhydrite.

A suite of seven magnesium borates characterizes the German Zechstein deposits, although recent discoveries show also the occurrence of three strontium or calcium-strontium borates. The boron is clearly stated by Braitsch (1960a, p. 13) to have been derived from sea water.

*England and New Mexico.*—Borate minerals in lesser abundance and variety have been found with halite and potash salts of Permian age in England and New Mexico. In Yorkshire, England, boracite and veatchite occur in the form of small crystals and grains, probably contained within rock salt (Guppy, 1944; Stewart et al., 1954). Veatchite is associated also with polyhalite and occurs in one well through a vertical interval of 190 feet. In the extensively worked potash field near Carlsbad, New Mexico, lueneburgite has been identified at many localities. It occurs as small white blebs in halite and in clay, associated with sylvite (Schaller and Henderson, 1932, p. 47).

*Nova Scotia.*—The oldest bedded marine evaporites known to contain borate minerals belong to the Windsor series of Late Mississippian age in Nova Scotia and New Brunswick, in the Maritime Provinces of Canada. In this district five borate minerals occur as replacement nodules or cavity encrustations in massive gypsum and anhydrite. Three of the minerals are calcium borates (inyoite, ginorite, and howlite), one is Na-Ca borate (ulexite), and one is calcium boro-silicate (danburite). All the minerals contain calcium and boron, but magnesium borates are absent. According to Bell (1929, p. 45-56) the gypsum and anhydrite strata are interbedded with fossiliferous limestone and brick-red argillaceous shale of the Windsor series, estimated to be at least 1,550 feet thick. The evaporites occur with about 5,000 feet of shales, grits, and arkoses of Mississippian and Triassic age. In this sequence there are no extrusive volcanic rocks. The borate-containing evaporite beds in Nova Scotia are locally contorted, steeply dipping, or overturned, and in places they are accompanied by thin veins that carry purple fluorite (Goodman, 1952, p. 45). Except for their local structural complexity and the introduction of hydrothermal solutions, as shown by the presence of fluorite in veins, these borate-evaporite occurrences are geologically much like those in western Oklahoma.

*Comparison of major features.*—A clearly unifying mineralogy and mode of association binds together the Permian borates of Germany, Russia, England, and New Mexico. The borate minerals themselves are chiefly magnesium compounds, or, in the case of the Inder district, magnesium borates were originally pres-



ent but have been partly replaced by calcium borates. Moreover, they are invariably associated with sodium and potassium salts, with the resultant implication that evaporation had proceeded to an advanced stage. At the latest stage, according to the experiments of Van't Hoff, salts of potassium, magnesium, and boron are precipitated from sea water, so that borate minerals are an expectable product in an environment of potassium and magnesium salts.

In both respects the borate occurrences in the Permian of Oklahoma are exceptional, for the minerals are sodium-calcium and calcium borates (magnesium borates are unknown), the host rocks are exclusively gypsum, and there is certain knowledge that the accompanying evaporites include only a small amount of sodium chloride, with no indication whatever of potassium salts. It is therefore clear that evaporation had advanced to the sulfate stage and barely into the sodium chloride stage, but never reached the stage of precipitation of potassium or magnesium salts. The Oklahoma borate minerals derived their boron from the sulfate stage, and the minerals themselves are built of calcium and sodium because these were the dominant cations available. A close comparison can be made with the borates in the Mississippian of Nova Scotia, where calcium-boron minerals occur in a gypsum-anhydrite sequence that is not accompanied by rock salt or potash salts. Here also the boron is related to the sulfate stage of evaporation, and similarly the calcium is supplied by the reorganization of gypsum and anhydrite.

There is no geologic difficulty in appealing to sea water as the source of boron in sulfate evaporites. Normal sea water of 35,000 ppm dissolved solids contains 4.8 ppm boron (Green, 1959). Upon evaporation the boron is concentrated, increasing to 88 ppm boron in sea water of a tidal pool adjoining the Gulf of Mexico that contains 270,000 ppm dissolved solids (Frederickson and Reynolds, 1960, p. 205). Salt lies at the bottom of the tidal pool, so that the water is saturated in sodium chloride. A similar determination from the Gulf of California by Moore (1960, p. 38) showed 40 ppm boron in sea water from a pool encrusted by gypsum, the water containing 286,000 ppm dissolved solids. These data indicate that approximately 129 to 283 ppm (0.013-0.028%)  $B_2O_3$  is

present in sea water at the time sulfates are being precipitated. Of great interest is the knowledge that these values correspond to an average content of 232 ppm  $B_2O_3$  in Permian anhydrite from Oklahoma.

*Oklahoma.*—The boron enrichment of Permian seas, discussed on an earlier page, is evident in evaporites of both Middle and Late Permian time in western Oklahoma. The manner in which the boron was contained in the original evaporites is not known, as there has been a complex history of boron reorganization and final concentration in the form of borate minerals. From the distinctive and unvarying mode of occurrence it is obvious that these minerals are forming as epigenetic replacement nodules in gypsum during the modern cycle of erosion, deriving their boron from associated beds of anhydrite. No borate minerals have been found in the anhydrite, and the anhydrite itself is believed to have been formed by dehydration of an original gypsum precipitate.

The critical relations in Oklahoma are summarized as follows:

1. Probertite, ulexite, and priceite occur as replacement nodules in bedded gypsum, localized chiefly along bedding partings.
2. Borate minerals are restricted in their occurrence to the Nescatunga gypsum member of the Blaine formation (Middle Permian) and to the lower 50 feet of the Cloud Chief gypsum (Upper Permian). Between the Blaine and Cloud Chief is 600 feet of red shales and sandstones containing no evaporites and no borates. The Nescatunga is 15 feet thick and is the only one of four gypsum members in the Blaine formation that contains borate minerals.
3. The borate minerals are strictly localized in that part of the gypsum which is close to a contact with bedded anhydrite. Invariably they are in the first ten feet of gypsum nearest the anhydrite-gypsum interface, and mostly they are in the first five feet. Where anhydrite occurs as a tongue or residual lens in gypsum, the borate minerals are distributed as a halo around the anhydrite.
4. Borate minerals are not present in weathered gypsum outcrops. Small open cavities that formerly contained nodular

borates are present, but the borate minerals have been dissolved by acidic surface waters resulting from the solution of gypsum.

5. All the gypsum at or near the ground surface is derived by hydration of anhydrite during the present cycle of erosion. The evidence for this conclusion is overwhelming. In Blaine County anhydrite alone occurs at depths greater than 400 feet, and on the outcrop gypsum invariably replaces anhydrite, incorporating residual masses both large and small (Muir, 1934). In the Weatherford area only gypsum crops out, thick anhydrite beds are present at shallow depth, and the gypsum-anhydrite contact is approximately parallel to present topography (pl. II; Ham and Curtis, 1959, pl. II).

6. No borate minerals were found in anhydrite.

7. The distribution of borate minerals within favored zones of the gypsum is irregular. It is partly related to the boron content of associated anhydrite beds but partly it is the result of ground-water transportation.

8. Pyroclastic sediments, lava flows, and intrusive igneous rocks are absent, and the Permian strata are essentially flat-lying. A volcanic or hydrothermal source for the boron is considered most unlikely.

9. The gypsum and the borate minerals alike are forming through slow hydration of anhydrite by cold ground waters in the modern zone of vadose circulation.

10. The Permian anhydrite of western Oklahoma is a recrystallized rock of medium- to coarse-crystalline texture (plate III E, F), and, following Conley and Bundy (1958), it is believed to have originated by dehydration through depth of burial from original beds of gypsum.

Perhaps the most striking feature of the Oklahoma deposits is the absolute restriction of the borate minerals to a gypsum host rock. This relation occurs without a single exception. It is well shown on a regional scale in figure 2, the section of which is 9 miles long; it is shown on a smaller scale in individual quarries as illustrated in figures 3 and 4; and it is confirmed on the scale of hand specimens from the quarries. Figure 17 shows a specimen from the Nescatunga gypsum at the Universal Atlas quarry, taken from the interlayered contact between an anhydrite bed four feet

thick and an overlying bed of gypsum. Gypsum is forming by the hydration of anhydrite, the process originating by the introduction of water along bedding partings in the contact zone. The dark-colored layers of gypsum locally cut across anhydrite and enclose isolated lenticular masses of it, as shown at two places in figure 17. The end result of the process is complete gypsification of the anhydrite. During gypsification borate minerals are formed, and the white nodule of probertite seen in the upper part of the figure lies entirely within the newly formed gypsum.



FIGURE 17. White nodule of probertite in gypsum (dark gray) that is altering along incipient bedding planes from anhydrite (light gray), x2, Nescatunga member of Blaine formation, quarry of Universal Atlas Co., SE $\frac{1}{4}$  SW $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 27, T. 17 N., R. 11 W., Blaine County.

All the field relations plainly indicate that the Oklahoma borate minerals are derived from anhydrite and are deposited as replacement nodules in associated beds of gypsum. The gypsum and anhydrite are composed of sulfate minerals admixed with small amounts of dolomite and calcite. Clay minerals are almost entirely absent. Silty reddish-brown shales occur as well-defined beds above and below the nearly pure sulfate rocks, but the formation of borate minerals is governed solely by gypsum-anhydrite contacts, and has absolutely no relation to shale beds. Clay min-

erals thus do not participate in any manner in the genesis or precipitation of Oklahoma borate minerals.

The widespread occurrence of boron in shales of all geological ages, especially those of marine origin, has been known for 30 years. The determined boron content has been found to range from 50 to 1,000 ppm  $B_2O_3$  in normal marine shales and to be as much as 5,000 ppm in clays occurring with rock salt in the Permian of northern Germany (Goldschmidt, 1954, p. 285). Determinations of boron in selected Permian shales from cores in western Oklahoma show a similar content, ranging from 515 to 933 ppm  $B_2O_3$  and averaging 707 ppm (table 5). No systematic variation was observed in this preliminary study of bulk samples, but it is noteworthy that the highest value is from a shale bed low in the Blaine formation, whereas the lowest value is from shale incorporated within halite near the top of the same formation.

TABLE 5.—BORON IN PERMIAN SHALES OF WESTERN OKLAHOMA  
(determined on total rock samples from cores)

<i>Sample description</i>	$B_2O_3$ (ppm)
Reddish-brown silty shale, depth 85.0 feet in core hole WCG-19, Custer County. Lower Cloud Chief.	837
Medium-brown shale masses in halite, depth 1,301 feet, Shell Oil Co. No. 1 LPG Yelton, Beckham County. Upper Blaine.	515
Reddish-brown silty shale above basal anhydrite of Blaine formation, Sunray-Midcontinent Oil Co. No. 1 Baker relief well, Blaine County, depth 500 feet.	933
Reddish-brown silty shale of upper Flowerpot, 4.5 feet below base of Blaine, depth 510 feet, Sunray-Midcontinent No. 1 Baker relief well.	644
Same, lower Flowerpot, depth 754 feet, Sunray-Midcontinent No. 1 Baker relief well.	605

As shown by Frederickson and Reynolds (1960 p. 211), most of the boron in marine shales is contained in the clay mineral illite (hydromica) and, once fixed in the illite space lattice, it stays there “. . . in substantially the same quantities when the sediment is subjected to other processes normally occurring in sedimentary rocks.” This conclusion substantiates the field observations that boron-containing shales play no part in the formation of borate minerals in western Oklahoma.

## BORON IN ANHYDRITE AND GYPSUM FROM OKLAHOMA

Preliminary tests indicated that measurable amounts of boron are present in anhydrite and gypsum from the Blaine and Cloud Chief formations, and a spectrographic method was devised for making quantitative estimates in samples from western Oklahoma. The method, described in a later section by J. A. Schleicher, is believed to have a probable error not exceeding  $\pm 5$  percent within the range of 30 to 1,600 ppm  $B_2O_3$ .

The first determinations on samples from Blaine and Custer Counties indicated that the Permian anhydrites contain approximately 100 to 700 ppm  $B_2O_3$ , whereas the associated gypsum beds contain approximately 50 ppm  $B_2O_3$ . The investigation was then broadened in an attempt to characterize the Blaine and Cloud Chief evaporites in all parts of western Oklahoma. Boron determinations were made on a total of 140 samples, including 24 anhydrites and 39 gypsums from the Blaine together with 30 anhydrites and 47 gypsums from the Cloud Chief. The results are summarized in table 6.

The outstanding result of the investigation is the consistently high boron content of Blaine and Cloud Chief anhydrite over a region of approximately 20,000 square miles in western Oklahoma. Fifty-four samples from cores, well cuttings, and outcropping strata have an average  $B_2O_3$  content of 232 ppm and a range of 62 to 692 ppm. The Cloud Chief anhydrite has a higher boron content than the anhydrite of the Blaine, averaging 280 ppm  $B_2O_3$  and ranging between 154 and 692 ppm, whereas Blaine anhydrite samples average 171 ppm  $B_2O_3$  and range from 62 to 428 ppm (fig. 18).

A second and corollary result is that gypsum associated with anhydrite of the Blaine and Cloud Chief formations, and derived from it by hydration in the present cycle of weathering, contains an average of 43 ppm  $B_2O_3$  while having a narrow range of 26 to 74 ppm. The average gypsum thus contains about one-fifth as much boron as the average anhydrite. The 86 samples of gypsum analyzed are mostly of high purity. They were taken as channel samples from outcrops and quarries, and as composite samples of continuous cores or cuttings from exploratory wells. In Blaine

and Custer Counties the gypsum beds locally contain borate minerals, and an attempt was made to exclude these minerals from the investigated samples so that misleading and abnormally high boron-content determinations would not be obtained. The attempt was successful in all samples except 10225, a core representing 16.6 feet of Cloud Chief gypsum in core hole WCG-9, which contained fragments of probertite nodules that increased the  $B_2O_3$  content to 1,030 ppm. Sample 10244 also is abnormal in having 113 ppm  $B_2O_3$ . It consists of surface cuttings of the Cloud Chief gypsum and contains 14.19 percent  $SiO_2$  plus  $Al_2O_3$ , present as admixtures of boron-containing clay and silt. Samples 10225 and 10244 have been excluded in calculating the range and average given above.

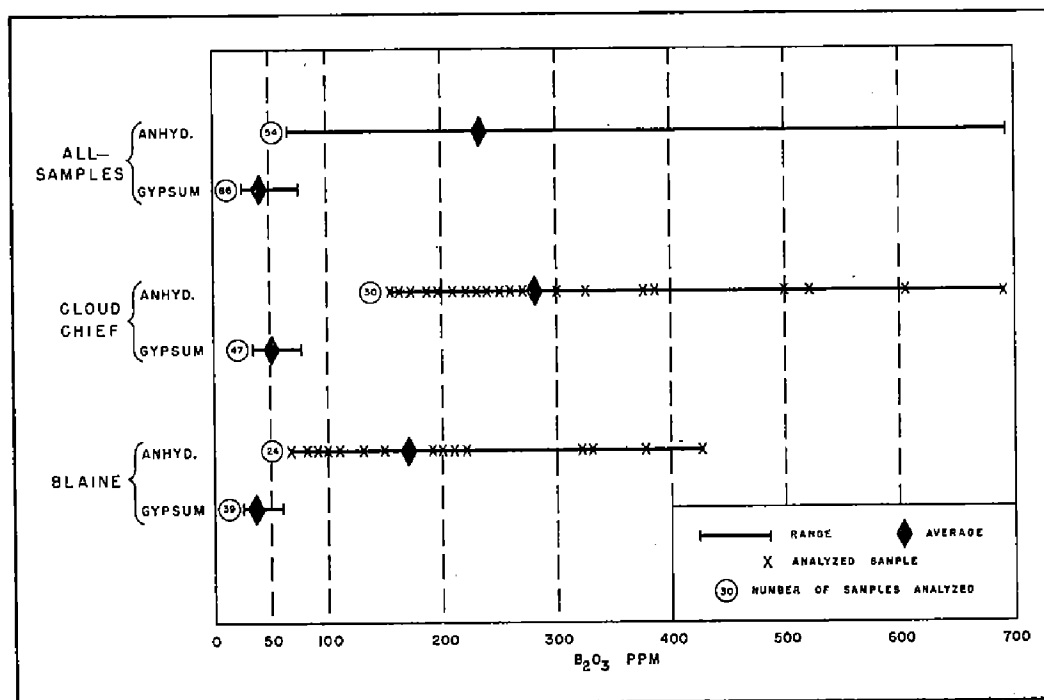


FIGURE 18. Summary of boron content in analyzed samples of gypsum and anhydrite from Blaine and Cloud Chief formations.

Analyses from selected cores are illustrated graphically in figure 19. It shows examples of the high content but wide range of  $B_2O_3$  in anhydrite, and the sharply contrasting low content of  $B_2O_3$  in gypsum. The four anhydrite members of the Blaine formation in the Baker relief well contain respectively 97, 195, 322, and 93 ppm  $B_2O_3$ , showing how the boron content can differ

stratigraphically at a single locality. In the Cloud Chief formation at core hole WCG-15, the basal anhydrite is 36 feet thick and shows a similar range of 228 to 377 ppm, yet 4.5 miles away in core hole WCG-28 the same basal anhydrite averages approximately 500 ppm. The gypsum beds above the anhydrite and interbedded within it show an abrupt decrease in  $B_2O_3$  content to less than 50 ppm, illustrating a fundamental difference in the lithologic distribution of boron.

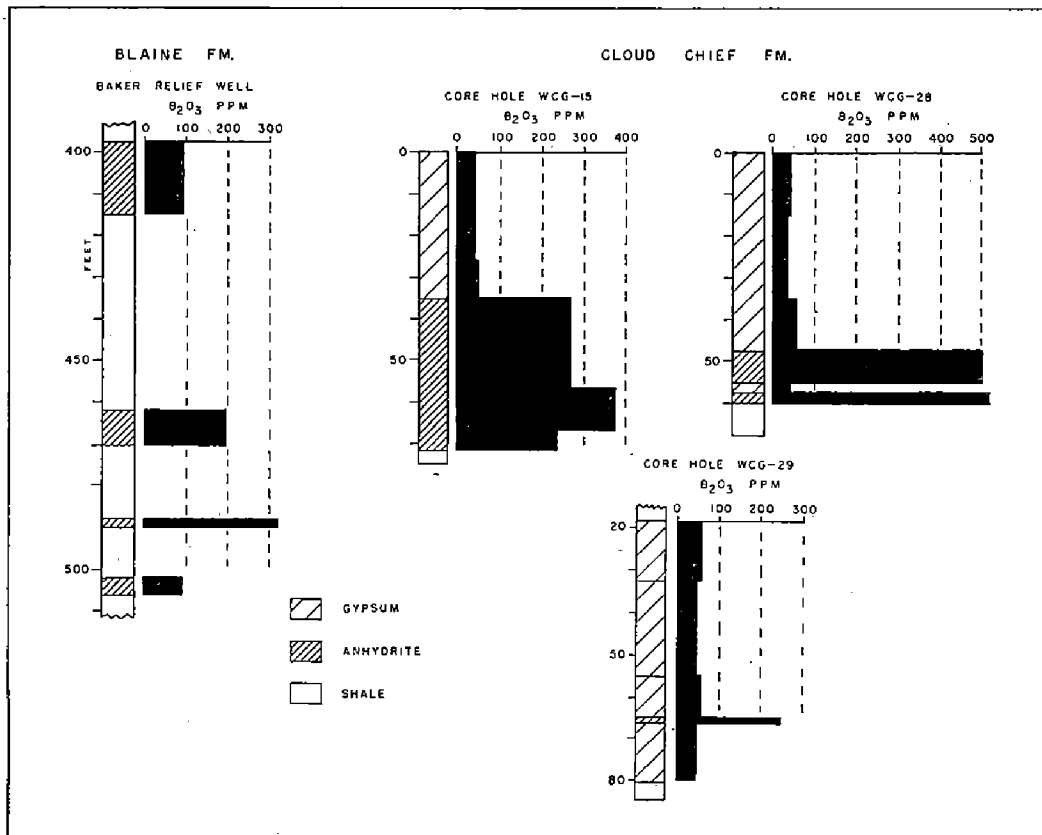


FIGURE 19. Boron content in selected cores of gypsum and anhydrite from Blaine and Cloud Chief formations. Blaine formation in Sunray Mid-Continent No. 1 Baker relief well, NW $\frac{1}{4}$  SE $\frac{1}{4}$  SW $\frac{1}{4}$  sec. 36, T. 14 N., R. 13 W., Blaine County, is 108 feet thick and contains four anhydrite members. The members show a range in  $B_2O_3$  content from 93 to 322 ppm and an average of 177 ppm, which is normal for the range and average of the formation in western Oklahoma. Second member below top is the Nescatunga, upper half of which, on outcrop, is gypsum containing borate minerals.

Anhydrite from the Cloud Chief formation contains approximately twice as much boron as the average anhydrite from the Blaine, the illustrated cores showing a range from 228 to 520 ppm  $B_2O_3$  and an average of 356 ppm. Associated gypsum beds, derived by hydration of the anhydrite, contain approximately 50 ppm. This consistent and abrupt change shows a basic difference in tolerance of boron by gypsum and anhydrite, and explains how the weathering of boron-rich anhydrite results in the formation of boron-poor gypsum and the simultaneous concentration in the gypsum of borate minerals. For locations of Cloud Chief core holes see table 6.



The distribution of boron in anhydrite from the Cloud Chief formation was investigated in the Weatherford district of Custer County; utilizing the cores and cuttings from systematically drilled holes of an earlier investigation (Ham and Curtis, 1958). Outcropping massive gypsum covers 35 square miles in this area, and anhydrite was found, by drilling, to occur at or near the base of the gypsum over approximately 25 square miles. Anhydrite does not occur at depths shallower than 33 feet, nor does it occur where stream valleys have cut through the evaporite sequence. It has the form of lenticular bodies as much as 40 feet thick, three miles wide, and at least five miles long, and these bodies are distributed beneath a thick cover of gypsum where hydration is retarded to a slow rate. Where anhydrite is present its thickness varies inversely with that of gypsum, the thickness of the evaporite body as a whole being nearly uniform.

Boron content was determined on anhydrite samples from the 21 holes in which anhydrite was found, and the results are illustrated on plate I in the form of an isobor map.\* Although the total range in  $B_2O_3$  is from 154 to 510 ppm, the isobor lines show in the east-central part of the area a definite curvilinear band of concentration greater than 250 ppm. This band of concentration is not related to topography, thickness of the anhydrite, regional dip, or local structure, but evidently reflects the original distribution of boron in the sea water from which it was precipitated. From the information available it appears that the greatest boron values lie toward the east, in the direction of the reconstructed shore line and therefore near the region of maximum sea-water evaporation and concentration. Values less than 200 ppm  $B_2O_3$  lie to the west, in the direction of the open sea, during Permian time, where there would have been more circulation and less concentration. The westward diminution in boron content is confirmed by the determination of 164 ppm  $B_2O_3$  in anhydrite of the Cloud Chief formation from a well drilled 40 miles west-southwest of the Weatherford area (Sample B-46, table 6).

On plate II are shown five geologic sections through the Cloud Chief evaporites. These sections illustrate the form and occurrence of anhydrite bodies beneath the gypsum, the  $B_2O_3$  content of the an-

---

\*Isobor means equal boron. As used in this report, an isobor map shows by lines of equal  $B_2O_3$  content the distribution of boron in a stratigraphic unit.

hydrite, and the occurrences of borate minerals. When viewed in conjunction with plate I, it is seen that borate minerals occur near anhydrite with concentrations of 154, 161, 196, 235, 245, 248, and 510 ppm  $B_2O_3$ . Only one of the seven occurrences lies within the belt of maximum boron concentration ( $>250$  ppm  $B_2O_3$ ), four lie just outside this belt (approximately 200-250 ppm  $B_2O_3$ ), and two are in the zone of minimum concentration (154-161 ppm  $B_2O_3$ ). As these values represent the complete range of boron content in anhydrite of the Weatherford area, it is clear that borate mineral occurrence is not related solely to boron content of the source rock, but probably also is governed by a redistribution of the boron by ground waters.

*Comparison with the Zechstein of Germany.*—Through the excellent and comprehensive work of Harder, which is the outstanding investigation of the occurrence of boron in evaporites, it is possible to compare the Permian anhydrites from Oklahoma with Zechstein anhydrites of equivalent age from Germany. Harder (1959, p. 167-175) made boron analyses of numerous samples of rock salt, potash salts, anhydrite, and associated clays. His samples included 61 anhydrites from the four evaporite cycles of the Zechstein of northern Germany, named in ascending order the Werra series (Z I), Stassfurt series (Z II), Leine series (Z III), and Aller series (Z IV). As determined from Harder's tables, the average value of the 61 anhydrite samples is 70 grams of boron per metric ton, which is equivalent to 70 ppm boron or 225 ppm  $B_2O_3$ . This matches almost exactly the 232 ppm  $B_2O_3$  obtained as the average value for the 54 samples of Permian anhydrite from western Oklahoma, and thereby strongly indicates that "normal Permian anhydrite" contains approximately 230 ppm  $B_2O_3$ .

Harder was able to demonstrate that the Basal Anhydrite of the Stassfurt series (Z II) has a notably higher content of boron than anhydrite from the other three evaporite series of the Zechstein. Thirteen samples of the Basal Anhydrite have an average value of 182 ppm boron (592 ppm  $B_2O_3$ ), whereas the 48 samples of anhydrite from the Werra, Leine, and Aller series have an average of 40 ppm boron (129 ppm  $B_2O_3$ ). The greatest value obtained was approximately 500 ppm boron (1,600 ppm  $B_2O_3$ ), from the Basal Anhydrite at Pöthen, Volkenroda, Thuringia, which is more than twice the 700 ppm  $B_2O_3$  found as the maximum value in Oklahoma.

In Oklahoma also it is possible to characterize the evaporite series by their boron content, as the younger Cloud Chief anhydrite averages 280 ppm  $B_2O_3$  whereas the older Blaine anhydrite averages 171 ppm  $B_2O_3$ .

Regarding the origin of boron in the Zechstein evaporites, Harder cited the presence of borate minerals, which locally contribute to the relatively high values in some of the potash salts, but he also stated that the boron content is generally greater where these salts are rich in sulfates, and further that the anhydrite beds themselves can be high in boron. A hydrothermal origin does not appear to be probable, because, he argued, if this were the origin the deeper Werra anhydrite should be richer in boron than the geologically younger Basal Anhydrite. Harder concluded by accepting as highly probable that the boron of the Basal Anhydrite was precipitated primarily with the calcium sulfate, and that the boron content of the Zechstein deposits is not higher than would be expected from the evaporation of sea water. These same conclusions are reached independently by the present investigation of boron in the Permian evaporites of western Oklahoma.

*Genetic relation of borate minerals to anhydrite.*—The distribution of boron as found in Permian gypsum and anhydrite of western Oklahoma is compatible with the occurrences of borate minerals, and strongly suggests a close genetic relationship. The average anhydrite contains 232 ppm or 0.023 percent  $B_2O_3$  and is the obvious source of boron for the borate minerals. Solution of anhydrite during weathering results in the simultaneous formation of gypsum, but, as shown empirically, the gypsum accepts only about 40 ppm or 0.004 percent  $B_2O_3$ , leaving in solution nearly 200 ppm  $B_2O_3$  from the original anhydrite. Small amounts of halite shown to be present in the anhydrite also dissolve in the weathering process and yield sodium ions, so that sodium, boron, and calcium are normally in solution while gypsum is being formed. The greatest concentration of these ions is at the anhydrite-gypsum interface, and it is exactly at this zone of the gypsum where borate minerals are found. Once dissolved out of the anhydrite, the boron remains within the gypsum phase until sufficiently concentrated to be precipitated, normally as pro-

bertite but less commonly as ulexite and very rarely as priceite. Priceite evidently is formed where NaCl is rare or absent as an original constituent of the anhydrite.

If the borate minerals were not readily soluble in acidic solutions, they would remain indefinitely in the gypsum host rock. They should be present, and perhaps even concentrated as ore deposits, in the uppermost surface layers. Borate minerals, however, have not been found in outcropping gypsum in Oklahoma. In the quarries of Blaine County they are at a depth of 15 to 30 feet, having been uncovered by stripping and quarrying operations; and in the core holes in Custer County they occur only within a depth range of 34.5 to 72.6 feet. The upper part of the gypsum in all areas is notably leached, containing open cavities that are lined with secondarily precipitated crystals of selenite. At the time of leaching the ground waters contain principally calcium sulfate and are acidic, with the result that borate minerals are dissolved. All stages in the solution of probertite have been observed in the quarries of Blaine County, and one example is illustrated in figure 20.

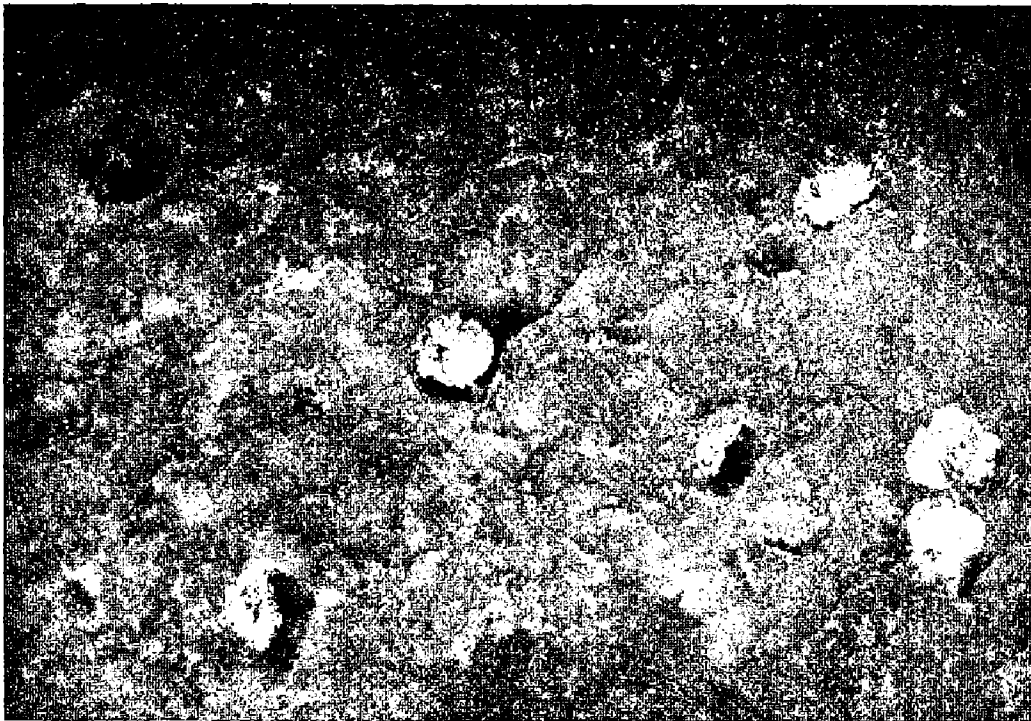


FIGURE 20. Compact white nodules of probertite in fine-grained Nescatunga gypsum, x3, quarry of U. S. Gypsum Co., locality 3, S $\frac{1}{2}$  SW $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 3, T. 18 N., R. 12 W. Peripheral edges of the three nodules at right are partly dissolved; in lower part of photograph are two nodules that are about half dissolved; and at upper left is a cavity from which the entire probertite nodule has been dissolved.

There appears to be a net loss of boron when it is liberated from anhydrite during weathering, and presumably it is carried away by ground waters. If all the boron were retained, and the anhydrite were of average composition with 0.023 percent  $B_2O_3$ , borate minerals should be everywhere present in gypsum at shallow depth near anhydrite. At many expected localities borates are either absent or exceedingly rare, and virtually all the boron has been removed. Part of the boron, however, is transported elsewhere and deposited as borate minerals. The two localities of maximum probertite concentration are at the Universal Atlas quarry and at locality no. 1 of the U. S. Gypsum Company. Channel samples of the probertite-containing gypsum showed  $B_2O_3$  contents of 0.16 and 0.10 percent, respectively. The larger value, 0.16 percent  $B_2O_3$ , corresponds to 1,600 ppm and is equivalent to a concentration nearly seven times that of the average anhydrite. Obviously there has been some circulation of boron-containing waters, much of it probably taking place along gypsum-anhydrite contacts by lateral movement on gently inclined beds.

#### LABORATORY INVESTIGATIONS OF THE NATURE OF BORON IN ANHYDRITE

As the borate minerals in Oklahoma are definitely related in a genetic sense to anhydrite, and as anhydrite is not ordinarily considered as a carrier or collector of boron, a series of investigations was carried out in an attempt to determine the mode of occurrence of boron in the anhydrite rocks. The Permian anhydrites were tested for inclusions of borate minerals and none was found. Water-soluble boron is present in significant but variable amounts, probably in the form of borate ions contained within liquid inclusions. Most of the boron in the anhydrite rocks investigated is believed to be contained as a space-lattice substitute of borate ( $BO_4^?$ ) for  $SO_4$ , and partial confirmation of this theory was obtained by the laboratory precipitation of boron-containing anhydrite. The amount of substitution within the range 50-700 ppm  $B_2O_3$  is, however, insufficient to be reflected in X-ray diffraction properties.

*Tests for inclusions of borate minerals.*—Borate minerals occur in anhydrite in other areas of the world (howlite in Nova Scotia

and boracite in Germany) and they might be expected in Oklahoma. A careful search of Oklahoma anhydrite by examination with a binocular microscope, and in thin sections under the petrographic microscope, has failed to reveal a single specimen of a borate mineral. As a further test, insoluble residues from 10.0 grams of coarsely crushed anhydrite in 3-percent NaCl solution were made from two specimens of the Nescatunga, containing respectively 428 and 90 ppm  $B_2O_3$ , and from a specimen of the Cloud Chief anhydrite that contains 692 ppm  $B_2O_3$ . The residues consist of authigenic dolomite grains together with detrital quartz and flakes of colorless mica (table 7). No authigenic minerals other than dolomite were found, and borate minerals are absent. Magnesium, calcium, and strontium borate minerals should be concentrated and recovered by this means, if they are present, as has been done by Braitsch (1960a) from the Zechstein of Germany.

TABLE 7.—INSOLUBLE RESIDUES FROM OKLAHOMA ANHYDRITE  
(dissolved in 3-percent NaCl solution)

<i>Sample</i>	<i>Horizon</i>	<i>B<sub>2</sub>O<sub>3</sub>, ppm</i>	<i>Insoluble residue Weight %</i>	<i>Description</i>
B-38	Cloud Chief	692	0.8	70% dolomite occurring as grains 0.05-0.10 mm in diameter, partly in euhedral flat hexagonal prisms with basal pinacoid faces; 20% detrital quartz; 10% colorless flakes of hydromica (illite).
B-4	Nescatunga	428	0.5	75% dolomite as irregular grains 0.05-0.20 mm in diameter; 20% quartz; and 5% colorless flakes of hydromica.
B-3	Nescatunga	90	<0.2	Carbonate dust.

*Water-soluble boron in anhydrite.*—The Oklahoma anhydrites are known from thin section studies to contain small fluid inclu-

sions, and it was inferred that boron might be present as boric acid or as borate ions dissolved in the fluid of these inclusions. Two samples of boron-rich anhydrite, one each from the Blaine and Cloud Chief formations, were finely ground and leached at room temperature with distilled water (table 8). When ground to less than 20-micron grain size the  $B_2O_3$  loss of the leached anhydrite ranged between 9.8 and 20.8 percent, but the largest grains still contained a few inclusions, and a finer grain size was sought for testing. Grains less than 8 microns in diameter, obtained by sedimentation, showed a total loss in  $B_2O_3$  of 16.6 percent for the Blaine anhydrite and 37.0 percent for the Cloud Chief anhydrite. Although these losses are substantial, and confirm the presence of water-soluble boron, approximately 350 ppm  $B_2O_3$  remains in the anhydrite after maximum leaching. This boron is believed to be contained within the space lattice of anhydrite, and probably will be held there until the anhydrite itself is dissolved.

TABLE 8.—LOSS OF  $B_2O_3$  FROM OKLAHOMA ANHYDRITE BY WATER LEACHING

		$B_2O_3$ (ppm)	Percent loss from original
Blaine (Nescatunga) anhydrite	Original sample	428	----
	Ground —20 microns	386	9.8
	Sedimented —8 microns	357	16.6
Cloud Chief anhydrite	Original sample	557	----
	Ground —20 microns	441	20.8
	Sedimented —8 microns	351	37.0

*X-ray diffraction data.*—An attempt to verify this supposition was made by an investigation of X-ray diffraction properties of boron-containing anhydrite, within the boron range of Oklahoma specimens. Carefully made diffractograms of well-crystallized anhydrite containing respectively 62, 90, 219, 428, 520, 608, and 692 ppm  $B_2O_3$  showed no significant difference in spacing, intensity, or breadth of the diffractogram peaks for reflections from  $2^\circ$  to  $90^\circ$ . An internal standard of pure quartz was used to check the spacing measurements. These data unfortunately neither prove nor disprove the presence of boron in the anhydrite lattice.

*Laboratory precipitation of boron-containing anhydrite.*—A further test was made by precipitating anhydrite from boron-containing solutions in the laboratory. The adopted method consists of dissolving reagent-grade powdered gypsum in hot 2N  $H_2SO_4$ , to which different amounts of  $H_3BO_3$  are added, and precipitating anhydrite by evaporation. The resulting anhydrite, repeatedly washed with distilled water, is of extremely fine grain size. It contained as much as 148 ppm  $B_2O_3$ , but no linear relationship could be established. When the original solution contained less than 1 percent boric acid (2.5 g  $H_3BO_3$ , 250 ml  $H_2SO_4$ , 2 g  $CaSO_4 \cdot 2H_2O$ ), the precipitated anhydrite contained 35 to 51 ppm  $B_2O_3$ , whereas at higher concentrations of boron (2.5 to 15.0 g  $H_3BO_3$ ) the anhydrite contained 90 to 148 ppm  $B_2O_3$ . The precipitated product is known to be anhydrite by X-ray diffraction methods, and electron photomicrographs of the anhydrite show no fluid inclusions. It is therefore to be concluded that a lattice uptake of boron is possible in anhydrite, but from our own experiments we have not determined the maximum limit of uptake, and further we have not been able to show how the boron is contained as a lattice unit. Additional work is continuing on this most interesting problem.

#### SUMMARY

This report of borate minerals from undisturbed gypsum beds of Middle and Late Permian age in western Oklahoma marks the first recorded occurrence of sodium-calcium and calcium borates in Paleozoic bedded marine evaporites of the United States. The deposits are exceptional in that the dominant borate mineral is probertite,  $NaCaB_5O_9 \cdot 5H_2O$ , hitherto known only from nonmarine bedded borate deposits of Tertiary age in California and Nevada. Magnesium borates, typical of the bedded Permian evaporites in Germany, Russia, England, and New Mexico, are not present in Oklahoma, and the normally associated potassium salts also are absent.



A uniform mode of occurrence as replacement nodules in gypsum at or near contacts with boron-containing anhydrite, characterizes the borate minerals in both of the stratigraphically and geographically separated formations, showing that all the borate minerals of the region have a common mode of origin. Beds and major lenses of anhydrite, even now being converted by hydration into gypsum, contain about five times more boron (average 232 ppm  $B_2O_3$ ) than the resulting gypsum (average 43 ppm  $B_2O_3$ ), so that boron in the amount of nearly 200 ppm  $B_2O_3$  is released in solution during the normal process of gypsum formation. This boron is precipitated as a replacement of gypsum near the anhydrite-gypsum interface, chiefly as sodium-calcium borate minerals. Sodium cations are derived by the solution of small amounts of rock salt contained in the anhydrite beds. Locally, where boron is at an exceptionally low concentration, the sodium is redeposited as thenardite ( $NaSO_4$ ).

Boron was originally derived from the Permian seas. The anhydrite beds of the earlier Blaine formation contain 171 ppm  $B_2O_3$ , in comparison with 280 ppm  $B_2O_3$  in anhydrite of the later Cloud Chief formation, and this relation suggests an enrichment of boron in the younger Permian sea. An isobor map of Cloud Chief anhydrite shows the greatest concentration of boron to be in the eastern part of the Weatherford area, nearest the reconstructed shore line where concentration through evaporation would have been at a maximum. The average content of 232 ppm  $B_2O_3$  in Permian anhydrite of Oklahoma matches almost exactly the value of 225 ppm  $B_2O_3$  found by Harder (1959) in Zechstein anhydrite from Germany, and these values compare with observed concentrations of 129 to 283 ppm  $B_2O_3$  in pools of modern sea water where sulfates have been precipitated.

Although the main elements of borate mineral formation in western Oklahoma can be satisfactorily explained in terms of present knowledge, there remain unanswered two important questions about the origin and occurrence of boron in anhydrite. First, what was the original form of the boron when it was concentrated out of the sea? It seems quite probable that the primary sulfate was

gypsum, and that the boron was associated at first with this mineral. Through burial and diagenesis the gypsum would be converted into anhydrite. Whatever boron was present with the gypsum and in the accompanying connate waters was evidently incorporated in anhydrite during the anhydritization process.

The second question concerns the mode of occurrence of boron in anhydrite. Does borate substitute for sulfate in the anhydrite lattice, and if so does it occur as the relatively unknown  $\text{BO}_4$  grouping? Experimental data show that boron uptake in anhydrite can be induced through laboratory precipitation, and our investigations of boron-rich natural anhydrite similarly indicate that at least 350 ppm  $\text{B}_2\text{O}_3$  must belong in some structural way to the anhydrite lattice. Regardless of the final outcome of further investigation, however, it is plain that anhydrite from the Permian of Oklahoma is no less than a carrier of boron and at the same time is the direct ancestor of the associated borate minerals.

## EMISSION SPECTROGRAPHIC DETERMINATION OF BORON IN GYPSUM AND ANHYDRITE

The analytical determination of boron may be made by standard wet methods, by flame photometry, or by emission spectrographic techniques. At the beginning of the investigation these methods were evaluated as to suitability for boron determination in approximately 200 samples of Permian gypsum and anhydrite from western Oklahoma, judged to contain boron within the range of 10 to 1,000 ppm (0.001 to 0.100 percent)  $B_2O_3$ .

The standard wet methods, normally used for borate minerals and compounds containing several percent  $B_2O_3$ , were considered unsuitable because the separation of small amounts of boron from other ions by these methods is subject to serious losses of boron, especially by volatilization.

Preliminary investigations of about 40 samples, using flame photometry and an oxy-hydrogen flame, failed to give satisfactory results, owing to the low concentrations of boron in the dissolved samples. Although it is possible that greater sensitivity can be obtained by using acetylene gas, the method was discarded in favor of emission spectrographic techniques. We are grateful to Dr. A. F. Frederickson of the Pan-American Research Laboratory, Tulsa, Oklahoma, for discussing with us their laboratory method for the spectrographic determination of boron in silicate clay minerals. The method, using beryllium as an internal standard, has been successfully adapted in our laboratory to the determination of boron in sulfate rocks. It has a probable error of 5 percent within the range of 10 to 500 ppm boron (32-1,600 ppm  $B_2O_3$ ).

The successful use of beryllium as an internal standard for determining boron in fertilizers has been reported by earlier investigators (Melvin and O'Conner, 1941), with a reproducibility of 5 percent. In addition to the decided advantage afforded by the close proximity of the primary Be line at 2494.6 Å to the B lines

at 2496.8 and 2497.7 Å, the excitation characteristics of the two elements are quite similar (Ahrens, 1950, p. 274, 276):

		<i>Excitation potential</i>	<i>Ionization potential</i>
Beryllium	2494.6 Å	5.4 volts	9.28 volts
Boron	both lines	4.9 volts	8.28 volts

*Preparation of samples.*—A ready source of beryllium was a few hand-picked crystals of the mineral beryl, which, from its theoretical composition of  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , is calculated to contain 5.03 percent beryllium. The beryl crystals were ground in a fused alumina capsule and ball, vibrated by a Spex Mixer-Mill until 100 percent of the material passed 170 mesh. Samples of the ground beryl examined spectrographically were found to contain no detectable amount of boron. Beryl powder was diluted with special-purity graphite powder to a final concentration of about 250 ppm beryllium. Samples of finely ground gypsum or anhydrite were weighed accurately at 0.2000 gram, and added to 0.1000 gram of the beryl-graphite mixture. A homogeneous final mixture was prepared by shaking for 20 seconds with a Wig-L-Bug, the sample being mixed and ground by a small plastic ball in a plastic capsule.

*Preparation of standards and analytical curves.*—Spectrographically standardized calcium carbonate (Johnson-Matthey and Co., Ltd.) was treated in platinum dishes with a small excess of cold, previously boiled, dilute sulfuric acid, added drop by drop. After all  $\text{CO}_2$  and water had been driven off at low temperature on a Temco hotplate, the temperature was raised to 400° F to fume off the excess acid. The residue was ignited in a muffle furnace at 900° C. The finely crystalline  $\text{CaSO}_4$  was ground to pass 100 mesh. J-M Specpure boric acid was ground to pass 200 mesh and added to a portion of the prepared  $\text{CaSO}_4$  to a boron concentration of 500 ppm B. Dilution of this standard with additional  $\text{CaSO}_4$  to a boron concentration of 200 ppm, and dilution of portions of the second standard to 100, 50, and 10 ppm, provide the five standards necessary for making the analytical curves.

*Technique and equipment.*—The spectrograph used was a Jarrel-Ash Co. 1.5-meter wide-angle, Wadsworth-mount grating

spectrograph, with a model 4075 Custom Varisource power supply. The D. C. arc is autoignited by a high-frequency spark. The microphotometer used was the JACo Console model. The electrodes were special-purity National Carbon Co. preforms, 0.25-inch diameter, standard undercut shallow-crater type, with center-post platforms as counter electrodes. An evaporated filter of about 25 percent transmission was interposed in the light path, and the primary slit was 25 microns. The film used was Eastman Spectrum Analysis No. 1.

The electrodes were loaded in small increments, alternately tamped with a flat-faced glass rod, until the crater was nearly level full. The electrodes filled with unknown samples were baked in a drying oven at 120° C for one hour to eliminate excess water from the particles and thus minimize spattering in the arc. The standards, however, were anhydrous and needed no drying. A moving-film spectrum of the 500 ppm standard showed that both beryllium and boron persisted in the arc for approximately 120 seconds, or until the sample was completely volatilized, whichever was earlier. Experimentation with the unknown samples showed that the small amount of water remaining in the samples after drying, together with small amounts of carbonate mineral present in some of the samples, caused the loss of significant amounts of sample by spattering if the ignition temperature was initially high. Accordingly, the arc was ignited at 2.5 amps and allowed to preheat the sample at this current setting for ten seconds. Then, the Varisource allowing continuous adjustment of arc current during ignition, the current was increased smoothly and rapidly over the next seven seconds to a maximum of 10.5 amps, where it was maintained for the remaining ignition time of 113 seconds. The total ignition time was 130 seconds, the exposure began with the initial ignition, and throughout the ignition the analytical gap was maintained at 4 mm, with the sample electrode as anode.

The film was developed for 3.0 minutes in Eastman D-19, shortstopped for 10 seconds in 3 percent acetic acid, and fixed for one minute in Kodak Rapid Liquid Fixer With Hardener. After a one-minute wash in running tap water, the film was rinsed twice on each side with distilled water, the excess sponged off, and the film was dried on an Applied Research Laboratories forced-air infra-red film drier.

The densities of the three lines were measured with the microphotometer. It was found necessary to use the two line pairs Be 2494.6: B 2496.8 and Be 2494.6: B 2497.7 because of the wide range of concentrations of boron present in the unknowns. The maximum concentration was found to be more than 20 times the minimum. The latter line pair was adjudged to be more stable, but a few of the higher concentrations of boron produced a B 2497.7 line too dark to be measured, and the line at 2496.8 Å had to be used. At the lower concentrations found, the 2496.8 line was too light to be accurately determined by the densitometer.

Three or four samples of each of the five standards were ignited, and the percent transmission of the two analysis lines and the internal-standard line was measured. Obtaining the relative intensities of the wavelength emitted by means of an emulsion calibration curve for this wavelength region, curves were drawn that related the intensity ratios to the concentration of boron in the standards. In the same manner, the unknown samples of gypsum and anhydrite were ignited and the relative intensities obtained. As calculated from variations in the standard samples, reproducibility ranged from 2.0 to 7.0 percent and averaged about 5.5 percent.

## REFERENCES

- AHRENS, L. H., 1950, Spectrochemical analysis: Cambridge, Mass., Addison-Wesley Press, 269 p., 72 tables.
- BELL, W. A., 1929, Horton-Windsor district, Nova Scotia: Canada, Geol. Survey, Mem. 155, 268 p.
- BRAITSCH, OTTO, 1960a, Mineralparagenesis und Petrologie der Stassfurt-salze in Reyershausen: Kali und Steinsalz, no. 1, p. 1-4.
- 1960b, Die Borate und Phosphate im Zechsteinsalz Südhannovers: Fortschr. Mineralogie, vol. 38, no. 2, p. 190-191.
- CLIFTON, R. L., 1942, Invertebrate faunas from the Blaine and the Dog Creek formations of the Permian Leonard series: Jour. Paleontology, vol. 16, p. 685-699.
- CONLEY, R. F., and BUNDY, W. M., 1958, Mechanism of gypsification: Geochim. et Cosmochim. Acta, vol. 15, p. 57-72.
- DUNBAR, C. O., et al., 1960, Correlation of the Permian formations of North America: Geol. Soc. America, Bull., vol. 71, p. 1763-1806.
- EAKLE, A. S., 1929, Probertite, a new borate: Amer. Mineralogist, vol. 14, p. 427-430.
- FAY, R. O., 1958, Permian stratigraphy of Blaine County—a preliminary report: Okla. Acad. Science, Proc. 1957, vol. 38, p. 82-86.
- FOSHAG, W. F., 1924, Probertite from Furnace Creek, Inyo County, California: Amer. Mineralogist, vol. 9, p. 11-13.
- 1931, Probertite from Ryan, Inyo County, California: Amer. Mineralogist, vol. 16, p. 338-341.
- FREDERICKSON, A. F., and REYNOLDS, R. C., JR., 1960, Geochemical method for determining paleosalinity, *in* Swineford, Ada, ed., Clays and clay minerals, volume 8, Proceedings of the Eight National Conference on Clays and Clay Minerals: New York, Pergamon Press, p. 203-213.
- GODLEVSKY, M. N., 1937, Mineralogical investigation of the Inder borate deposits: Mémoires de la Société Russe de Minéralogie, vol. 66, p. 345-368.
- GOLDSCHMIDT, V. M., 1954, Geochemistry: Oxford, Clarendon Press, 730 p.
- GOODMAN, N. R., 1952, Gypsum and anhydrite in Nova Scotia: Nova Scotia Dept. Mines, Mem. 1, 75 p.
- GRABAU, A. W., 1920, Geology of the non-metallic mineral deposits, vol. I, Principles of salt deposition: New York, McGraw-Hill Co., 435 p.
- GREEN, D. A., 1936, Permian and Pennsylvanian sediments exposed in central and west-central Oklahoma: Amer. Assoc. Petroleum Geologists, Bull., vol. 20, p. 1454-1475.
- GREEN, JACK, 1959, Geochemical table of the elements for 1957: Geol. Soc. America, Bull., vol. 70, p. 1127-1184.
- GUPPY, E. M., 1944, Boracite from a boring at Aislaby, Yorkshire: Mineralog. Mag., vol. 27, no. 187, p. 51-53.

- HAM, W. E., 1960, Middle Permian evaporites in southwestern Oklahoma: Internat. Geol. Cong., 21st, Copenhagen, Proc. Sec. 12, p. 138-151.
- HAM, W. E., and CURTIS, N. M., JR., 1958, Gypsum in the Weatherford-Clinton district, Oklahoma: Okla. Geol. Survey, Mineral Rept. 35, 32 p.
- HAM, W. E., CURTIS, N. M., JR., and SCHLEICHER, J. A., 1958, A new occurrence of probertite in Oklahoma: Okla. Geol. Survey, Okla. Geology Notes, vol. 18, p. 24-27.
- HAM, W. E., MANKIN, C. J., and SCHLEICHER, J. A., 1960, Borate minerals in Permian gypsum of western Oklahoma [abstract]: Geol. Soc. America, Bull., vol. 71, p. 1878-1879.
- HARDER, HERMANN, 1959, Beitrag zur Geochemie des Bors, Teil II, Bor in Sedimenten: Göttingen Univ., Akad. Wiss., II. Math.-Physikal. Kl., Nachr., no. 6, p. 123-183.
- MELVIN, E. H., and O'CONNOR, R. T., 1941, Spectrochemical analysis of trace elements in fertilizers: Indus. Eng. Chemistry, Anal. Ed., vol. 13, p. 520.
- MOORE, G. W., 1960, Origin and chemical composition of evaporite deposits: Ph.D. dissertation, Yale University, *also* open file report, U. S. Geol. Survey, Washington, D. C.
- MUESSIG, SIEGFRIED, 1958, Primary borates in playa deposits: minerals of high hydration [abstract]: Geol. Soc. America, Bull., vol. 69, p. 1619.
- MUIR, J. L., 1934, Anhydrite-gypsum problem of Blaine formation, Oklahoma: Amer. Assoc. Petroleum Geologists, Bull., vol. 18, p. 1297-1312.
- MURDOCH, JOSEPH, 1945, Probertite from Los Angeles County, California: Amer. Mineralogist, vol. 30, p. 719-721.
- PALACHE, C., BERMAN, H., and FRONDEL, C., 1951, Dana's system of mineralogy, vol. II: New York, John Wiley and Sons, 1124 p.
- POITEVIN, E., and ELLSWORTH, H. V., 1921, Inyoite from New Brunswick: Canada, Geol. Survey, Bull. 32, 21 p.
- SCHALLER, W. T., 1930, Borate minerals from the Kramer district, Mohave desert, California, *in* Shorter contributions to general geology, 1929: U.S. Geol. Survey, Prof. Paper 158, p. 137-170.
- , 1937, Borax and borates, *in* Industrial minerals and rocks, 1st ed.: New York, Amer. Inst. Min. Metall. Engineers, p. 149-162.
- SCHALLER, W. T., and HENDERSON, E. P., 1932, Mineralogy of drill cores from the potash field of New Mexico and Texas: U. S. Geol. Survey, Bull. 833, 124 p.
- SMITH, W. C., 1960, Borax and borates, *in* Industrial minerals and rocks, 3rd ed.: New York, Amer. Inst. Min. Metall. Petroleum Engineers, p. 103-118.
- STAPLES, L. W., 1948, Origin of Oregon priceite [abstract]: Geol. Soc. America, Bull., vol. 59, p. 1382.
- STEWART, F. H., CHALMERS, R. A., and PHILLIPS, R., 1954, Veatchite from the Permian deposits of Yorkshire: Mineralog. Mag., vol. 30, no. 225, p. 389-392.



## INDEX

Ahrens, L. H. (cited)	68
"Alabaster" gypsum	9
anhydrite	
artificial precipitation	64
boron content	54-58, 61, 62, plate II, table 6
Cloud Chief formation	11
genetic relation of boron minerals	59-61
insoluble residue	62
Nescatunga gypsum	38, 39
ascharite	46
authigenic minerals	62
Bell, W. A. (cited)	48
Berman, Harry (cited)	46
beryllium	67, 68
beta ascharite (szaibelyite)	46, 47
Blaine formation (see also Nescatunga gypsum)	9, 10, 11, 18, 28, 38, 53
boron content	54-58, 63, table 6
Blosser, W. I.	8
boracite, Permian	7, 43, 46, 47, 48, 62
borate minerals	
absence in anhydrite	51
Argentina	41
California	7, 14, 22, 23, 33, 36, 37, 41, 64
Chile	41
comparison of major features	48-50
distribution	51
economic possibilities	41-42
England	43, 45, 48, 64
genetic relation to anhydrite	59-61
geologic setting	8-11
Germany	7, 43, 45, 47, 62, 64
Italy	7, 41
Kashmir, India	7
Kerch Peninsula	7
marine	7, 43-53
Nevada	7, 64
New Brunswick	43
New Mexico	48, 64
nonmarine	7, 43
Nova Scotia	7, 43, 48, 61
Oklahoma	7, 11-42
areal extent	9, plate II
chemical analyses and formulas	22, 23, 26, 33, 36, 38, 40, 46
stratigraphic range	9
summary	64-66
Oregon	36
origin	43, 47, 48-49, 50, 51, 52, 64
Permian	7, 8
relation to gypsum-anhydrite interface	50, 59, 65
replacement nodules	13, 52, 65

- Russia 41, 43, 45, 47, 64  
 solution 50-51, 60  
 South America 7  
 stratigraphic range 9, 45  
 Tertiary 7, 14, 43  
 Tibet 7  
 Turkey 7, 36, 41  
 uses 41  
 volcanic association 7, 43, 48  
 world occurrence 44, 46  
 x-ray diffractograms 23-25, 34, 35, 36, 37, 63
- borax 7, 17, 33, 41
- boron  
 areal distribution 54-58, plate II  
 content in anhydrite 54-58, 61, 65, plate II, table 6  
 content in gypsum 54-58, 61, 65, table 6  
 content in shales 53  
 content in Permian anhydrite of Germany 58-59  
 content in tidal pools 49-50, 65  
 genetic relationships 61  
 laboratory investigations 61-64, 67, 68  
 lithologic distribution 54-58, plate I, table 6  
 stratigraphic distribution 54-58
- Braitsch, Otto (cited) 46, 47, 62
- Bundy, W. M. (cited) 51
- carnallite 47
- celestite 13, 38, 39, 40
- cephalopods 9
- Chalmers, R. A. (cited) 46, 48
- Clifton, R. L. (cited) 9
- Clinton 10
- Cloud Chief gypsum 8, 9, 11, 10, 28, 40-41, 50, 53  
 boron content 54-58, 62, 63, table 6  
 priceite, absence of 41  
 probertite 8, 12, 20, 21, 31, 41  
 selenite 41  
 thenardite, absence of 41  
 ulexite 8, 12, 31, 34, 35, 41
- colemanite 14, 17, 36, 46, 47
- Conley, R. F. (cited) 51
- Curtis, N. M., Jr. (cited) 8, 14, 21, 28, 31, 41, 51, 57
- danburite 46, 48
- Dog Creek shale 10
- Doxey shale 10
- Eakle, A. S. (cited) 14, 16, 17
- Ellsworth, H. V. (cited) 46
- emission spectrograph 67-68
- Fay, R. O. 8, (cited) 9
- Flowerpot formation 53
- Flowerpot shale 10
- fluorite 48
- Foshag, W. F. (cited) 14, 17, 26, 36
- Frederickson, A. F. (cited) 49, 53, 67
- FrondeL, Clifford (cited) 46

ginarite	46, 48
Godlevsky, M. M. (cited)	7, 26, 45, 46, 47
Goldschmidt, V. M. (cited)	53
Goodman, N. R. (cited)	26, 48
Grabau, A. W. (cited)	7
Green, D. A. (cited)	9
Green, Jack (cited)	49
Guppy, E. M. (cited)	46, 48
Gyp Siding	28
gypsum	
"Alabaster"	9
Blaine	9, 38
boron content	54-58, 61, table 6
Cloud Chief formation	9, 40-41, 50
Medicine Lodge	9
Nescatunga	9, 41, 50, 51
origin	13, 38, 51, 65
percent of Blaine formation	9
Shimer	9, 38
halite	40, 47, 48, 59, 65
Ham, W. E. (cited)	7, 8, 14, 21, 28, 31, 41, 51, 57
Harder, Hermann (cited)	58, 59, 65
Henderson, E. P. (cited)	46, 48
howlite	46, 48, 61
hydroboracite	46, 47
hydromica	53
hydrothermal activity	7, 11
illite	53
inderborite	46
inderite	46
insects	9
insoluble residues	62
inoite	46, 47, 48
isobor	57, 65, plate I
kaliborite	46
kernite	17, 33
kurnakovite	46
laboratory techniques	61-64, 67-70
Leonardian	9
lueneburgite	43, 45, 46, 48
Medicine Lodge gypsum	9, 28
Melvin, E. H. (cited)	67
molluscs	9
Muessig, Siegfried (cited)	26
Muir, J. L. (cited)	51
Murdoch, Joseph (cited)	14, 17, 26
Nescatunga gypsum	9, 11, 41, 50, 51
anhydrite	38, 39
boron content	54-58, 62, table 6
celestite	38-39
priceite	8, 36, 37
probertite	8, 13, 18, 20, 28, 38, 39, 52, 57, 60
ulexite	8, 13, 28, 30, 34, 35

O'Conner, R. T. (cited)	67
Palache, Charles (cited)	46
Pan-American Research Laboratory	67
pandermite (priceite)	8, 11, 21, <b>36-37</b> , 41, 46, 47, 50, 60
pelecypods	9
Phillips, R. (cited)	46, 48
pinnoite	46
Poitevin, Eugene (cited)	46
pollen	9
polyhalite	48
priceite (pandermite)	8, 11, 21, <b>36-37</b> , 41, 46, 47, 50, 60
probertite	11, 13, <b>14-25</b> , 46, 50, 59, 60, 61, 62
absence of borate associates	21
abundance	18
California	14, 16, 17, 22, 23, 24, 25
chemical analyses	22, 23
Cloud Chief gypsum	12, 20, 21, 31, 41
distribution	18
formula	14
habit	16, 17, 19-21
Nescatunga gypsum	8, 13, 18, 20, 28, 38, 39, 52, 57, 60
nodules, dimensions of	16, 19-21, 38, 39
replacement by ulexite	26, 27, 31-32
solution	20, 60
x-ray diffractograms	23-25
psuedomorphs, ulexite	26, 27, 31-32
p-veatchite	46
Reynolds, R. C., Jr. (cited)	49, 53
Reynolds, W. D.	8, 27
sample preparation	68
Schaller, W. T. (cited)	7, 8, 14, 17, 26, 33, 43, 46, 48
Schleicher, J. A. (cited)	8, 14, 28
selenite	30, 31, 41, 60
Shimer gypsum	9, 28, 38
shark teeth	9
Smith, W. C. (cited)	26, 41
sodium chloride (halite)	40, 47, 48, 59, 65
Southard	8, 10, 11, 15, 18, 27, 28, 30, 34, 35, 36, 38, 41
spores	9
Staples, L. W. (cited)	36
Stewart, F. H. (cited)	46, 48
strontioiginorite	46
strontiohilgardite	46
sulfoborite	46
sylvite	47, 48
szaibelyite (beta ascharite)	46, 47
thenardite	36, 38, 40, 41
ulexite	8, 11, 13, 14, 17, 21, <b>26-35</b> , 46, 47, 50, 60
California	26, 33, 34, 35
chemical composition	33
Cloud Chief gypsum	8, 12, 31, 34, 35, 41
formula	26
habit	30, 31
Mississippian	26

Nescatunga gypsum	13, 30, 34, 35
Nevada	26
Nova Scotia	34, 35, 48
nodules, dimensions of	26, 29, 30, 31
psuedomorphs	26, 27, 31-32
Tertiary	26
world distribution	26
x-ray diffractograms	34, 35
Underwood, D. F.	8
United States Gypsum Co.	8, 15, 18, 19, 27, 29, 30, 38, 41, 60, 61
Universal Atlas Cement Co.	11, 15, 18, 20, 28, 38, 51, 52, 61
veatchite	43, 46, 48
vertebrate fossils	9
Walton, S. A., & Son	20, 28
Watonga	10, 15
Weatherford	8, 10, 11, 14, 28, 31, 34, 35, 51
Weatherford-Clinton district	8, 9, 11, 14, 15
Whitehorse group	10
x-ray diffractograms	23-25, 34, 35, 36, 37, 63

