SECONDARY SELENITE CRYSTALS IN TERTIARY STRATA IN TEXAS

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INTRODUCTION

Occurrences of selenite in the Tertiary formations of the Coastal Plain of Texas have been known for many years. Considerable discussion as to the origin and theoretical significance of these deposits has been advanced. As a result of early studies a number of hypotheses regarding the climates of the Tertiary epochs and geologic conditions under which the gypsum-bearing sediments may have been formed were advanced. Many early writers assumed that the selenite deposits were of primary origin. With this assumption the writer disagrees. Evidence derived from a study of one of these deposits which may be considered typical is presented in support of this contention. Interesting crystallographic features including numerous penetration twins and a rare crystal form, the positive hemiorthodome ($\bar{1}03$), to which the letters *ee* are assigned are described and illustrated.

DESCRIPTION OF OCCURRENCE

The selenite crystals here described are found on a branch of White Creek, three miles south of College Station, Texas. At this place erosion has produced a cliff about 30 feet high in which the crystals occur.

The section exposed is given below:

		Surface soil	3 ft.
		Cross bedded sandy clay	20 ft.
Pleistocene.	Terrace material	Basal conglomerate (pebbles 2 mm. to 1 cm. in diameter)	2 to 6 in.
Eocene.	Cockfield formation	Bedded, lignitic, clayey, porous sandstone	1 ft.

The detritus at the foot of the cliff is composed essentially of the same materials as the formations exposed higher on the cliff and has no doubt resulted from the slumping of these formations. The selenite crystals were first seen protruding from the dry surface of the detrital heap. The outer surface of the heap when dry forms a moderately hard surface composed of a matrix of sandy clay. On digging into this material one finds that the crystals decrease in

size and increase in numbers and in completeness of crystallization as depth increases. All gradations in size from minute specimens of microscopic size to the large skeletal crystals of about eight centimeters maximum dimension were found within a depth of approximately ten centimeters. The moisture content of the matrix also increases as depth increases. At the inner edge of the zone of crystallization the clayey sand was wet almost to the point of saturation. This condition indicates that calcium sulphate-bearing waters of the porous formations are slowly diffusing outward and subsequently evaporating, depositing near the surface crystals of selenite. The innermost margin of the zone of crystallization—a depth of approximately ten centimeters—is a plane determined by the loci of points at which the solution in its outward passage has lost a quantity of its solvent sufficient to reduce it to the point of saturation. Along this plane, which approximately parallels the outer surface of the matrix, precipitation is rapid, a large number of centers of crystallization are formed, and innumerable small crystals result. As the crystals are small and the supply of calcium sulphate is large, these crystals are completely developed. Moving progressively outward, diffusion and crystal growth become progressively slower and therefore larger crystals are produced. Development of the larger crystals has taken place first along certain crystallographic planes; while certain areas between these planes remain to be filled in. Development of crystals is then first as a skeleton which given sufficient time would no doubt result in a complete crystal.

The solvent bearing the calcium sulphate in solution is evidently vadose waters. Their abundance increases during rainy seasons and decreases during dry periods. The calcium sulphate in the waters is being dissolved from the underlying gypsiferous formations (Cockfield at this locality) through which it has been disseminated as the result of the chemical action of pyrite-derived sulphuric acid on the lime carbonate present in the form of fossil shells and lime nodules in some layers of this and similar formations. After every rainy period a thin, white powdery coating of gypsum may be observed on the face of cliffs of creeks of the vicinity. This coating is noticeable in a zone about four to eight inches wide about six inches to one foot above the level of the creek, and is presumably deposited from gypsiferous vadose waters percolating out of the porous formations along the water table in the valleys.

CHEMISTRY

Numerous writers have discussed the origin of the gypsum in the Cockfield and similar lithologic units in the Coastal Plain. The best and most logical explanation of these deposits was given by Penrose in his discussion of the gypsum in the Fayette beds. His account of the formation of gypsum in these beds is quoted here.

. . . Sulphur and gypsum are of very frequent occurrence, the latter often being found as twin crystals in the shape of an arrowhead. The beds frequently contain carbonate of lime in the shape of nodules, or impregnating the strata. One of the most marked characteristics of the clays, and especially of the chocolate covered beds, is a white bleached appearance on the surface, while, a few inches in, they regain their dark color. This, and the presence of sulphur and gypsum, are intimately connected phenomena, and can be easily explained by the combined decomposition of the iron pyrites, carbonate of lime, and the vegetable coloring matter of the dark clays. The iron pyrites decompose with the formation of sulphate of iron and sulphuric acid; the sulphuric acid attacks the carbonate of lime, forming gypsum and carbonic acid; the former is deposited as crystals, and the latter goes in the air and surface waters. The sulphate of iron attacks the organic matter in the clays and is again reduced to iron pyrites with the evolution of sulphuretted hydrogen and oxygen. The oxygen forms carbonic acid with the vegetable matter, and rapidly goes off into the air. This reaction repeats itself until the clay finally becomes devoid of all vegetable material, and hence of coloring matter, and exposes a white surface. The sulphur, which originally formed a part of the sulphuretted hydrogen, but which has now lost its hydrogen, is deposited as a yellow or white crust on the surface and in the cracks of the strata.[1]

The oxidation of pyrite or marcasite, primary minerals of deposits rich in organic matter, to ferrous sulphate, sulphuric acid, and free sulphur is expressed chemically by the following equation:

(1) $$6FeS_2 + 15O_2 + 2H_2O = 6FeSO_4 + 2H_2SO_4 + 4S.$$
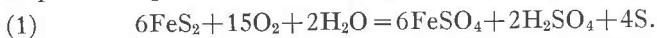
The formation of ferrous sulphate is confirmed by the presence of the mineral melanterite, $FeSO_4 \cdot 2H_2O$, in the vicinity and at numerous other localities in these sediments. The production of sulphuric acid is proved by the presence of calcium sulphate in the form of gypsum. Sulphuric acid would be present as such only momentarily, as the lime carbonate in the sediments would immediately be attacked by any acid that might be introduced in the sediments from any source whatever. According to equation 1, it is theoretically possible for free sulphur also to be formed in the process of oxidation. When natural ferrous sulphides are powdered and

[1] Penrose, R. A. F., Jr., A preliminary report on the Geology of the Gulf Tertiary of Texas from the Red River to the Rio Grande: *Geological Survey of Texas*, E. T. Dumble, *First Annual Report, Austin*, **1899**, p. 48.

treated with nitric acid, a strong oxidizing agent, in a test tube, free sulphur is produced. *It has, however, been impossible to confirm the formation of free sulphur in the natural oxidation of these sulphides by its presence in enclosing sediments.*

No authentic report of free sulphur unquestionably identified as such occurring in these deposits has been found. It is reasonable to suppose that if sulphur had been present in the free state it would still be present as such at some localities. Tests on numerous sands and several brown shales which are impregnated with malanterite have failed to reveal the presence of native sulphur.

Due to the presence of melanterite and gypsum (derived from sulphuric acid) and the absence of sulphur, the following equation seems the more logical explanation of the decomposition of the iron sulphides:

(2) $$2FeS_2 + 7O_2 + H_2O = 2H_2SO_4 + 2FeSO_4.$$
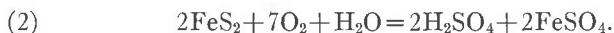
A yellow coating occurring on rocks and in crevices in coastal plain sediments has been identified as the mineral copiapite, $2Fe_2O_3 \cdot 5SO_3 \cdot 17H_2O$. This mineral occurs in minute tetragonal crystals and ranges in color through several shades of yellow. It might have been easily confused with sulphur in the absence of confirmatory optical and chemical tests. Equation 3 indicates how the two compounds, copiapite and sulphuric acid, may be formed by the action of oxygen on the ferric sulphides.

(3) $$4FeS_2 + 15O_2 + 20H_2O = 2Fe_2O_3 \cdot 5SO_3 \cdot 17H_2O + 3H_2SO_4.$$
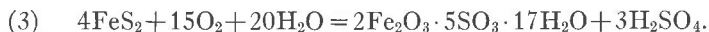
Since the products called for in equations 2 and 3 have been confirmed by their presence or by the presence of their salts, it seems logical to accept these two equations as being the true expression of the processes in action in these sediments. *The formation of free sulphur is therefore open to question and cannot be definitely settled until observation confirms without doubt the actual presence of sulphur in the free state, or as a compound which is known to be derived in situ from free sulphur in these sediments.*

For the formation of gypsum from shell material or lime nodules the following equation may be written:

(4) $$CaCO_3 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + CO_2 + H_2O.$$

CRYSTALLOGRAPHY

All specimens show essentially the same forms although the degree of development varies in different individuals. The smaller

crystals exhibit more nearly complete development than do the large ones. The smaller crystals are elongated in the direction of the c axis while the large ones are elongated in the direction of the a or clino-axis. Figure 1 illustrates the forms recognized. In the illustration b is the clinopinacoid $\{010\}$; m is the prism $\{110\}$; l is the unit hemi-bipyramid $\{111\}$; e is the positive hemiorthodome $\{\bar{1}03\}$; (see also Pl. 2, Fig. 7, lower right); and ee is the positive hemiorthodome $\{\bar{1}02\}$ (see also Pl. 2, Fig. 7, upper left).
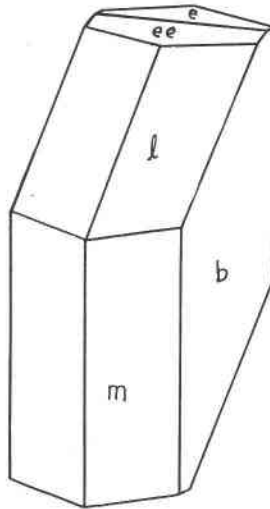

FIG. 1. Drawing illustrating crystallography of selenite.

Table I is a list of the forms present and crystallographic measurements made on them with a contact goniometer.

Cleavage is best developed parallel to b (010) and yields along this plane thin, polished folia with excellent glassy luster. Cleavage parallel to the direction of the plane (100) produces an irregular conchoidal surface. Many irregularities are present in these surfaces due to inclusions of foreign material. Cleavage fragments parallel to the plane ($\bar{1}01$) (form t, which is not present on these specimens) have a fibrous structure. The surfaces produced by this cleavage resemble the fibrous surfaces of satin spar.

Numerous inclusions of foreign particles are present in the crystals the most abundant of which are masses of clay and sand grains. One crystal was noted which had embedded within it a small

TABLE I. SUMMARY OF FORMS PRESENT AND CRYSTALLOGRAPHIC DATA

Form	Miller Symbols	Angular Relationships	Remarks
l	$\{111\}$	$111/1\bar{1}1=36°$	Deeply concave in large skeletal crystals.
m	$\{110\}$	$110/1\bar{1}0=68°\ 30'$	Moderately concave in large skeletal crystals.
b	$\{010\}$	$110/010=56°\ 30'$	Slightly concave in skeletal crystals.
e	$\{\bar{1}03\}$	edge $1\bar{1}0-\bar{1}\bar{1}0/\bar{1}03=87°$	Rounded; convex. Very poorly developed. Not recognizable on large incomplete specimens.
ee	$\{\bar{1}02\}$	edge $1\bar{1}0-\bar{1}\bar{1}0/\bar{1}02=97°$	Poorly developed on small specimens.

The form *e* (positive hemiorthodome $\bar{1}03$), is barely recognizable on the forms on which it is best developed. This face is convex and rounded making the determination of its angular relationships with known crystallographic directions difficult and of doubtful accuracy. The angle which the form $\bar{1}03$ makes with the interfacial edge $1\bar{1}0$–$\bar{1}10$—and hence with its parallel, the *c* axis—is 84°49'.[2]

Measurements made on a number of selenite crystals included in this study show a considerable range in value for this angle. These values are, however, well within the limits of error in measurements for an angle between such poorly developed forms. Determinations made on a selected few of the smaller specimens on which another face is fairly well developed yield a mean value for the angle made with the interfacial edge $1\bar{1}0$–$\bar{1}10$ of 97°. Calculations based on this value are suggestive of another positive hemiorthodome having the Miller symbols $\{\bar{1}02\}$. An examination of reference books on mineral crystallography shows the positive hemiorthodome $\{\bar{1}03\}$ to be fairly common on crystals of selenite, while no case of the positive hemiorthodome $\{\bar{1}02\}$ occurring on this mineral is recorded in these lists. According to Dr. Charles Palache,[3] this form has been reported by Cesaro on a crystal from Italy, but the form yielded only approximate measurements. In view of the fact that this form has not been designated by letters, the letters *ee* are now assigned to it.

The form *b* (010) is well developed on the small crystals and is moderately concave but well outlined by interfacial edges on the large skeletal forms. The forms *m* $\{110\}$ and *l* $\{111\}$ are also well developed on the smaller crystals and deeply concave, but well outlined by interfacial edges, on the larger skeletal specimens. Crystallization in the large skeletal forms has taken place along the symmetry plane (plane of the *a* and *c* axes) and from the center outward the following interfacial edges are developed:

b:*m*; *b*:*l*; *l*:*l*; *m*:*m*; and *m*:*l*, Plate 1. Figs. 1, 2, 3, 4, 5, and 6.

[2] Rogers, A. F., Introduction to the study of minerals, McGraw-Hill, *New York*, **1912**, p. 36.
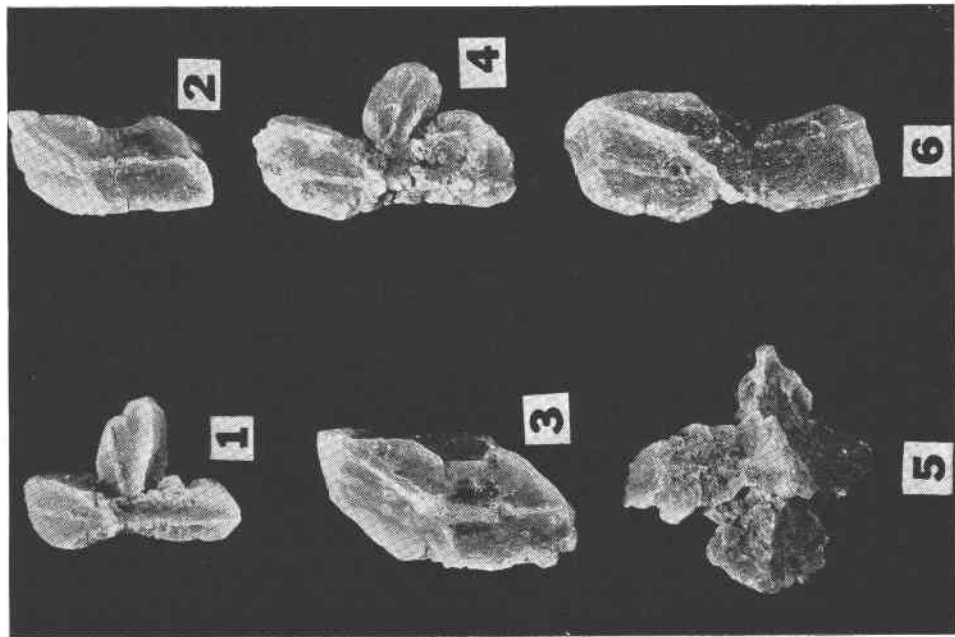
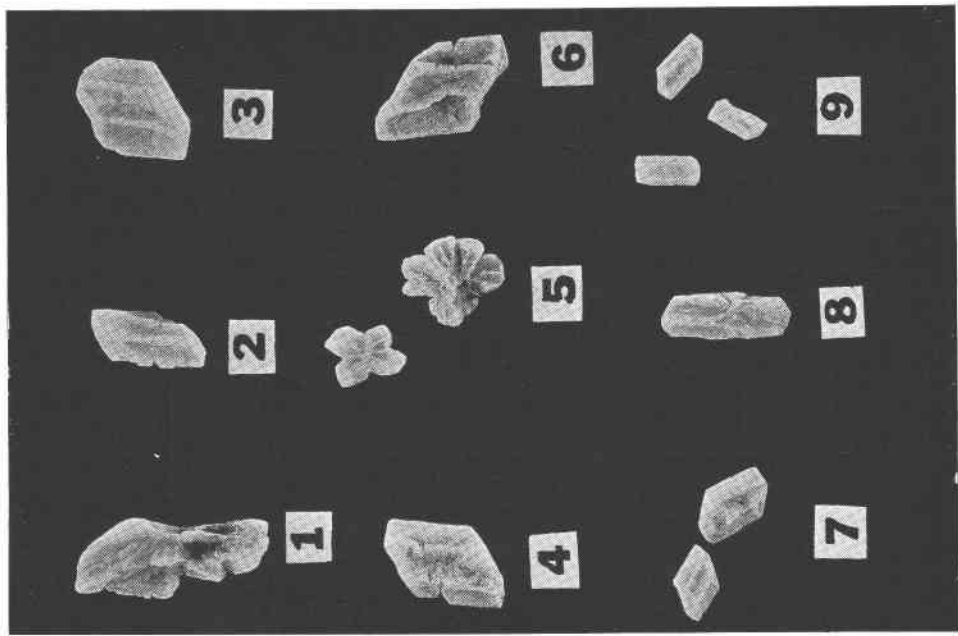[3] Letter of Jan. 17, 1933 to J. T. Lonsdale.

PLATE 2.—Selenite crystals: Figs. 1 and 6 skeletal crystals showing irregularities due to inclusions; Figs. 2, 3, 4, 7, 8, and 9 small completely developed crystals; Fig. 5 (upper left) complete

PLATE 1.—Large skeletal, individual and twinned crystals of selenite.

well-rounded pebble of jasper, presumably derived from the conglomerate at the base of the terrace deposit. The clay and sand grains included in the crystals resemble the materials of the sediments in which the selenite crystals are found. The presence of these inclusions derived from enclosing deposits of Tertiary and Pleistocene ages is evidence favoring the contention that the selenite deposits are not primary in origin.

TWINS. Many of the selenite crystals are in the form of twins exhibiting essentially the same crystal forms as the single individuals described in the preceding section. Penetration twins forming crosses by the intergrowth of two individuals and rosettes by the intergrowth of more than two individuals are common. In some cases both individuals of the cross exhibit equal development, Pl. 2, Fig. 5., while in others one individual may be deficient in size in comparison to its twin, Pl. 2, Fig. 1. In a few specimens one end of an individual may be deficient in size in comparison to its counterpart on the opposite side of its twin, Pl. 1, Fig. 5. Rosettes formed by the development of from three to five individuals radiating from a common center are very conspicuous, Pl. 1, Fig. 5. All twins from this locality are considered to be paragenic in origin. It is clear that the different individuals of any group have developed from a common center of crystallization. The so-called "fish tail" twins (twinning plane 100) which are very common in Coastal Plain gypsum deposits and which are metagenic in origin were not found in the vicinity of this locality. The small crystal illustrated in Pl. 2, Fig. 5, upper left, is the nearest perfect twin found. It consists of two equally developed individuals one of which has been rotated through an angle of approximately 45°. The other crystal in the same figure is a deformed rosette of five skeletal crystals developed from a common center, four of which are in the same plane, while the fifth is perpendicular to that plane. Plate 1, Fig. 1, is a cross penetration twin (plane of 011) of two skeletal individuals with the end of one crystal broken off, while Plate 1, Fig. 4, illustrates a skeletinized cross twin with only one end of an inferior twin developed. Plate 1, Fig. 5, is a rosette of three approximately equally developed skeletal individuals, one of which is perpendicular to the plane of the other two.