THE ORIGIN OF THE SULPHUR DEPOSITS
OF SICILY.

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INTRODUCTION.

The occurrence and associates of sulphur in nature are so varied that difficulty is frequently encountered in determining the exact manner of their formation. In some instances, the agencies which appear to have been unusually active in one locality, cannot be shown positively to have played even a minor rôle in another district. It is evident that general methods do not apply equally well to all deposits, but that rather each district must be considered as an individual unit and its geological and structural features thoroughly studied before some intelligent conception may be gained as to the probable origin of the sulphur in that particular locality.
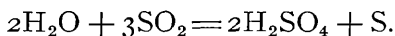
GENERAL TYPES OF SULPHUR DEPOSITS.

Depending upon general methods of formation and occurrence, economic geologists and mineralogists are accustomed to differentiate four distinct types of sulphur: (a) metallic sulphide, (b) solfatara, (c) mineral spring, and (d) sulphate.

Metallic Sulphide Type.—It has frequently been observed that the decomposition of metallic sulphides, especially pyrite, marcasite, galena, sphalerite, and stibnite, have produced thin crusts of sulphur, either in a pulverulent form or as masses of small aggregated crystals, which fill the crevices of the rock or line the walls of small geodes. This type is merely of mineralogical interest, as the thin layers of sulphur which result rarely exceed a few inches in thickness.

Solfatara Type.—Issuing from a volcano simultaneously with certain gases, are numerous substances, which, although gaseous at high temperatures, are deposited in a solid form upon cooling.

Among these substances, which are known as sublimates, sulphur is one of the most conspicuous. However, the sulphur thus formed cannot always be distinguished from that produced by secondary changes, namely from the interaction of liberated gases. Most of the analyses of the gases given off from either active or extinct volcanic vents reveal varying amounts of either H_2S or SO_2. From the H_2S thus given off, sulphur may be formed by incomplete oxidation according to the equation: $2H_2S + O_2 = 2H_2O + 2S$. The formation of sulphur in solfatara regions was formerly considered to be due largely to a reaction between H_2S and SO_2, whereby water and free sulphur were formed. This reaction, while taking place readily in the laboratory, has been shown by A. Brun[1] to be practically impossible in nature. Also, in a consideration of the agencies operating in solfataric regions, reference should be made to the experiments of C. Geitner,[2] and of E. Jungfleisch and L. Brunel.[3] These investigators have shown that SO_2 and water vapor react out of contact with air even at ordinary temperatures, the action being accelerated by heat and concentration of SO_2. Above 160° C. sulphur and sulphuric acid are produced according to the following reaction:

$$2H_2O + 3SO_2 = 2H_2SO_4 + S.$$

Below 160° C., $H_2S_2O_4$ is formed as an intermediate product which, upon heating or standing, breaks down to S and H_2SO_4.

Mineral Spring Type.—Sulphur deposits are also quite common around mineral springs, where, by the action of oxygen from the air upon the aqueous solution of H_2S, the sulphur is slowly displaced and appears usually in the form of a fine whitish powder. The mineral associates of this type are usually some form of $CaCO_3$, as limestone, calcite, aragonite, or travertine, and gypsum. However, the chemistry involved in the deposition of sulphur from mineral springs is not quite as simple as that just indicated. More involved changes are also taking place which cannot be so easily traced step by step, but which con-

[1] *Chem. Zeitung,* No. 15, p. 127, 1909.
[2] *Ann. der Chem. u. Pharm.,* Vol. 129, p. 350, 1864.
[3] *Compt. rend.,* Vol. 156, p. 1719, 1913.

tribute toward producing the sulphur and associated minerals mentioned. A. Bechamp[4] has shown that when H_2S is passed into water containing suspended $CaCO_3$, the CO_2 is replaced and two soluble calcium compounds are formed:

$$2CaCO_3 + 2H_2S = Ca(SH)_2 + H_2Ca(CO_3)_2.$$
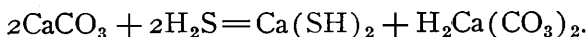
C. Palmer[5] has shown that the sodium and potassium salts, which are always present in mineral springs, increase this solvent action of a hydrogen sulphide water on calcium carbonate. The calcium hydrosulphide formed will, upon the escape of the H_2S, deposit gypsum, or calcite or aragonite according to the following reactions:

$$Ca(SH)_2 + 2O_2 + 2H_2O = CaSO_4.2H_2O + H_2S$$
$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + H_2S.$$
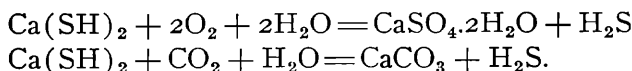
Another force which is usually active in the mineral spring type is the rôle played by small organisms that live and thrive in sulphureted water, and that S. Winogradsky[6] has named sulphur bacteria. These organisms possess the power of oxidizing H_2S to H_2SO_4, and of storing free sulphur in their cells when an excess of this gas is present. The H_2SO_4 so formed attacks in turn the calcium bicarbonate taken into the cell from the water, and returns it to the medium in the form of calcium sulphate. Still other reactions might be mentioned in connection with the mineral spring type. Soluble polysulphides and thiosulphates, which often accompany the sulphides in natural waters, are decomposed by CO_2 with the liberation of H_2S and S. Finally, Raffo and Marncini[7] have shown that colloidal sulphur can be carried in solution, and that a solution is stable which contains S, H_2SO_4, and Na_2SO_4 in the following proportions: S (colloidal) 2.79–2.60 per cent., H_2SO_4 6.43–7.00 per cent., and Na_2SO_4 3.75–3.92 per cent. Any change in the concentration of the salt will cause a precipitation of the sulphur. It will thus be seen that many factors are operative in the mineral spring

[4] *Ann. chim. phys.,* 4th ser., Vol. 16, p. 234, 1869.
[5] Bull. U. S. Geol. Surv., No. 340, p. 455, 1908.
[6] *Botanische Zeit.,* Vol. 45, Nos. 31–37, 1887.
[7] *Zeitschr. Chemie Ind. Kolloide,* Vol. 9, p. 58, 1911.

type, each one contributing either directly or indirectly to the production of sulphur and the associated minerals.

Sulphate Type.—Sulphur is commonly found intimately mixed with, or in the vicinity of, bituminous gypsum, which in turn is associated with other sedimentary rocks. It is usually assumed that the bituminous matter of the gypsum causes a reduction of the sulphate of calcium to the sulphide with the production of CO_2 and H_2O. The resulting sulphide is then further decomposed by CO_2, H_2O, and O_2, yielding calcium carbonate and sulphur. Sulphates are, however, very stable compounds and their reduction at ordinary temperature by lifeless organic material is to be seriously questioned. On the other hand, it has been known for some time to bacteriologists that certain living micro-organisms are capable, under certain favorable conditions, of reducing sulphates in solution with the liberation of hydrogen sulphide. This important biochemical reaction has been only recently alluded to in geological literature[8] and then but briefly.

OBJECT OF THIS INVESTIGATION.

The sulphur deposits of Sicily occupy the south-central portion of the island and are distributed over an area extending from Centuripe in the east to Gibellina in the west, approximately 160–170 km. in an east-west direction, then south to the coast, with a maximum width of about 90 km. The sulphur bearing stratum is not continuous over this entire area but is restricted to isolated, basin-like deposits. After the deposition of the sedimentary rocks with their disseminated sulphur, violent terrestrial movements have broken and tilted the layers leaving some of them in an almost vertical position (see Fig. 94). Subsequent erosion of these disturbed earth blocks has not only, in some instances, made it extremely difficult to correlate corresponding strata in even adjoining districts, but has destroyed some of the deposits as well, so that it is extremely probable that the sulphur area was more extensive in earlier geological periods than at present. In other places, the sulphur bearing layers are still con-

[8] O. Stutzer, "Die Wichtigsten Lagerstätten der Nicht-Erze," Vol. I, p. 259, 1911.

cealed by more recent sedimentary deposits. The mines are concentrated in groups where the ore is richest and the expense of extraction least (see Fig. 84).

With reference to the origin of these sulphur deposits, numerous and diverse theories have been at various times proposed by different investigators. Some have argued for an explanation
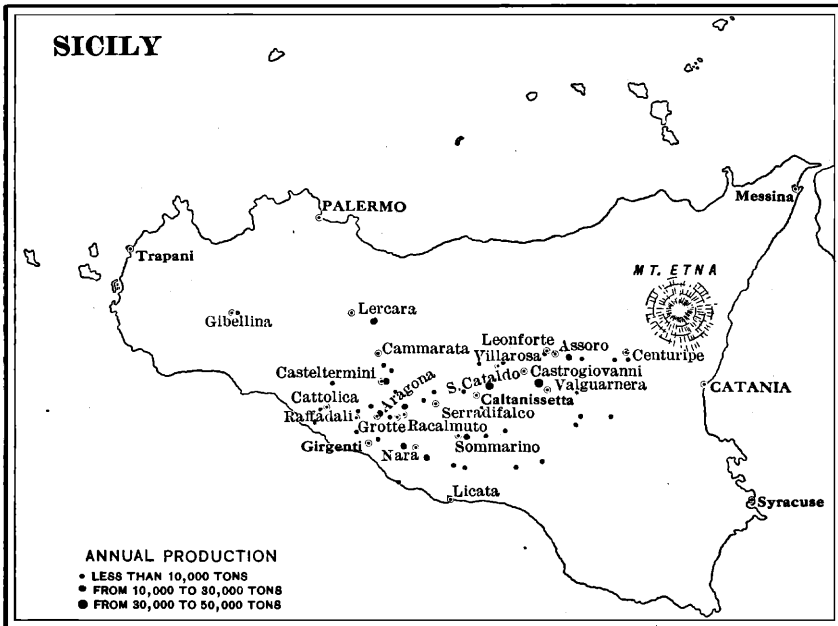

SICILY

PALERMO
Messina
Trapani
MT. ETNA
Gibellina
Lercara
Cammarata
Leonforte Assoro
Villarosa Centuripe
Casteltermini
Castrogiovanni
S. Cataldo Valguarnera
Cattolica Aragona
Caltanissetta
CATANIA
Raffadali
Serradifalco
Grotte Racalmuto
Girgenti
Nara
Sommarino
Licata
Syracuse

ANNUAL PRODUCTION
• LESS THAN 10,000 TONS
● FROM 10,000 TO 30,000 TONS
● FROM 30,000 TO 50,000 TONS

FIG. 84. Map of Sicily showing location and relative productive importance of sulphur mines. Scale 1 : 3,000,000. (After Baldacci.)

based on solfataric action, others were firmly convinced that these deposits were typical mineral spring types, while still others have endeavored to utilize the gypsum in an attempt to explain these enormous, although not exceedingly rich, deposits, which have been worked more or less continuously for the past three centuries.

Within recent years, the research work carried on along biological-chemical lines has been extremely fruitful, and the mineralogist and geologist have, at present, at their disposal a much

larger fund of information than was available when the majority of these theories were proposed. In view of the many conflicting theories which have been advanced, the rather early date of many of them, and the strides of science latterly, a reëxamination was considered very desirable. It was in an endeavor to explain these sulphur deposits in the light of modern biological-chemical reactions and under normal conditions, especially with reference to temperature, that this investigation was undertaken.

GEOLOGY OF THE SULPHUR DISTRICTS OF SICILY.

Before taking up the origin of the sulphur deposits, with which we are more especially concerned, we must consider very briefly the main geological strata of that section of the island of Sicily in which the sulphur mines occur. For the interpretation of the geology of this exceedingly complex region we are largely indebted to S. Mottura[9] and L. Baldacci,[10] whose memoirs are always quoted on works dealing with Sicilian sulphur. Stelzner-Bergeat[11] and O. Stutzer[12] have rendered the data of these noted Italians more accessible by their clear, summarized accounts in German.[13]

The succession of the formations here given cannot be considered absolutely constant in all sections of the sulphur-bearing district. In some places one or even several members of the series may be entirely lacking, while in other places the order

[9] " Sulla formazione tertiaria nella zona solfifera della Sicilia," *Memoire R. comitato geologico d'Italia*, Vol. I, 1871; reprinted: Caltanissetta, 1910, edito a cura della Societa dei Licenziati della R. Scuola Mineraria di Caltanissetta.

[10] Descrizione geologica dell' Isola di Sicilia," *Memorie descrittive della Carta geologica d'Italia*, Vol. I, Rome, 1886.

[11] " Die Erzlagerstätten," Vol. I, p. 457, 1904.

[12] " Die Wichtigsten Lagerstätten der Nicht-erze," Vol. I, p. 197, 1911.

[13] See also: G. von Rath, *Neues Jahrb. f. Min. Geol. und Pal.*, pp. 584–603, 1873; Ch. Ledoux, *Annales des mines*, (7), 7, pp. 1–84, 1875; A. V. Lasaulx, *Neues Jahrb. f. Min., Geol. und Pal.*, pp. 490–517, 1879; E. Stoehr, " Notizie preliminari su le piante ed insetti fossili della zona solfifera della Sicilia," *Boll. R. Com. geol.*, No. 9–10, 1875; Ref. *Neues Jahrb.*, p. 321, 1877; *Neues Jahrb.*, pp. 169–171, 1874.

may vary slightly from that given below which might be considered, however, as the normal sequence, especially in the south-central portion of the Island.

UPPER PLIOCENE.

Yellow Sands and Sandstones.—In the sulphur bearing section the youngest formation which is usually encountered is that of the yellow sands of the Upper Pliocene. The sands are more or less cemented, the binding material being in some cases calcium carbonate, and in others, silicious material. These sands contain numerous marine fossils and may reach a maximum development of over one hundred meters.

Shell Breccia.—Below the yellow sands and sandstones is a formation known as the shell breccia (tufo calcareo o breccia conchigliare). It is a limestone formation of an earthy yellow color, abounding in fragments of fossil shells. The thickness of this formation varies considerably, from a few meters to over one hundred meters. The shell breccia rests in turn upon *blue clays,* which also contain marine fossils. This series, from the blue clays at the bottom to the yellow sands at the top, is usually nearly horizontal, with a slight dip to the south. It rests almost always unconformably upon the Lower Pliocene. Fig. 85 illus-
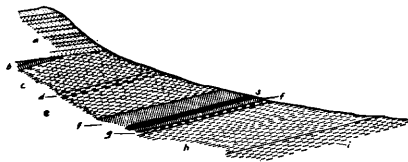

FIG. 85. Profile of strata near Caltanisetta. (After Ledoux.)

a = sandstones, 100 meters; b = shell breccia, 100 meters; c = blue clay, 60 meters; d = foraminiferous marls, 10 meters; e = gray clay, 60 meters; f = gypsum and clay, 25 meters; S = sulphur ore, 4 meters; g = calcareous tripoli, 5 meters; h = saliferous clay, 80 meters; i = gray clay, 200 meters.
Scale 1 : 15,000.

trates only in a general manner the succession and thicknesses of the various strata near Caltanissetta. The profile, however, does not reveal the unconformity at the close of the Lower Pliocene.

LOWER PLIOCENE.

Foraminiferous Limestone.—This formation is also known as the " trubi " and has a variable composition, passing from an impure clay to a true limestone. It is stratified and conformable with the underlying gypsum-sulphur formation, and from this fact it might be inferred to belong to the same period as the latter (upper Miocene), but the fauna, according to Baldacci, is decidedly Pliocene in character. It has a maximum thickness of 150 meters. In some localities beds of clay are found between these limestones and the gypsum underneath (see Figs. 2 and 10).

UPPER MIOCENE.

The Gypsum-sulphur Formation[14] *(Serie gessoso-solfifera).*— This formation is by far the most important, commercially, of the entire geological series, as it is in this series of rocks that the deposits of sulphur are located. They rest directly upon the tripoli and generally in perfect conformity, indicating that the formations succeeded one another without any violent terrestrial
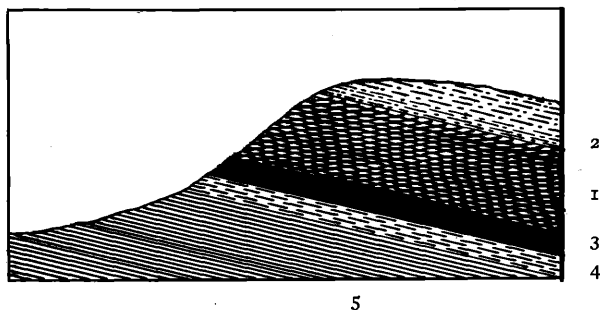

FIG. 86. Cross-section of a sulphur mine southeast of Castrogiovanni. (After Mottura.)   The gypsum-sulphur formation rests conformably upon the tripoli.   1 = Foraminiferous limestone (or "Trubi") ; 2 = Gypsum; 3 = Sulphur rock; 4 = Tripoli; 5 = Marl.
Scale 1 : 1500.

disturbances. Fig. 86, representing a cross section of a sulphur mine southeast of Castrogiovanni, illustrates this conformity.

[14] E. Kayser places this formation in the Lower Pliocene. " Lehrb. d. Geol." Part 2 (Formationskunde), 3d ed., p. 592, 1908.

The gypsum, which comprises the upper member of the gypsum-sulphur series, is very extensive, in its horizontal as well as in its vertical extent. It covers an area of over 800 sq. km., and possesses in a number of places a thickness of over 100 meters. It not only conceals the true sulphur bearing rock beneath, but extends into areas in which the sulphur is entirely absent. The fossils that have been found in the gypsum, while not very abundant, indicate, however, marine conditions.

Sometimes the sulphur is found in small, irregular, lens-shaped masses scattered through the gypsum. When thus found it is very pure, but so limited in extent that it is mined only when it is in the proximity of the true sulphur beds. The beds or zones which contain the sulphur of economic importance occur in al-
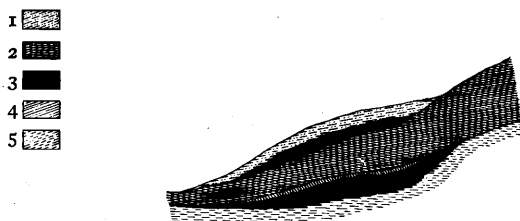

FIG. 87. Mine Zubi (San Cataldo). Sulphur beds near the top as well as the bottom of the gypsum formation. 1 = Foraminiferous limestone (or "Trubi"); 2 = Gypsum; 3 = Sulphur rock; 4 = Calcareous or Sandy gypsum; 5 = Tripoli.

Scale 1 : 8,000.

most every case toward the base of the gypsum formation. At times, however, a sulphur zone is found near the top as well as near the bottom of the gypsum, as is seen in Fig. 87, which represents a vertical section of a mine near San Cataldo and for which I am indebted to Mr. A. G. Oliveri.

The individual sulphur beds vary in thickness from one meter to, in rare instances, almost thirty meters. Generally in a given locality three or four beds are encountered, one above the other, separated from each other by narrow, sterile layers of bituminous, salty clays and shales (tufi). These sterile intercalations rarely exceed one meter in thickness. A cross section of one of the mines at Sommatino, Solfara Grande, Fig. 88, reveals six

independent beds varying in thickness from 2 to 8.5 meters and possessing an aggregate thickness of over 30 meters. The sulphur content in beds 2 and 12 averages 18 per cent.; in beds 4 and 10, 22 per cent.; and in 6 and 8 about 26 per cent. The bituminous, and more or less salty shales (tufi) which separate the various sulphur beds are also found interspersed through the gypsum above. The distribution of the sulphur zones and their relation to the gypsum-sulphur formation can, perhaps, be best
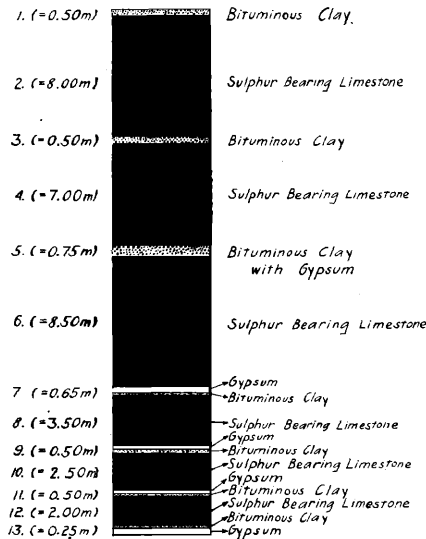

FIG. 88. Cross-section of *Solfara Grande di Sommatino*. (After Mottura.)
Scale 1 : 500.

illustrated by a more detailed account of a few typical localities.

Numerous sulphur mines are to be found in the vicinity of Racalmuto and Grotte. Best known are those of Mount Cimicia and Pernice-Cannatone. With the exception of small, isolated lenses of sulphur scattered here and there through the gypsum, the occurrence at Mt. Pernice consists of two rich zones. The upper (stagnone) lies between the gypsum and "trubi." It has an average thickness of 10 m. with a sulphur content of 30 per cent. and dips 25° E.S.E. Below this zone is a massive bed of gypsum (127 m.) with interbedded shales. Below this bed of

gypsum a 1.30 m. layer of bituminous shale is found with a small amount of sulphur, and then the second sulphur zone is encountered, which is separated into beds by "tufi." Here the dip varies from 35–40° SE. and the sulphur content from 15–25 per cent. Then follows the customary silicious limestone and finally the tripoli.

On Mt. Cimicia we find the Giona, Mendola, and Cozzo Tondo mines. Here the sulphur bearing bed varies from 2–3.5 m. and the sulphur from 18–20 per cent. Characteristic of these mines is the impregnation of the sulphur zone with an unusually large amount of bituminous matter. As a result, the crude sulphur is dark colored, containing 6–8 per cent. bitumen.

Near Racalmuto are to be found the Tulumello, Bordonaro, and Alfano mines. Here the sulphur bearing zone is about 4 m. in thickness and extends for about 250 m. in an E-W direction. The sulphur content varies from 20–23 per cent. and the rocks have a dip from 65–70° to the south. Another important group of mines is to be found near Naro, consisting of Virdilio, Min-
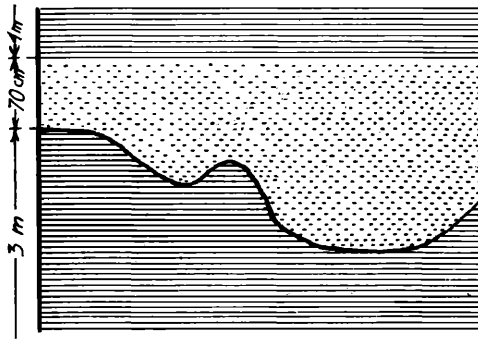

FIG. 89. Shale unconformable with lower sulphur bed. (After Stutzer.)

tina and Mintinella. The sulphur bed, which in this district is about 15 m. in thickness, is overlain by "trubi" and underlain by silicious limestone. The dip is 25° to the south and the average sulphur content is approximately 50 per cent., reaching, however, in isolated places as high as 80–90 per cent.

Some of the most productive mines of the entire Island are located in the vicinity of Caltanissetta. One of the main pro-

ducers in this section is the Trabonella. Here the dip measures 30° to the south, but not far distant it is increased to 52°. The aggregate thickness of the sulphur bearing strata reaches 22 m., while the sulphur averages 18 per cent. At the Gessolungo-Trigona Mine, located also near Caltanissetta the sulphur occurs in two beds separated by bituminous shale and limestone. It was at this mine that O. Stutzer reported a cross bedding of the limestone and sulphur bearing strata with erosion of the lower sulphur bed before the deposition of the over-lying shale. The second sulphur bed, however, lies conformably upon the shale (see Fig. 89).

Near Sommatino the following mines are to be found: Solfara Grande, Solfarella di Sommatino, and Solfara del Fiume de Riesi. The occurrence of the sulphur at the Solfara Grande di Sommatino has already been referred to. At the Solfarella di Sommatino we observe the following cross section:

	Meters.
Sulphur bed of varying thickness	
Bituminous shales	40.00
Sulphur bed ("Vanella bianca")	6.00
Bituminous shale	0.50
Sulphur bed ("Vanella soriata")	5.00
Bituminous shale	0.50
Sulphur bed ("Vanella bastarda")	6.00
Tripoli and silicious limestone	12–20

The aggregate thickness of the sulphur beds is about 20 meters while the sulphur content appears to be in the vicinity of 31 per cent. It is apparent that the sulphur content of the sulphur rock is far from constant and that it varies greatly. This fact is illustrated by the following table:

	Per Cent.
Montedoro	13–25
Pernice at Racalmuto	30
Muculufa	17–18
Naro	50
Licata	15
Juncio Group at Caltanissetta	20–22
Trabonella	18
Madore (Lercara)	20
Grottacalda (Valguarnera)	25–27
Sommatino	18–26
Cimicia (Racalmuto)	21

In the above descriptions reference has been made to the sulphur bed or zone, but nothing has been said as to the nature or occurrence of the sulphur in these beds. The sulphur occurs disseminated throughout the limestone, which, in some instances, is rather cellular, and again, quite compact. The limestone, grayish, brownish or light yellow in color, is more or less impure from admixture of clay, gypsum, or bituminous matter. At intervals thin seams or bands of pure sulphur, from 5 mm. to 2 cm. in thickness, are seen extending parallel to the bedding (see Fig. 90). Frequently small pockets and veins of secondary sulphur
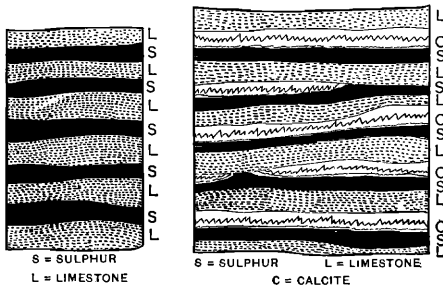

FIG. 90.   FIG. 91.

FIGS. 90 and 91. Diagrammatic sketches, illustrating occurrence of sulphur in limestone. (After Mottura.)

occur which cut through the limestone without any regularity. At times above the sulphur seams are open spaces which permit crystals of secondary calcite to attach themselves to the hanging wall with their sharp points projecting downward (Fig. 91). The walls of small geodes and fissures in the limestone are often completely covered with beautiful crystals of sulphur, calcite, aragonite, gypsum, celestite, barite, quartz and melanophlogite.

Considering the lens or basin-like character of the sulphur formation, the large number of deposits, their independence and their small extent, Mottura suggested that deposition must have taken place in restricted basins or lagoons. Near Villarosa, the sulphur formation has a length of approximately 7 km.; at Caltanissetta, not over 5–6 km.; at San Cataldo, less than 2 km.; and at Grottacalda, 3.5–4 km. The width of the formation varies from 300 m. to 1 km. An average would probably approximate 500 m. Through the courtesy of Mr. A. G. Oliveri, the follow-

ing sketches were obtained, illustrating the character of the sulphur formation at the Aronica, Severino, Bosco and Stincone mines (Figs. 92 and 93).

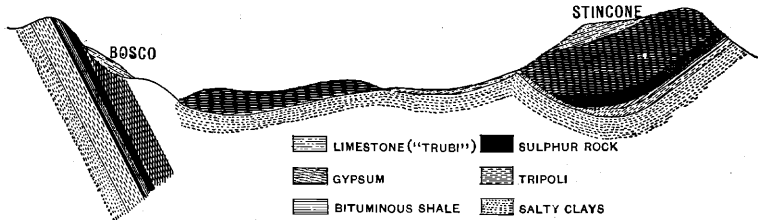Below the gypsum-sulphur formation there often occurs a

FIG. 92. Character of sulphur formation at Bosco and Stincone mines (Serradifalco).
Scale 1 : 12,000.

compact limestone which at its base becomes silicious and grades into the underlying tripoli. Its thickness is occasionally 50–60 meters, but usually only 1–3 meters.

Tripoli.—This deposit reaches a maximum development at Racalmuto, where it is 150 meters in thickness. Generally, how-
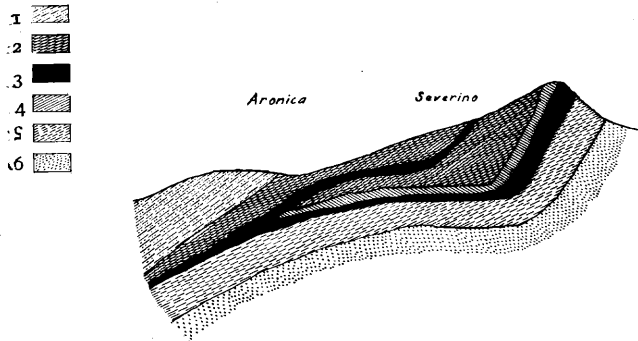
FIG. 93. Mines Aronica-Severino (Castrogiovanni). Character of the Sulphur formation at Aronica and Severino mines. 1 = Foraminiferous Limestone (or "Trubi"); 2 = Gypsum; 3 = Sulphur Rock; 4 = Calcareous or Sandy Gypsum; 5 = Tripoli; 6 = Clays, Salty and Bituminous.
Scale 1 : 8000.

ever, it does not exceed 60 m. and frequently is only 2–3 m. thick. Its color varies from white or gray to a dark brown. It has a loose and mealy texture and consists largely of fragments of
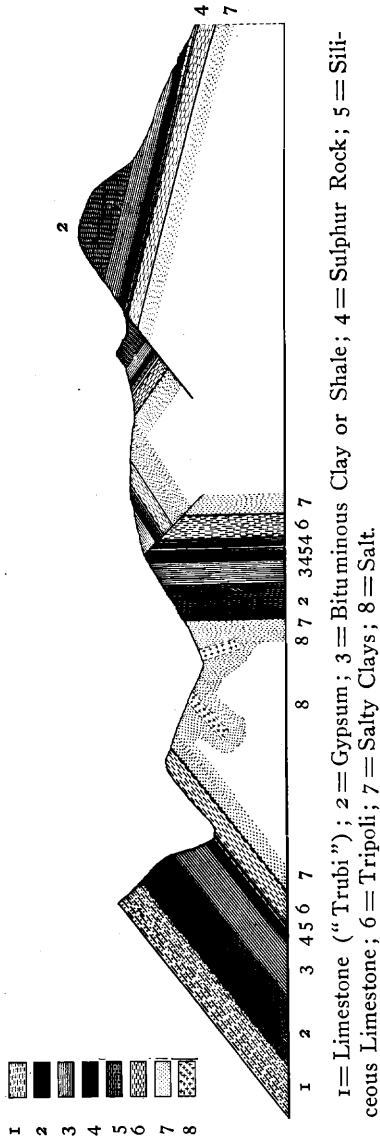
FIG. 94.   Cross-section near Racalmuto, illustrating salt deposits in the salty clays below the tripoli, as well as the disturbed character of the strata.   (After Oliveri.)   Scale 1 : 15,000.

1 = Limestone ("Trubi"); 2 = Gypsum; 3 = Bituminous Clay or Shale; 4 = Sulphur Rock; 5 = Siliceous Limestone; 6 = Tripoli; 7 = Salty Clays; 8 = Salt.

radiolaria, diatoms and sponges.   This formation contains a considerable number of fossil fish, insects, plant remains, and and occasionally some lignite.

Salty, Arenaceous Clays.—Finally, below the tripoli, lie salty,

arenaceous clays that contain a great deal of gypsum. This formation may reach the enormous thickness of over 1,000 meters. The clays are salty to the taste and at times contain lenticular masses of pure salt. This is especially true in the vicinity of Racalmuto and Grotte, figure 94, as well as farther to the northwest, between Casteltermini and Cammerata (Fig. 95).
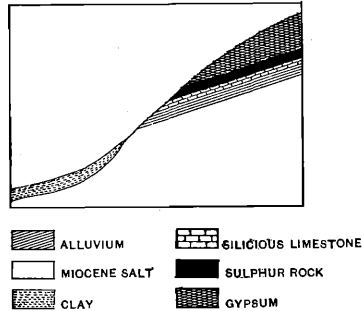

FIG. 95. Sulphur and salt deposits at the Antinori mine near Casteltermini. (After Mottura.)
Scale 1 : 18,000.

These clays contain interbedded layers which are rich in bituminous material and petroleum.

In the above descriptions no attempt has been made to treat exhaustively the geology of any one of the individual regions, as the main object of incorporating a general survey of the strata is to render the discussion of the origin more intelligible.

ORIGIN OF THE SULPHUR DEPOSITS.

With the above discussion of the sequence and character of the formations in the sulphur-bearing districts, the distribution of the sulphur in the limestone and its relation to the accompanying gypsum in mind, the origin of the sulphur may be more easily discussed. It is but natural that the mines, located as they are in a region easily accessible to Europeans, should have been frequently visited and that numerous theories should have been advanced concerning them.

The earlier theories are of sufficient interest to warrant a brief survey.

Earlier Theories.[15]—F. Hoffmann[16] seems to have been one of the first to hazard an opinion upon the origin of the sulphur. He considered it the result of volcanic activity, formed in the same manner as that found at the Solfatara Pozzuoli near Naples, or that produced on the Islands of the Lipari. According to M. Maravigna[17] the sulphur is the result of the decomposition of H_2S dissolved in water which likewise carried marls in suspension. A. Paillette[18] and G. Bischof[19] noted the association of bituminous gypsum with the sulphur and concluded that the latter was due to the decomposition of H_2S, produced by the action of CO_2 and water vapor upon CaS, the origin of which should be attributed to the reduction of gypsum by means of organic material. It should here be noted that although water heated to a temperature of approximately 44° C. is sufficient to decompose CaS, a temperature approaching 700° C. is required for the reduction of calcium sulphate by carbonaceous material,[20] a temperature entirely inconsistent with the existence of the associated minerals, especially gypsum. Not a single feature is present in the sulphur beds to warrant an explanation involving elevated temperatures.

S. Mottura,[21] who in the year 1871 published the first of his comprehensive memoirs, interpreted the beds of tripoli, as well as the sulphur-bearing limestone with its associated gypsum, as lacustrine and not marine deposits. He was led to this belief by the number, independence, small extent, and structure of the sulphur beds, as well as by the presence, especially in the lower horizons, of some fossils of fresh-water fish. These fresh or

[15] Some of the earlier theories will be found in Baldacci's Monograph, p. 331.

[16] Karsten's und von Dechen's Archiv, Vol. 13.

[17] *Compt. rend.,* Vol. 7, p. 304, 1838.

[18] *Compt. read.,* Vol. 16, p. 988, 1843.

[19] Bischof claims priority with reference to the reduction theory, *Chemische und physikalische Geologie,* 2, pp. 144–164, 1851.

[20] H. O. Hofman and W. Mostowitsch, *Bull. Am. Inst. Min. Eng.,* Vol. 47, pp. 917–939.

[21] " Sulla formazione terziaria nella zona solfifera di Sicilia," *Mem. Com. Geol.,* Vol. 1, 2, 1871 and 1872; also " Formation solfifere de la Sicile," *Bull. d. soc. d'industr. min.,* (2), 10, 147, 1881.

brackish water lakes were supposed to have been fed by springs bringing the sulphur and calcium carbonate in one of two possible forms, either as H_2S and the bicarbonate of calcium, or else as a monosulphide of calcium. Mottura was likewise of the opinion that the CaS was the result of the reduction of the sulphate by organic matter under the influence of internal heat. Like Mottura, A. von Lasaulx[22] considered fresh-water basins the recipients of thermal springs which contained both H_2S and $CaCO_3$. G. Spezia[23] has developed a similar theory, believing, however, that thermal springs carrying $SrSO_4$, SiO_2, as well as $CaCO_3$ and H_2S in solution deposited their load in shallow sea basins.

According to L. Baldacci[24] the gypsum found associated with the sulphur must be regarded as the result of concentration of marine water in broad, shallow lagoons. This gypsum, which is considered the source of the sulphur, is thought to have been reduced to the sulphide by the action of the hydrocarbon methane, which was discharged in the lagoons by mud volcanoes (maccalube). However, if methane is to act as a reducing agent, it must itself in turn be oxidized. Inasmuch as a temperature of approximately 500° C. is required to induce CH_4 to unite with free oxygen, it would hardly seem probable that this gas could withdraw oxygen from a sulphate at an ordinary temperature. The theory of the reduction of gypsum by hydrocarbons finds another advocate in R. Travaglia.[25] He does not, however, consider the origin of the hydrocarbons the product of maccalube, but rather the result of the decay of concentrated organic matter.

O. Stutzer[26] emphasizes the sedimentary origin of these de-

[22] *Neues Jahrb.,* p. 490, 1879.

[23] " Sull'origine del solfo nei giacimenti solfiferi della Sicilia, Torino," 1892; ref. *Neues Jahrb.,* I, p. 281, 1893; also *Ztschr. f. Kristallogr.,* Vol. 24, pp. 412–414, 1895.

[24] " Descrizione geologica dell'Isola di Sicilia," *Mem. descritt. d. Carta geol. d'Italia,* I, pp. 331–374, 1886.

[25] " Contributo agli Studii sulla genesi dei giacimenti di solfo," *Boll. d. R. Com. Geol. d'Italia,* Vol. 20, pp. 110–118, 1889; ref. *Neues Jahr.,* Vol. 2, p. 74, 1892; also F. Fuchs and L. De Launay, " Traité des Gites Minéraux et Metallifères," Vol. I, p. 273, 1893.

[26] " Die Wichtigsten Lagerstätten der Nicht-erze," Vol. I, pp. 254–262, 1911; *Zeit. deut. geol. Ges.* (Monatsb.), pp. 8–12, 1911.

posits, additional proof of which he finds in the Gessolungo-Trigona Mine, near Caltanissetta. Here he noted two sulphur beds, the lower three meters in thickness, the upper four meters. The two beds are separated by 70 cm. of sterile shale. The new features observed are a cross bedding of some of the strata, and an unconformity in some places between the lower sulphur and overlying shale (Fig. 6). According to Stutzer the sulphur was due to the oxidation of the H_2S but some difficulty is experienced in finding a suitable explanation of the origin of this gas. Two sources are suggested: first, from organic material by putrefaction, and second, from inorganic sulphates through reduction, attention being called to the fact that the organic material necessary for the reduction is never absent from the sulphur beds. We are led to believe from a statement made on page 259 of his "Lagerstätten der Nicht-erze" that his theory for the Sicilian deposits involves reduction by ascending gases, for he refers in the following words to the reduction of sulphates, the italics are the writer's: "Die bei diesen Prozessen notwendige organische Substanz liefert entweder die gleichzeitig lebende Tier- und Pflanzenwelt oder sie wird in Form von Gasen von unten her zugeführt. *Destillation bituminöser Sedimente, z. B. in Sizilien;* Entgasung von Steinkohlenflozen, z. B. bei Kokoschütz in Oberschlesien."

A theory that would seem in harmony with geological facts should explain not only the presence of the sulphur beds in the limestone and their absence in the gypsum above, but also their formation at normal temperature and under circumstances which will confine the formation and deposition of the sulphur to these land-locked basins or lagoons, the general outlines of which, although badly faulted and eroded, are still nevertheless somewhat retained.

BACTERIAL REDUCTION THEORY.

If we abandon the volcanic idea as the source of the H_2S, we are practically forced to admit that the major portion of this gas must, by some means, be derived from sulphates. It has been shown that the reduction of sulphates by means of CH_4

does not seem probable, and it has also been pointed out that a temperature of approximately 700° C. is necessary for the reduction of calcium sulphate by carbonaceous material. Thus, the inquiry is naturally raised as to whether sulphates are capable of reduction at ordinary temperatures, and if so, what evidence we have of this reaction in nature.

Our attention was first called to the reduction of sulphates at ordinary temperatures, with a resultant liberation of H_2S, by the observations of L. Meyer,[27] F. Cohn,[28] E. Plauchud,[29] A. Etard and L. Oliver.[30] These pioneer investigators failed, however, to distinguish between the microörganisms which possess the power of reducing sulphates with an evolution of H_2S, and the bacteria which thrive in a medium of H_2S, and oxidize this gas to S and H_2SO_4. In the instances referred to, beggiatoa (sulphur bacteria) were believed to cause both reduction and oxidation. It remained for S. Winogradsky[31] to prove conclusively that beggiatoa can perform only the latter function, namely, the oxidation of H_2S to H_2SO_4, and that, in so doing, they accumulate sulphur in their cells as an intermediate product. These organisms are, however, incapable of producing any of the sulphureted hydrogen.

For the first exhaustive study on the sulphate-reducing bacteria, we are indebted to W. M. Beyerinck.[32] In 1895, he was attracted to this problem in an endeavor to explain the abundant liberation of H_2S in the ditches of Amsterdam, especially during the months of July, August and September. As a result of his efforts he was able to isolate one of the anaërobic bacteria capable of causing such a reduction. To it he assigned the name "*Spirillum desulfuricans.*" Beyerinck isolated it in a liter of ditch water to which were added small amounts of mineral salts, sulphates, and traces of organic substances. This addition of or-

[27] *Journ. f. prakt. Chemie,* Vol. 91 p. 5, 1864.

[28] *Ber. botan. Sektion der Schles. Gesellsch. f. Vaterländ. Kultur,* f. 1876, p. 115; ref. *Der Naturforscher.,* Vol. 10, p. 340, 1877.

[29] *Compt. rend.,* Vol. 84, p. 235, 1877; *Compt. rend.,* Vol. 95, p. 1363, 1882.

[30] *Compt. rend.,* Vol. 95, p. 846, 1882.

[31] *Botanische Zeit.,* Vol. 45, Nos. 31–37, 1887.

[32] *Centralbl. f. Bakt.,* 2d Abt., Vol. 1, pp. 1, 49, 104, 1895.

ganic material was essential, since the energy necessary to bring about the reduction of sulphates can be supplied only by the oxidation of this organic material. The reducing powers of his cultures were tested accurately by titrating the H_2S evolved with a standard solution of iodine. Of the numerous experiments described by Beyerinck, in which various sulphates and organic materials were tested, we will refer only to one, which is of especial interest inasmuch as the sulphate reduced was gypsum. Trench water (Grabenwasser) was saturated with gypsum, and to each liter of this solution were added 50 mg. sodium malate (to furnish some organic food stuffs for oxidation), 50 mg. asparagin (to furnish some nitrogen), 100 mg. potassium phosphate, and 1 gm. sodium carbonate. In a few days spirillum desulfuricans caused a noticeable reduction. In less than three weeks the reduction increased to almost 60 mg. H_2S per liter, equivalent to the reduction of 140 mg. SO_3. Beyerinck is convinced that it is immaterial which sulphate is employed. The conditions necessary for an exceedingly flourishing growth of this sulphide ferment are the absence of oxygen, the presence of sulphates, mineral salts, and organic material, and a temperature of about 25–30° C. Some reduction will take place, however, when the temperature is as low as 12° C., or as high as 40° C. The mixed cultures are somewhat more active in producing H_2S than the pure cultures. In nature this organism is found in the slimes, which consist essentially of calcium phosphate and carbonate, with more or less organic material. If iron phosphate is present the slime soon turns black as the result of the formation of a colloidal iron sulphide precipitate.

A. van Delden[33] continued the investigations of Beyerinck, in an endeavor to explain the strong H_2S development in the estuaries (Wadden) bordering the coasts of Holland, where the slime often reaches a thickness of several meters. In order to familiarize himself with the behavior of *Sp. desulfuricans* in fresh water before attempting to isolate the organism responsible for the reduction in sea water, he grew cultures of spirillum desulfuricans and studied the reduction carefully. Some very im-

[33] *Centralbl. f. Bakt.*, 2d Abt., Vol. 11, pp. 81, 113, 1903.

portant facts were here brought to light. In one case, it was found that the trench water contained sufficient organic food material to cause the entire elimination of sulphates from solution. In other instances, when the evolution of H_2S ceased, the addition of more organic material caused the evolution of this gas to be renewed, and the development of sulphureted hydrogen continued as long as sulphates remained in solution. Since unusual interest is attached to the reduction of calcium sulphate, gypsum, we may here cite a few of the experiments using this substance.

Culture Solution.		No. of Days.	Mg. H_2S Liberated per L.	Mg. SO_3 Reduced per L.
Ditch water ....500.00 gms.		7	93.5	220
Potassium hydrogen phosphate	0.250			
Sodium lactate..............	2.500			
Asparagine	0.500			
Gypsum...................	0.150			
Same as above with gypsum..	0.300	7	110	260
Same as above with gypsum..	0.450	7	122	288
Same as above with gypsum..	0.600	26	187	440

On another occasion, again using gypsum (0.500 gm.), van Delden found that after a period of forty-one days the mixed cultures liberated 246 mg. H_2S per liter, an amount equivalent to that resulting from the reduction of 580 mg. SO_3. Thus it will be seen that large quantities of this gas can be set free without producing injurious effects upon the organisms themselves. Investigations with pure instead of mixed cultures gave quite analogous results, as in one instance the H_2S titrated was equivalent to 238 mg. per liter. It is van Delden's opinion that the organic compounds found in nearly all polluted waters can be utilized by these organisms during the process of reduction. The earlier work of Beyerinck on the reduction of sulphates at room temperatures is fully substantiated by this later investigation.

By employing practically the same culture solutions as were used with *Sp. desulfuricans,* with the addition, however, 3 per cent. sodium chloride, van Delden was able to obtain pure

cultures of the specific organisms active in the reduction of sulphates in sea water. The sulphide ferment active in sea water, although very similar to that of *Sp. desulfuricans,* is nevertheless sufficiently different in its behavior towards sodium chloride solutions to be considered an independent species. To this organism van Delden assigned the name of *Microspira æstuarii.* In the experiments employing mixed cultures of *Microspira æstuarii* the H_2S content evolved totaled in several instances almost four times the maximum noted with *Sp. desulfuricans* in fresh water. Two interesting cases in which mixed cultures were used will be here cited.

Culture Solution.		No. of Days.	Mg. H_2S Liberated per L.	Mg. SO_3 reduced per L.
Sea water from the Helder ...500.00 gms. K_2HPO_4..................... 0.25 Asparagine .... 0.50 Sodium lactate.............. 2.50 Slime from the Dollard		27	843	1984
Tap water..................500.00 NaCl .... 15.00 K_2HPO_4..................... 0.25 Asparagine .... 0.25 Sodium lactate............. 5.00 $MgSO_4.7H_2O$ 4.00		19	1030	2424

From results of this character, one is amazed at the enormous quantities of H_2S liberated per liter of solution. In the second experiment quoted above, the amount of sulphate reduced exceeds the average sulphate content of sea water. Thus it will be seen that if organic food stuffs are sufficient the sulphates of the ocean can be completely eliminated. If pure instead of mixed cultures were used, similar results were obtained, a maximum of 952 mg. H_2S per liter being recorded, an amount equivalent to that derived from the reduction of 2,240 mg. SO_3.

Van Delden pointed out that *Sp. desulfuricans* and *Microspira æstuarii* are two distinct species and not modifications of the same one, and he found proof of this fact in their behavior towards solutions of NaCl. The following table strikingly illustrates the effect of varying amounts of NaCl upon each.

Per Cent. of NaCl Solution.	o	½	1	1½	2	2½	3	6	8	10
Sp. desulfuricans, mg. SO$_3$ reduced per L.	532	500	528	532	320	80	0	—	—	—
M. æstuarii, mg. SO$_3$ reduced per L	0	240	1,000	1,200	1,140	1,108	1,280	1,440	600	200

From this table it is apparent that, while both organisms can flourish in brackish waters which contain only a small amount of NaCl (.5 to 1.5 per cent.), when the NaCl content exceeds 2 per cent. the reduction by *Sp. desulfuricans* rapidly diminishes, ceasing entirely at 3 per cent. *M. æstuarii*, on the other hand, continues briskly the evolution of the H$_2$S in salt concentrations up to 6 per cent. Beyond this point, with further addition of NaCl, the reduction is quickly checked.

That the reduction of sulphates is very general in nature at the present time is evidenced by numerous references in the literature. While only two specific organisms have thus far been thoroughly tested, others will probably be found to possess the same property, in fact, names have been assigned to species which are supposed to perform in a similar manner. As it does not seem necessary to discuss in detail further investigations along this line, brief statements of a few of the most striking instances may be of service in illustrating the universal occurrence of this reduction.

N. Zelinsky[34] examined samples of ooze from the bottom of the Black Sea at depths of 16, 40, 389, 870, and 1207 fathoms and succeeded in isolating an organism capable of reducing sulphates to sulphides under anaërobic conditions. This motile, somewhat elongated bacterium has received the name of *Bacterium hydrosulfureum ponticum*. E. Brusilowsky[35] reported in the estuary of Odessa, a bacterium active in reducing salts of sulphur and oxygen to H$_2$S. To this organism he assigned the name of *Vibrio hydrosulfureus*. Nadson[36] has pointed out a similar re-

[34] J. Russ, *Chem. Soc.*, Vol. 25, p. 298; ref. *J. Chem. Soc.*, Vol. 66, part 2, p. 200, 1894.

[35] *Russk. Wratsch,* pp. 717, 791, 819, 1890; ref. *Centralbl. f. Bakt.*, Vol. 10, p. 194.

[36] "Ueber die Schwefelwasserstoffgärung in Weissowo-Salzee und ueber die Beteiligung der Mikroorg. in der Bildung des Schwarzen Schlammes," Petrograd, 1903; ref. W. Omelianski, Lafar, "Handbuch der Technischen Mykologie," Bd. 3, p. 214, 1904–1906.

duction of sulphates by *Proteus vulgaris* and *Bac. mycoides* in the black slimes of the "Weissowo-Salzee" (Gouv. Charkow, Russia). N. Goslings,[37] likewise, while unable to obtain pure cultures of the organisms, was convinced that microörganisms were the cause of the H_2S noted in the Passugèr Ulricus water, a strongly alkaline and iron-bearing spring rich in sulphates. A microörganism quite similar to Beyerinck's *Sp. desulfuricans,* if not identical with it, was isolated by Anton Rank.[38]

In determining the cause of the excessive production of hydrogen sulphide in three sewage disposal plants, W. M. Barr and R. E. Buchanan[39] decided that the organic matter in normal sewage does not contain enough sulphur to produce the quantities of H_2S observed. Chemical analyses of the raw sewage and effluents were made and it was found that where the sulphates in the original water supply are high, there is a marked reduction in the amount of mineral sulphates found in the effluent, showing that a portion of these mineral sulphates had been reduced and removed from solution.

Another instance suggestive of reducing organisms came under the observation of the United States Geological Survey.[40] A quantity of water rich in sulphates, from one of the alkaline lakes of California was sent to the laboratory in a wooden barrel. When received, the water had become so saturated with H_2S and discolored by extract from the wood, as to be rendered unfit for analysis.

In the open sea, however, due to oceanic currents and the presence of large amounts of ferruginous clays, little opportunity is offered for the accumulation of the H_2S, formed by either reducing bacteria or the bacteria of decay. The sulphureted hydrogen evolved would be quickly dissipated in the vast expanse of water, or else would find combination with ferruginous compounds. While the low temperature of the oceanic depths no doubt retards the reduction, this process does, nevertheless,

[37] *Centralbl. f. Bakt.,* 2 Abt., Vol. 13, p. 385, 1904.

[38] "Beiträge zur Kenntnis der Sulfatreduzierenden Bakterien," Diss. phil. Zürich, 1907; ref. *Centralbl. f. Bakt.,* 2 Abt., Vol. 20, p. 6119, 1907–1908.

[39] *J. Ind. and Eng. Chem.,* Vol. 4, p. 564, 1912.

[40] F. W. Clarke, U. S. Geol.. Survey, Bull. 491, p. 101, 1911.

take place, especially in the waters of the sea bottom that are in contact with the "blue muds." J. Murray and R. Irvine[41] observed that in the water filtered from the "blue muds" the sulphur content was reduced from 25 to 50 per cent. of that originally present in the sea water. The soluble sulphates of the alkalies and alkaline earths in the waters of the sea bottom are thus removed from solution and largely replaced by carbonates and insoluble sulphide. It is this precipitate of iron sulphide which is the cause of the blue black color of the "blue muds."

Entirely different conditions are encountered when the same reactions take place in lagoons, or land locked basins, where oceanic currents are absent and when the iron salts are insufficient to combine with all the H_2S liberated. We are now approaching the conditions which we might very reasonably believe to have existed in the lagoons of the sulphur districts of Sicily. To prove that large accumulations of H_2S can result in lakes or land lock basins, one need only to observe what is taking place at present in the Weissowo-Salzsee (Gouv. Charkow, Russia) or the Black Sea.

In the ground water of the Weissowo-Salzsee we have a remarkable instance of H_2S concentration with depth. Nadson, who isolated reducing bacteria in the slimes of this lake, has reported the following amounts of sulphureted hydrogen in one liter of the water:

At a depth of 16 meters .... 5.91 c.c. H_2S.
At a depth of 18.1 meters .... 88.31 c.c. H_2S.
At a depth of 18.7 meters .... 184.96 c.c. H_2S.

These same biochemical forces are also operative at the present time in the Black Sea. In the latter case, however, due to the enormous volume of water involved, and the large influx from the Mediterranean by way of the Bosphorus, the quantity of H_2S per liter is not as large as in the preceding instance. Nevertheless, the Russian deep sea expedition of 1891 detected sulphureted hydrogen everywhere beginning at depths of about 200

[41] *Trans. Roy. Soc. Edinburgh*, Vol. 37, p. 481, 1895; also Challenger Rept., "Deep-sea Deposits," p. 254, 1891; W. N. Hartley, *Proc. Roy. Soc. Edinburgh*, Vol. 21, p. 25, 1897; Murray and Irvine, *idem*, p. 35.

meters. Below this level the amount of H_2S increased quite rapidly as was shown by A. Lebedinzeff.[42] The amount of this gas in 100 liters of water varied with the depth as follows:

At a depth of 213 meters .... 33 c.c. H_2S.
At a depth of 427 meters .... 222 c.c. H_2S.
At a depth of 2,026 meters .... 555 c.c. H_2S.
At a depth of 2,528 meters .... 655 c.c. H_2S.

From this table it will be seen that the bottom layers contain over twenty times as much H_2S as those nearer the surface. According to N. Zelinsky and E. Brusilowsky this development of gas is due to the action of anaërobic bacteria upon the sulphates in solution. Below the 200-meter level, all the higher forms of life disappear, as a result of the poisonous action of this gas and the absence of free oxygen in the water. As a consequence, only about 7 per cent. of the maximum depth of the Black Sea is habitable. N. Androussow[43] is inclined to believe that a portion of the H_2S is derived from decaying organic material. The poverty of the bottom layers in free oxygen and the stagnant condition of the water below the 200-meter level, is due to the prevention of normal vertical circulation, resulting from the increase of specific gravity with depth.

If the present be considered a " key to the past," the biochemical reactions which one may observe taking place to-day in the Black Sea are quite suggestive of what we might reasonably expect to have occurred in an earlier geological period in the lagoons of the sulphur districts of Sicily. There is, however, this difference to be noted between the Black Sea of the present time and land-locked basins of Sicily of late Miocene. In the former, we have an unusually large enclosed body of water reaching in places a depth of over 2,500 meters, and possessing an average annual temperature of about 10° C. In spite of the enormous volume of water and the comparatively low temperature, suffi-

[42] *Travaux de la Soc. des naturalistes à Odessa,* 1891, Vol. 16; ref. W. Omelianski Lafar, " Handbuch der Technischen Mykologie," Bd. 3, p. 214.

[43] *Bullétin de la Soc. Impér. de Géographie,* 1892, Vol. 28, p. 370; *Mémoires de l'Ac. Imp. Des Sciences de Petrograd,* 1894; Vol. 1, p. 1; " Guide des excursions du VII. Congl. géol. internat.," No. 29, 1897.

cient H_2S has been developed to destroy all the higher forms of life below the 200-meter level.   In Sicily, on the other hand, the lagoons or bays, while connected with the sea by shallow channels, were otherwise cut off from oceanic circulation by a bar. These lagoons were much smaller in extent, probably not over 12 km. in length and 2 km. in width, while the average temperature of the water, due to its geographical location, must have been considerably higher than that of the Russian lakes of the present time.   An extremely energetic liberation of H_2S would be the direct result of reduction in the warm waters rich in sulphates, as the experiments with *Sp. desulfuricans* and *M. æstuarii* have demonstrated a maximum liberation of gas when the sulphates were abundant and the temperature in the vicinity of 20–25° C. Inasmuch as the bodies of water were small and the reduction probably continued for several thousand years, not only would the lower levels of the basins become practically saturated with sulphureted hydrogen, but other important chemical reactions would result.

An attempt will here be made to trace the various chemical changes which very likley took place in the lagoons while the waters were being concentrated by solar evaporation and the soluble sulphates reduced by anaërobic bacteria.   Originally, the basins probably swarmed with marine life, and, by the death and resultant decay of these organisms, some H_2S was unquestionably developed.   In the process which we term putrefaction, the proteid material is acted upon by numerous bacteria, and, after passing through a series of intermediate stages, finally liberates H_2S.   The nitrogenous material which is also present in animal tissue would likewise break down, yielding ultimately NH_3, which combining with the CO_2, would form $(NH_4)_2CO_3$.   This salt is everywhere present in the ocean, owing to the decomposition of albuminoid material.   This alkali would possess the property of converting some of the sulphate and chloride of calcium, present in sea water, to the carbonate.   The equations for these reactions may be expressed as follows:[44]

[44] "Report on the Deep Sea Deposits," Challenger Expedition, 1891, p. 254.

(1) $CaSO_4 + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4,$
(2) $CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$
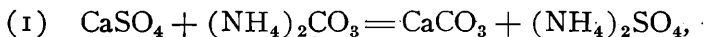
Thus, while some of the H_2S, especially in the early stages of the concentration, was undoubtedly derived from processes involving putrefaction, the comparatively few fossils found in the sulphur-limestone series, would preclude the possibility of the formation of all of this gas in that manner. The major portion of the sulphureted hydrogen must have been derived from another source, namely from the reduction of sulphates in solution through the action of anaërobic bacteria. The sulphates present in quantity in sea water are the sulphates of calcium, magnesium and potassium, and these salts must be considered the raw material for the development of the greater portion of the H_2S.

We are not familiar with the exact manner in which these organisms bring about reduction, but we have ample proof of the disappearance of the sulphates in solution, and of the generation of H_2S in quantity. If we assume, as seems plausible, an intermediate product, namely, a sulphide, and follow the suggestion of Murray and Irvine that the reduction is produced by the carbonaceous material of the protoplasm, the equation in the case of calcium sulphate would be expressed as follows:

(3) $CaSO_4 + 2C$ (living microörganisms) $= CaS + 2CO_2.$
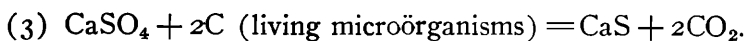
The CaS formed as an intermediate product, though only slightly soluble in water, is nevertheless hydrolyzed by it and yields soluble products.[45]

(4) $CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2.$
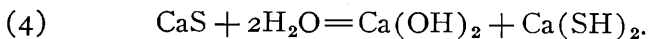
In all the investigations involving the reduction of sulphates by microörganisms the presence of some organic material is essential, as the energy necessary to bring about the reduction can only be secured by the oxidation of this organic matter. The dark-colored bituminous rocks of the sulphur horizon are sufficient proof of the existence of an adequate amount of this important

[45] R. Abegg's "Handbuch der anorganischen Chemie," Vol. 2, part 2, p. 117, 1905.

prerequisite. The CO_2 liberated by such oxidation would react upon the products of equation (4), forming compounds as expressed in equation (5).

(5) $Ca(OH)_2 + Ca(SH)_2 + 2CO_2 = 2CaCO_3 + 2H_2S.$
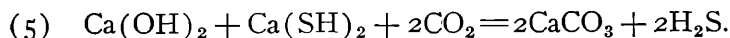
Hydrogen sulphide would thus be generated in the lower levels of the enclosed basin, and, at the same time, a precipitate of $CaCO_3$ would result.

The sulphate of potassium, which is also present in the sea water, would likewise be reduced and follow the reactions indicated above for the calcium salt. The K_2CO_3, however, by virtue of its solubility would not separate from solution. In like manner the magnesium sulphate would suffer reduction, but the $MgCO_3$ ultimately formed would be held in solution by the ammonium salts, especially the chloride, formed as illustrated in equation (2). Thus while the sulphates of calcium, magnesium and potassium are all subject to reduction, only the calcium carbonate would precipitate in quantity. The actual occurrence of the sulphur in a limestone is in harmony with this deduction. The H_2S liberated would soon poison the lower layers and drive the fauna to the upper levels. With the continued evolution of this gas and its diffusion upward, practically the entire land locked area would, in a short time, geologically speaking, be rendered unfit for marine habitation. It should be borne in mind that in the early stages of concentration, the H_2S was probably the result of the combined action of putrefaction and reduction. With the continued liberation of H_2S, the fauna would be removed from the depths and restricted to the surface levels. Their number being thereby largely reduced, the H_2S resulting from the putrefaction of a limited number would likewise be materially diminished. On the other hand, the evolution of H_2S as a result of the reduction of sulphates would become relatively more important with the disappearance of the fauna from the lagoons.

The H_2S in diffusing upward would, upon reaching the surface, be oxidized to water and sulphur.

(6) $H_2S + O = H_2O + S.$

This reaction can proceed as a purely chemical process although it is not at all improbable that the sulphur bacteria may have aided somewhat in the separation of free sulphur.

Part of the sulphur thus set free by the oxidation of the H_2S would slowly settle to the bottom of the basin and become disseminated throughout the limestone. Aside from occurring disseminated, the sulphur is also found in small horizontal bands or seams varying in thickness from 5 mm. to 2 cm. This observation would lead one to infer that at certain intervals a more copious precipitation of sulphur had taken place, and our next thought will be directed to a solution of this phase of the problem.

E. Divers and T. Shimidzu[46] have shown that calcium hydrosulphide reacts very readily with sulphur to form a calcium polysulphide, while at the same time H_2S is liberated. This observation, as will be seen, has a direct bearing upon the chemical reactions concerned in an explanation of the horizontal bands of pure sulphur. Some of the finely divided sulphur resulting from the oxidation of the H_2S would not reach the bottom of the enclosed basin, but would react with the $Ca(SH)_2$ which had been formed according to equation (4). This experiment was repeated by the writer, who used liter flasks, flowers of sulphur, calcium monosulphide and water in an endeavor to determine whether a polysulphide would be formed at room temperature. The dark amber color and increased specific gravity of the resulting solution, gave unmistakable evidence of a solution of some of the sulphur in the hydrosulphide, and of the formation of a polysulphide at a temperature which did not exceed $25°$ C. If the calcium hydrosulphide dissolves some of the finely powdered flowers of sulphur at room temperatures, freshly precipitated sulphur would react much more energetically. The experiments of R. H. Brownlee[47] and H. C. Cooke[48] have shown that freshly precipitated sulphur is considerably more active chemically than other forms of the same element. The calcium

[46] *Jour. Chem. Soc.,* Vol. 45, p. 283, 1884.
[47] *Jour. Am. Chem. Soc.,* Vol. 29, p. 1032, 1907.
[48] *Jour. Geol.,* Vol. 21, p. 25, 1913.

tetra or penta sulphide would probably be the result of the action of the freshly precipitated sulphur and calcium hydrosulphide, and the equation could be expressed as follows:[49]

$$(7) \qquad\qquad Ca(HS)_2 + 4S \rightleftarrows CaS_5 + H_2S.$$
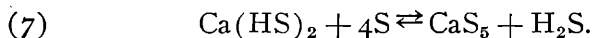
Divers and Shimidzu have pointed out that the reaction (7) between calcium hydrosulphide and sulphur is reversible, that is, the polysulphide of calcium is very unstable, and H_2S coming in contact with such a solution, would produce an exceedingly heavy precipitate of free sulphur. "The calcium becomes hydrosulphide, and if the solution is cold and sufficiently dilute, all polysulphide is destroyed as is seen from the bleaching of the solution." The polysulphide obtained by the writer by dissolving flowers of sulphur in an aqueous solution of calcium sulphide at ordinary room temperature, responded in the same manner when H_2S was passed through the solution. We now have what seems to be a satisfactory explanation of the banded structure observed in much of the Sicilian limestone. The formation of a polysulphide, followed by its immediate decomposition, would produce at intervals larger quantities of free sulphur, which would form the horizontal seams or bands in the calcium carbonate rock.

The maccalube or mud springs, which we may still see in operation in the vicinity of Girgenti and Caltanissetta, were probably more active in earlier geological periods. The intermittent discharge from these mud springs was probably the result of a derangement of the ground waters due to seismic disturbances. Salty, bituminous clays were thus brought from the lower horizons and deposited in the lagoons while the precipitation of sulphur was in progress. This material, which forms the sterile intercalations between the sulphur beds, has been given the name of tufi.

While the reduction of sulphates was taking place in these

[49] H. V. Tartar, *Jour. Am. Chem. Soc.*, Vol. 36, 495, 1914, has shown that calcium tetrasulphide is the lowest polysulphide formed when $Ca(OH)_2$ and S react in aqueous solution. When sulphur is in excess it combines with the tetrasulphide to form the pentasulphide.

land locked basins, evaporation of the enclosed water was likewise in progress. According to J. Usiglio,[50] when concentration of sea water equivalent to about one fifth of the original volume results, the saturation point of gypsum is reached and this mineral begins to separate out. That the saturation point of gypsum had been reached in the sulphur districts is clearly shown by the massive deposits of this mineral usually found above the sulphur-limestone series. At Comitini the concentration had even proceeded far beyond this point, for here rock salt has been found above the sulphur bed. With this concentration, due to solar evaporation, an additional factor is introduced which ultimately checks further reduction. The amount of solid matter present in solution in the oceanic waters varies considerably with location. Analyses of waters from the eastern Mediterranean,[51] collected during the voyages of the Austrian steamer "Pola," showed a salinity varying from 3.836 to 4.115. Of all the salts present in solution, sodium chloride is by far the most abundant single constituent, W. Dittmer's[52] estimate being 77.758 per cent. If we consider the salinity of the lagoons at the beginning of the concentration period at approximately 4 per cent., and if three fourths of all the soluble salts was sodium chloride, there would have been present at the outset about 3 per cent. NaCl in the water subjected to bacterial reduction. By the time the concentration had reached the stage at which gypsum began to precipitate—a concentration equivalent to about one fifth of the original volume—the salinity of the water in the lower levels of the basins must have increased about five fold. Likewise the sodium chloride content, at the time of the separation of the gypsum, must have experienced a like increase. We know that NaCl, in general, has an inhibitory action on bacterial growth,[53] especially when present in amounts exceeding 6 to 8 per cent. A. van Delden[54] has studied the effect of NaCl upon *M. æstuarii,* one of

[50] *Ann. chim. phys.,* (3), Vol. 27, pp. 92, 172, 1849.

[51] Analyst, K. Natterer, *Monatsh. Chemie,* Vol. 13, 1892, pp. 873, 897; Vol. 14, 1893, p, 624; Vol. 15, 1894, p. 530.

[52] Challenger Rept., "Physics and Chemistry," Vol. 1, p. 203, 1884.

[53] K. v. Karaffa-Koroutt, *Z. Hyg.,* Vol. 71, p. 162.

[54] *Centralbl. f. Bakt.,* 2 Abt., Vol. 11, p. 116, 1903.

the most active of the sulphate reducing organisms. From the table given on page 566, it will be seen that reduction was quickly checked when the sodium cholride content exceeded 6 per cent· Thus, by the time the gypsum began to separate from solution, the increased NaCl content had reached such proportions as to check completely further bacterial action. If this be correct, we have an explanation for the absence of true sulphur-limestone beds in the gypsum above. Occasionally sulphur is found in the gypsum, but only in very small, irregular, lens shaped masses of. pure sulphur which probably represents secondary accumulations. Mottura has called attention to the solvent action of oils emanating from the asphaltic material which permeates the limestone-sulphur zone. Likewise the natural etch figures seen on many of the sulphur crystals are further evidence that a solvent has been active in the transportation and formation of the secondary sulphur.

If, after the concentration had proceeded to the point of deposition of the gypsum, a subsidence of the land should take place or a severe storm destroy the bar which separates the water of the lagoon from oceanic circulation, the influx of water from the ocean would materially decrease the salinity and NaCl content to such a point that reduction might be renewed. We should then have developed a limestone-sulphur zone near the top as well as near the bottom of the gypsum formation, as is the case near San Cataldo, Fig. 4.

At the close of the Miocene, a gradual subsidence of the land took place, again establishing communication with the open sea. The subsidence continued until a noteworthy depth had been reached for in the sea foraminifera were abundant. This fact is revealed by the presence of a white foraminiferous limestone resting conformably upon the gypsum-sulphur-limestone series.

SUMMARY.

The sulphur deposits of Sicily constitute isolated, basin-like formations scattered throughout the south-central portion of the Island. The sulphur bearing stratum is usually underlain by

tripoli, while massive deposits of gypsum rest conformably upon it. That portion of the sulphur which is occasionally found in small, irregular lens-shaped masses enclosed in the gypsum, seems to represent secondary accumulations. These are so limited in extent as to be of economic importance only when found in the proximity of the true sulphur beds. The sulphur beds vary greatly in thickness, the average approaching probably three or four meters. Generally, in any given locality, three or four beds are encountered, one above the other, separated by narrow, sterile layers of bituminous, salty shales. These sterile intercalations rarely exceed three feet in thickness, and probably represent intermittent discharges from "maccalube" into the basins during the deposition of the sulphur. In the sulphur beds the sulphur occurs not only disseminated throughout a limestone, which is more or less bituminous in character, but also in bands of almost pure sulphur, from 5 mm. to 2 cm. in thickness, which extend parallel to the bedding.

The earlier theories proposed laid unusual stress upon the direct influence of volcanism with a resultant deposit formed under strictly igneous conditions. As the sedimentary character of the beds was unquestionably established, the idea of the influence of volcanism was partially relinquished, at least to such an extent as to permit a deposition under aqueous conditions.

While it has been universally accepted that the sulphur was the result of the oxidation of H_2S, the source of the sulphureted hydrogen has given rise to much speculation. Theories involving the reduction of gypsum by methane or by organic matter seem to have at present the largest number of adherents. It does not seem possible that either methane or lifeless carbonaceous material could possibly have reduced the gypsum at ordinary temperatures and there are no features present which would indicate unusual thermal conditions.

Numerous observations in nature of copious liberation of H_2S in both fresh and saline waters rich in sulphates, have led to the belief that living microörganisms are able to cause a reduction of sulphates in solution at ordinary temperatures. This belief

has been repeatedly verified in the laboratory by bacteriologists, who have isolated specific anaërobic bacteria capable of performing this function. The accumulation of H_2S set free by sulphate reducing bacteria has rendered the lower levels of some of the present lakes and enclosed basins uninhabitable for the higher forms of life. In the Black Sea, at the present time, only seven per cent. of the maximum depth is habitable as the result of the poisonous action of this gas.

These observations are unquestionably suggestive of what we may reasonably expect to have taken place in an earlier geological period in the lagoons of the sulphur districts of Sicily. The small size of the individual basins, the comparatively high average temperature of the water, due to its geographical location, the high sulphate content, and the period of years over which these bacterial reactions extended, probably caused a liberation of H_2S sufficient not only to saturate the lower levels, but also to bring about important accompanying chemical reactions. The oxidation of H_2S and the action of CO_2 upon $Ca(OH)_2$ and $Ca(SH)_2$, products formed by the reduction of calcium sulphate, would cause a simultaneous separation of the sulphur and a precipitation of calcium carbonate. Some of the sulphur would, however, be absorbed by the $Ca(SH)_2$ to form a polysulphide. This polysulphide is so unstable that even H_2S coming in contact with such a solution would produce a heavy precipitate of free sulphur. The formation of a polysulphide, followed by its immediate decomposition, would liberate at intervals sufficient sulphur to form the horizontal bands in the limestone. While the reduction was in progress, evaporation was likewise taking place. Thus, by the time the concentration had reached the saturation point of gypsum, the increased sodium chloride content of the basin had reached such proportions as to completely check further bacterial action. A destruction of the bar which separated the lagoon water from oceanic circulation, or a gentle subsidence of the land, might cause such an influx of water from the ocean as to decrease to a marked extent the salinity of the water. Reduction would then be once more renewed, after con-

siderable gypsum had been deposited. Ordinarily, however, the sulphur-limestone series is confined to the base of the gypsum formation.

Such a bacterial reduction theory, with its accompanying chemical reactions, would explain the presence of disseminated and banded sulphur in the limestone, the usual absence of the sulphur-limestone rock in the gypsum above, and the formation of the sulphur at normal temperatures and under conditions which would confine its formation and deposition to these land-locked basins.

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