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A study of the genesis of the Krueger zinc deposit and the near-by barite deposits of the Potosi quadrangle, Washington County, Missouri

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A STUDY OF THE GENESIS OF THE KRUEGER ZINC DEPOSIT AND THE NEAR-BY BARITE DEPOSITS OF THE POTOSI QUADRANGLE

WASHINGTON COUNTY, MISSOURI

BY

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A

THESIS

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ABSTRACT

This thesis deals with the study of the genesis of the Krueger zinc deposit and the near-by barite deposits of the Potosi quadrangle, Washington County, Missouri.

The rocks outcropping in the quadrangle embrace Pre-Cambrian and Lower Paleozoic formations, the Potosi and Eminence being the most important formations with regard to the studied deposits.

The few structures present in the area are of the vertical type and are more abundant in the southern part of the quadrangle.

Special emphasis is placed on the relationships between the barite, the associated sulfides, and the host rock.

Geometric and geochemical criteria are studied in detail and used to explain the local genesis of the ore deposits. Geometric evidences, either in the outcrops or in the drill cores, suggest the possibility of a syngenetic origin. The geochemistry of barium and the sulfides supports this mode of origin.

An attempt to solve the problem of the origin of the ore fluids was made. Both the supergene and hypogene theory are considered. More criteria appear to support the second one.

GENERAL INTRODUCTION - ACKNOWLEDGEMENTS

General Introduction

Interesting and important deposits of barite and associated sulfides have been known and mined in the Potosi quadrangle of Washington County, Missouri, for a century or more. The problem of their genesis has been subjected to controversial opinions during the years since their discovery.

The similarity of the Missouri deposits with other barite deposits in the United States and abroad has inspired a large series of publications. Most of these have been reviewed in this thesis and compared with the data collected in the field and studied in the laboratory by the writer. Literature of barite deposits from all parts of the world has been studied. This has provided a background of data and conditions found in other deposits of the same occurrence and has supplied many different ideas and theories on their genesis.

The approach to the problem involved two steps: first a careful study of outcrops in the area and second a petrographic analysis of the samples in the laboratory. It became necessary to apply new criteria and to elaborate on the conventional ones to permit a better understanding of the factors and causes of the origin of the barite deposits of Missouri.

The conclusions reached in the present thesis differ considerably from the previous interpretations and suggest new possibilities in regard to the genesis of the studied deposits.

Acknowledgements

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CHAPTER I

GEOGRAPHICAL AND GEOLOGICAL INTRODUCTION

The studied ore deposits are located in Washington County, one of the counties in the southeastern part of the State of Missouri. The Washington County barite district is the most important one in the state and includes all of the area belonging to Washington County and a few square miles of St. Francois County. A second district, in central Missouri, covers parts of several counties in the area of the Lake of the Ozarks. These barite deposits are smaller and could not be studied at this time.

The present work concentrated on the study of the barite deposits of the Potosi quadrangle, which lies in the center of Washington County.

Physical Geography of the Potosi Quadrangle

The Potosi Quadrangle is comprised between the 37°45' and the 38°00' parallels, north latitude, and between the 90°45' and 91°00' meridians, west longitude.

The whole quadrangle, about 22 km. (14 miles) wide, and 27 km. (17 miles) long, can be considered, in a general way, as a part of a wide plateau. The lowest and the highest points in the area are in proximity of the Town of Latty, in the valley of Fourch a Renault, about 215 m. (700 ft.) above sea level and the other, the Little Pilot, a porphyry knob, 365 m. (1200 ft.) above sea level in the northwestern side of the quadrangle.

The drainage of the whole area is a part of the Meramec River Basin. The tributary, in the Potosi Quadrangle, is the Big River and its smaller tributaries. The northwestern waters of the area are collected by the Curtois River, and other streams flowing directly into the Meramec River. The major part of the streams has a flat angle grade. Only in a few cases is the river bed as far below the average plateau surface as 60-90 m. (200-300 ft.). Because of the local characteristic of the rivers there are very few flood planes in the area and they occur only along the big streams.

The major part of the soils, as their study shows, is of the residual type, with a few small areas of the alluvial type close to the largest streams, as stated above. These residual soils, important and interesting for the purposes of the present study, are frequently rich in quartz and chert nodules. The richness in siliceous nodules is one of the main causes of the poor agricultural quality of the soils of the region.

The area under study is prevalently covered by forests of pines, oaks, and cedars. Agriculture is developed on the flood planes, with wheat and corn as principal crops.

The population consists mostly of farmers and is concentrated in the towns of Potosi and Caledonia or disseminated on farms.

<u>Stratigraphy of the Potosi Quadrangle</u>

Data for the geology of the Potosi Quadrangle have been taken mostly from C. L. DAKE's paper (1930)[1]. For the purposes of this study a general summary of the sequence of the formations outcropping in the area and a short illustration of the main tectonic events that have taken place in part or in all of these rock formations are described below.

C. L. DAKE and other geologists who have studied the area agree on the recognition of the following formations:

Quaternary	.Alluvium - residual soils and alluvium sensu strictu
Ordovician	.Roubidoux Formation - sandstone with a fair abundance of cherty material and thin lenses of dolomite
	.Gasconade Formation - cherty dolomite
Cambrian	.Eminence Formation - dolomite and chert
	.Potosi Formation - crystalline dolomite, quartz and chalcedony druses, chert
	.Derby-Doerun Formation - finely crystalline to earthy, but not cherty dolomite
	.Davis Formation - shale, limestone, and limestone conglomerate
	.Bonneterre Formation - crystalline dolomite, no chert
	.Lamotte Formation - sandstone with several shale layers
Pre-Cambrian	.Rhyolite porphyry and rhyolitic tuffs

As seen in this stratigraphic section, the formations present in the area belong to the Pre-Cambrian and to the Paleozoic.

1. All references are in bibliography.

Pre-Cambrian

The Pre-Cambrian rocks of the Potosi Quadrangle consist exclusively of rhyolite porphyry and rhyolitic tuffs. Granite, granite porphyry or basic dikes have not been found.

Rhyolite Porphyry. Outcrops of these rocks are found especially in the southern part of the Potosi Quadrangle, close to the border between Washington and Iron Counties. The porphyries form a series of relatively small knobs that become a definite range in the southern part. A small porphyry knob, named Little Pilot, is located in the northwestern part of the quadrangle and is the highest point of the area. The dark reddish-brown rhyolite porphyry contains small orthoclase and quartz crystals in a ground mass of very fine texture.

According to GEIJER (1931) and AMSTUTZ (1958), microscopic examinations revealed that some portions of the rhyolites are to be classified as keratophyric andesites.

Rhyolitic Tuffs. As reported by DAKE (1930), some thin bedded slabs of tuff were found just outside the northwestern corner of the Potosi quadrangle. They were, however, not in place.

Cambrian

The Cambrian system is represented by the six formations described below.

Lamotte Formation. The Lamotte consists prevalently of a sandstone, sometimes interbedded with thin layers of clays. The color of this sandstone is extremely variable because of the different amounts of iron oxides it contains. The formation outcrops only in a small area near Caledonia in the southwestern part of the quadrangle.

Bonneterre Formation. Sandstone, sometimes calcareous, and sandy dolomite constitute the biggest portion of the Bonneterre Formation. In the upper part it is prevalently formed by a massive and coarse dolomite. This formation also outcrops only in the southern part of the Potosi Quadrangle, particularly in the Belgrade and Belleview sections.

Davis Formation. The Davis Formation, outcropping sparsely in the southern part of the Potosi Quadrangle, consists principally of shales although some limestones and dolomites are frequently interbedded.

Derby-Doerun Formation. The Derby-Doerun Formation, as the Davis, is very scarcely represented in the area. It outcrops only in the south central part of the quadrangle in an area where tectonic movements occurred. Lithologically the formation consists of a very fine crystalline dolomite without chert. ULRICH united the two last formations under the general name of Elvins Formation.

Potosi Formation. The Potosi Formation, together with the Eminence, is the rock complex containing most of the barite deposits of the district. It is well represented in the whole quadrangle, but especially near the Town of Potosi and in the Palmer area, in the southwestern corner of the quadrangle. The major part of the outcropping barite is found in this formation, and also almost all of the barite mined in southeast Missouri is recovered from it. The thickness of the formation does not exceed 70-100 m. (250-300 ft.) and in many places its thickness is greatly reduced by erosion.

A light to dark brown, relatively crystalline, medium to fine grained, very cherty dolomite constitutes the bulk of the Potosi formation. Shales and sandstones are not represented at all. Very frequent druses are prevalently composed of chalcedony, coated in the interior by relatively large quartz crystals.

Eminence Formation. The Eminence is the most widely distributed formation throughout the Potosi Quadrangle and much of the barite is contained also in this formation. Barite is present in outcrops especially near the contact with the subjacent Potosi Formation. The Eminence Formation is formed by a series of massively bedded dolomite layers with fairly abundant chert. A property distinguishing the Potosi from the Eminence is the lighter color of the latter. Shales and sandstones are scarce and occur always as thin beds or lenses. Chert is very abundant and one of the main characteristics of the formation.

Ordovician

Only the lowest formations of the Ordovician are present in the area.

Gasconade and Roubidoux Formations. The top of the stratigraphic sequence in the Potosi Quadrangle is formed by the Gasconade and Roubidoux formations. They occupy the central part of the quadrangle and also the southern part, where they are in direct contact with the Bonneterre, Davis, and Derby-Doerun formations because of tectonic movements which originated a system of faults a few miles north of Belgrade.

Quaternary

The mature topography of the region makes difficult a separation between the old and the recent Quaternary deposits. The streams do not have a strong erosive action and the alluvial deposits are few. Only in proximity of the largest streams alluvial deposits can be found and their material is always derived from the Paleozoic Formations. The whole quadrangle is almost completely covered by residual soils originated by weathering of these formations.

Structural Geology of the Potosi Quadrangle

C. L. DAKE (1930) observed one major fault and two fault systems in the area and considers that they are normal vertical gravity faults. The only possible fold of the region may be the so-called Shirley syncline which may cause the preservation of the Roubidoux formation in the quadrangle.

This fault and the fault systems are, according to

DAKE, the Shirley fault and the faulted zone of Palmer. These are said to be probably of different age. The Shirley fault, which passes a few miles east of Shirley is said to be younger than the Roubidoux Formation, the youngest Paleozoic formation in the area. This fact is supported by DAKE's observation of an anomalous contact between Roubidoux and Eminence, reported from a few places only.

The Shirley fault is supposed to pass through the Krueger property and was assumed by various authors to have served as a channelway for mineralizing solutions. The present author has not seen this fault on the surface and the block diagrams (see tables 5, 6, 7) do not prove or strongly suggest its presence. The fault assumed to be present by previous authors (DAKE, 1930; BALLINGER, 1948; and others) was drawn into the block diagrams assuming that their assumptions were correct.

As will be discussed in more detail later in this thesis, the connections between the mineralized and/or brecciated portions of the drill holes, as reported by BALLINGER (1948) and as relogged by the writer, do not prove the presence of the fault. There is at the most a very slight suggestion that the northeastern part of the subterraneous breccia horizon is slightly (a few feet only) higher than the southwestern part. Yet this could be caused by a slight monocline or by an original stratigraphic elevation-difference of the breccia.

One of the two fault systems in the Palmer area was thought to be possibly of the same age as the questionable Shirley fault; the other is probably older and at least post-Eminence, DAKE, (1930).

CHAPTER II

GENERAL DESCRIPTION OF THE DEPOSITS

The barite deposits of the Potosi Quadrangle are located in two principal areas. The first, around the Town of Potosi, occupies the northeastern corner of the territory studied for this thesis; the second, on the central western edge, belongs to the Palmer and neighboring sections.

The following chapter offers a brief description of the outcrops visited, and the mode of occurrence of the barite in the field. The barite occurs as residual and as bedrock deposits. They will be discussed in this sequence:

Residual barite

Bedrock barite

Residual Barite

The residual barite is presented in soils and overburden as fragments of different sizes and shapes, from a few to several centimeters. The origin of this barite, frequently containing small cubes of galena, is not difficult to explain. During weathering and decomposition of the barite bearing dolomites, the insoluble residue, consisting mainly of quartz druses, chert, and barite, was concentrated in the soils where it is now found. The enclosing dolomitic sediments were decomposed and removed by the water.

The Cambrian barite bearing formations, like the Potosi and Eminence, have been directly in contact with atmospheric agents for a long time. They were subjected to a strong weathering action, which did not, or only to a negligible extent, act on the quartz, chert, and barite present in the formations (see figure 1). These factors made the large and commercially interesting concentration of barite in the residual material over almost the whole region present.

Residual barite has been and still is mined principally inside the following areas[2]:

Palmer area: 90°55'/91°00 west - 37°48'/37°52' north; sections 7, 8, 15, 21, 22, T.36 N., R.1 E., and sections 1, 12, 15, T.36 N., R.1 W.

Deposits along Missouri Highway No.114: 90°48' west - 37°58' north.

Superbar Company Deposits: along Missouri Highway No.8, northeast of Potosi.

Hornsey Bros. Mining Company: southwest rim of the Town of Potosi; 90°47' west - 37°46' north.

2. Except for the Palmer area the geographical coordinates refer to the central point of the area mentioned. No section, township, and range can be given for some of the cited localities because part of the Potosi Quadrangle is not sectionalized.

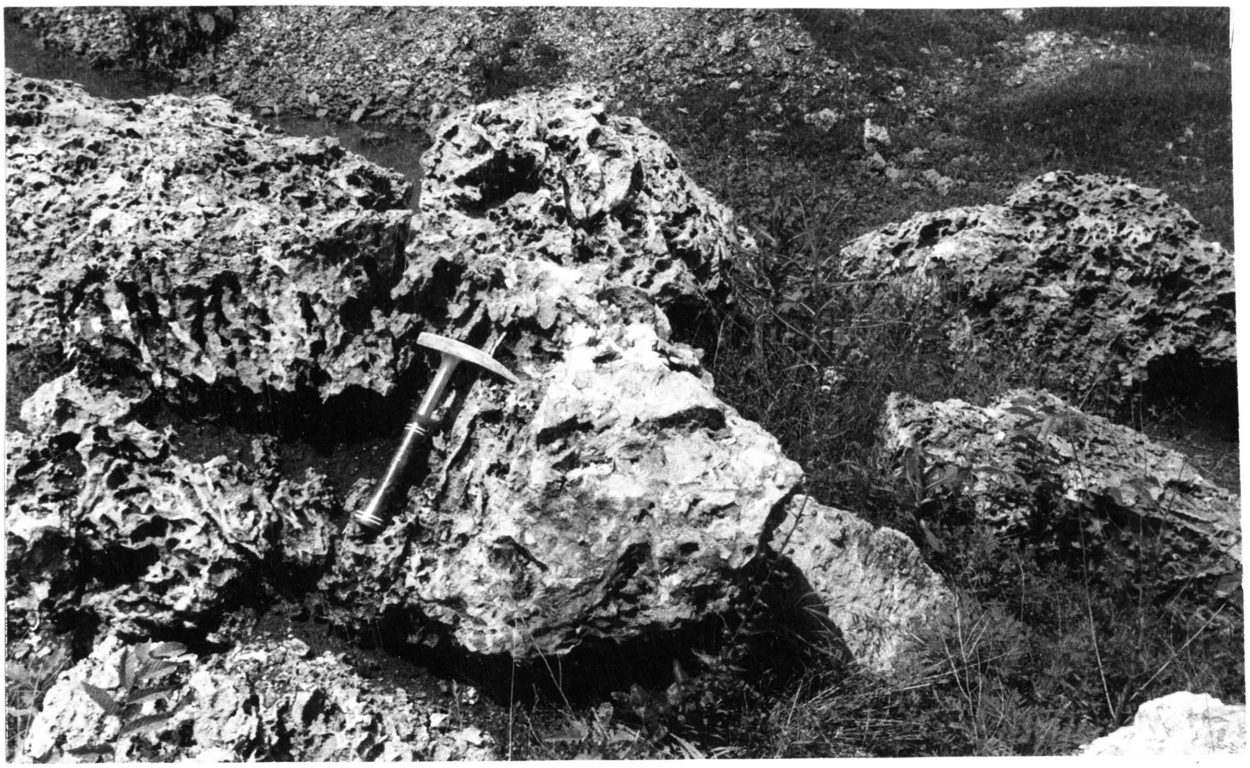


Figure 1 - Residual barite crystals and quartz druses along Missouri Highway No. 21 near Old Mines. Quartz forms a rigid network in which barite occurs.

Bedrock Barite

Any study of the genesis of ore deposits has to be based mostly on observations and considerations of the mineral in place, with particular reference to its relations to the surrounding rocks. In this case, special attention has been given to the few outcrops of barite and associated sulfides in bedrock present in the Potosi Quadrangle. The barite deposits of the area are here sub-divided as follows:

Krueger Property: 90°53' west - 37°55' north ; NE¼ Sec. 24, T.37N.R.1E.

Hornsey Bros. Mining Company Deposits: 90°48' west - 37° 56' north

Deposits along Missouri Highway No. 8: 90°48' west - 37°57' north

Krueger Property

The Krueger Property (see figures 2, 3) is located about six miles west of Potosi along Missouri Highway No. 8 and includes an area of about 160 acres on the orographic right side of the River Fourche a Renault, between the Middle and North Fork Creek in the NE¼, Sec. 24, T.37N.R.1E.

The surface rock in the area is predominantly of Eminence age and consists of a light gray, moderately granular, massively bedded, cherty dolomite. The contact between the Eminence and the Potosi formation is difficult to determine because of the strong similarity of the rocks of the two formations at the contact. This contact is actually transitional.

According to C. L. DAKE (1930), the Krueger Property is related to the Shirley fault which is said to go through the deposit at/or near the shaft. This point will be discussed later. The fault was not detected by the writer. In a few places, DAKE and others who surveyed the area were apparently able to recognize a displacement on the surface.

This ore deposit is associated with a dolomitic breccia. The minerals present are sphalerite, galena, marcasite, and barite. A relatively large amount of chert is also present. At the entrance of the open pit, just above the water, there are on the south side a few outcrops of dolomite in which only barite occurs. On the north side the short outcrop contains brecciated cherty material which shows some mineralization of sulfides in addition to barite.

Unfortunately it was impossible to observe the deposit underground. The only shaft present on the property was completely underwater during the earlier visits. Later the owner of the property had almost completely destroyed and filled the shaft.

Samples were collected on the surface and belong to material once taken out from the shaft. The study of the property is thus based on observations on the small outcrops at the shaft entrance, on the dump material, and on the drill hole records published by the United States Bureau of Mines, as well as on the logging of 19 drill holes by the writer in the Minneapolis Core Library of the U. S. Bureau of Mines.

Details of the mineralogy and paragenetic sequence of the minerals present in the brèccia are discussed in Chapter V.

Hornsey Bros. Mining Company deposits

These deposits are located on the southwestern rim of the Town of Potosi (see figure 4). They consist mostly of residual soils in which barite with some lead sulfide is found. Galena is frequently present as big crystals or aggregates.

A few outcrops of barite in bedrock were found close to the northern limit of the deposits on both sides of the road. Barite occurs here as a constituent of the matrix between pieces of dolomite rock, sometimes forming its major constituent. In the latter case it has the appearance of a barite network (see figure 5).

Sulfides, except galena, are not associated with the barite in this location.

Deposits along Missouri Highway No. 8

On Missouri Highway No. 8, about two miles west of Potosi, on the left orographic side of Baites Creek, several open pits can be seen on the side of the highway and in the wood. From these pits barite was mined several years ago. The pit with the largest outcropping face is pictured on figure 6. Details are shown in figures 7, 8a, 8b, 9a, 9b, 10.

Here barite occurs in considerable quantity, occasionally associated with galena. Barite is well exposed as small or large irregular patches in a light dolomite on a relatively large open pit wall, about 20 yards away from the highway. The dolomite is broken and fractured and some of the matrix space contains barite. Druses of quartz are present in small quantity. Some chert nodules occur in the outcrops along Highway No. 8, but there is no visible relation to the barite. Usually these nodules occupy a higher stratigraphic position (see figures 11a, 11b).

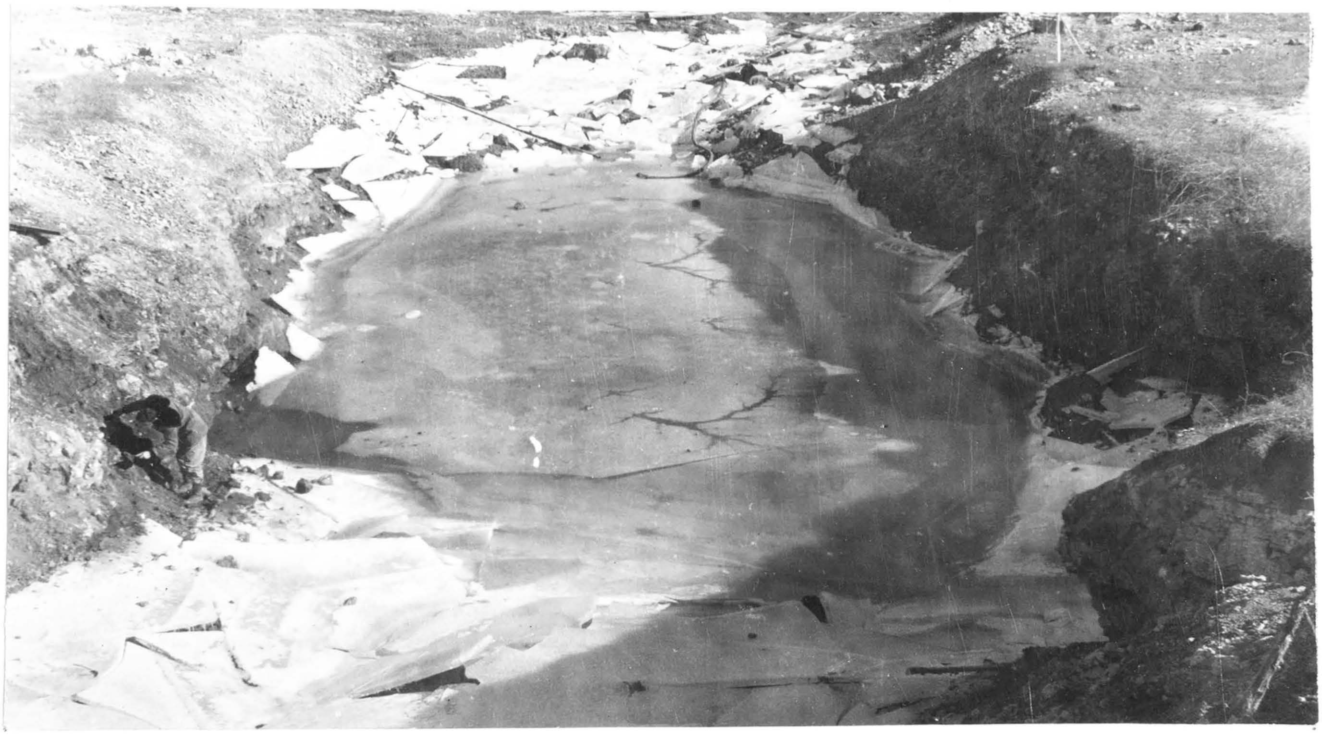


Figure 2 - View of the open pit of the Krueger Zinc Deposit. The old shaft is located a few feet to the right of the person looking at beds of cherty breccia with marcasite and sphalerite.

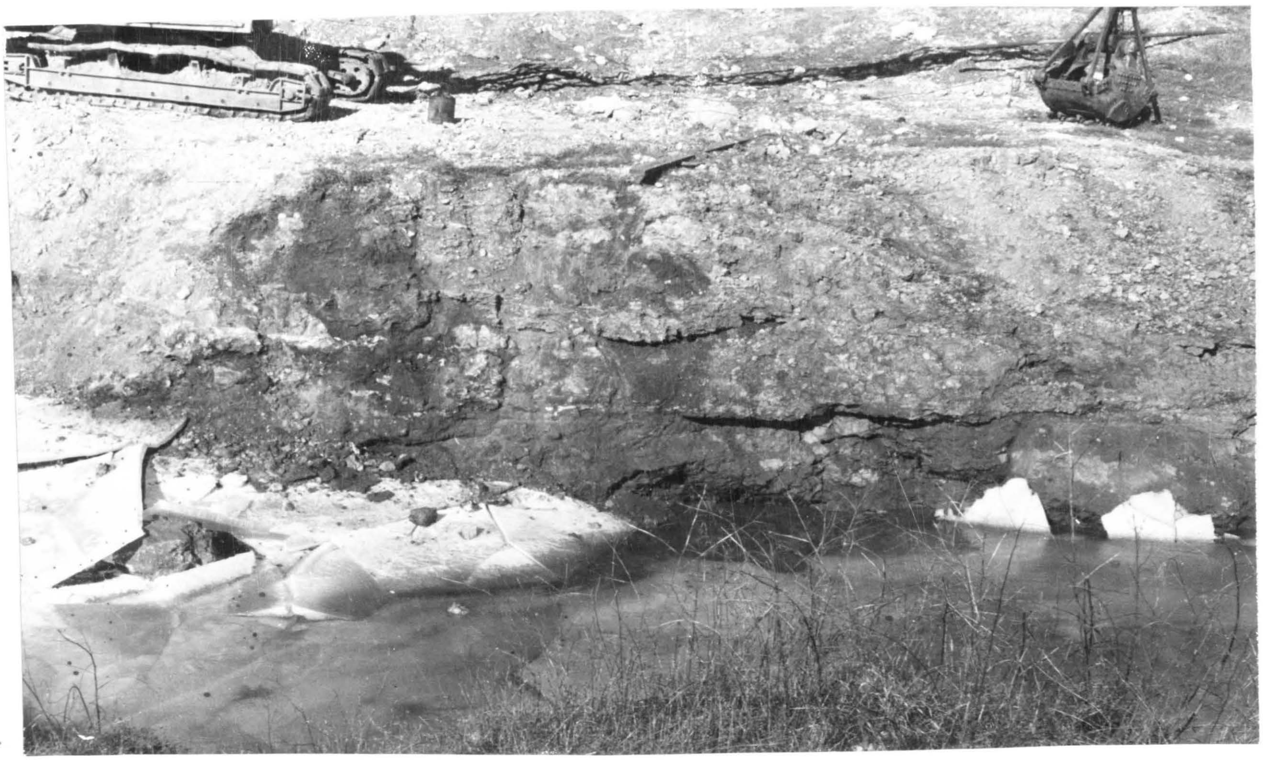


Figure 3 - Barite and dolomitic breccia outcropping in the open pit of Krueger Zinc Deposit. The horizontal resistant beds consist of dolomite, chert (mostly brecciated and cemented with some marcasite and sphalerite), and barite.

Figure 4 - Outcropping barite in an open pit of the Hornsey Bros. Mining Company. The complete absence of mineralization in the foot and hanging walls is well displayed.

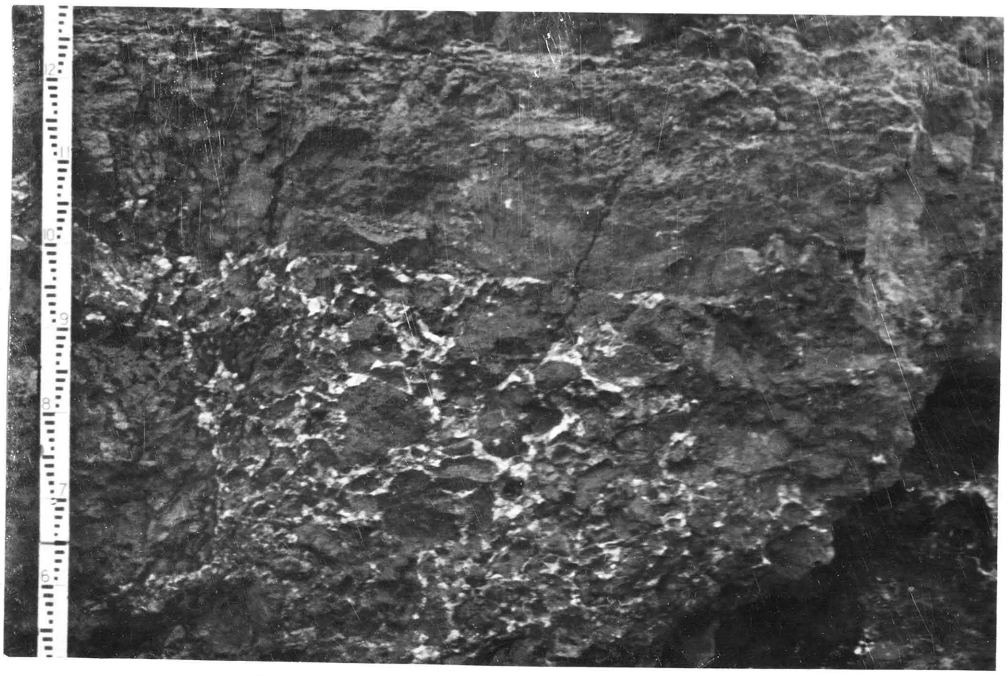
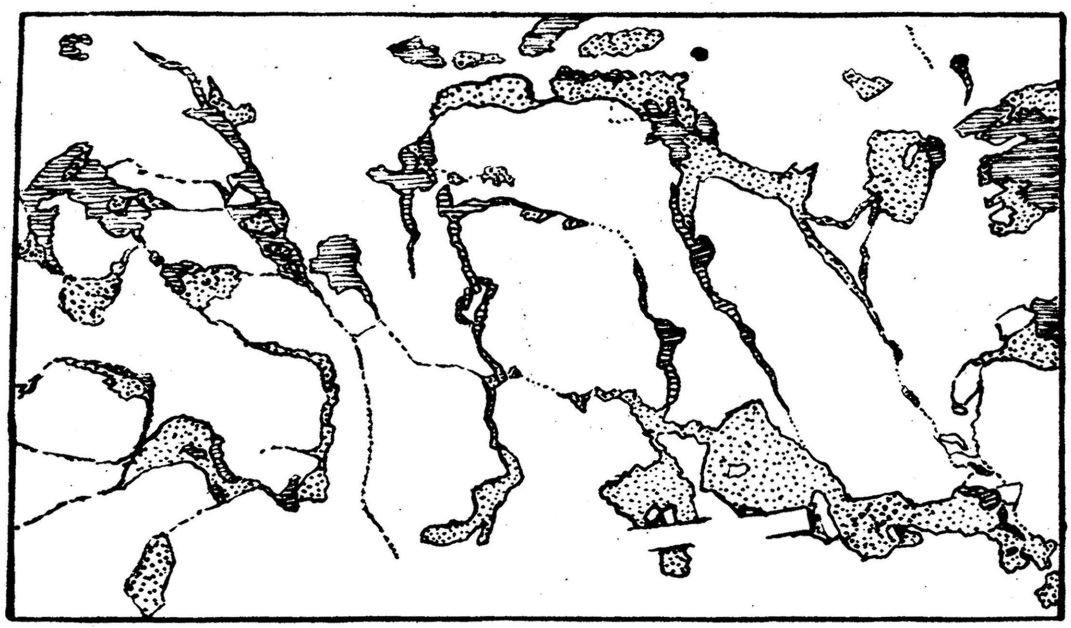


Figure 5 - Detail of the figure 4 showing the lack of mineralization in the hanging wall.

Figure 6 - Open pit with outcropping barite north of Missouri Highway No. 8.

Figure 7 - Detail of the outcropping barite in the open pit north of Missouri Highway No. 8 (the length of the knife is 2½ inches). Picture taken on vertical wall.

Figure 8 - Detail of the outcropping barite and limonite in the open pit north of Missouri Highway No. 8 (vertical outcrop). The Drawing shows the box-work of limonite.



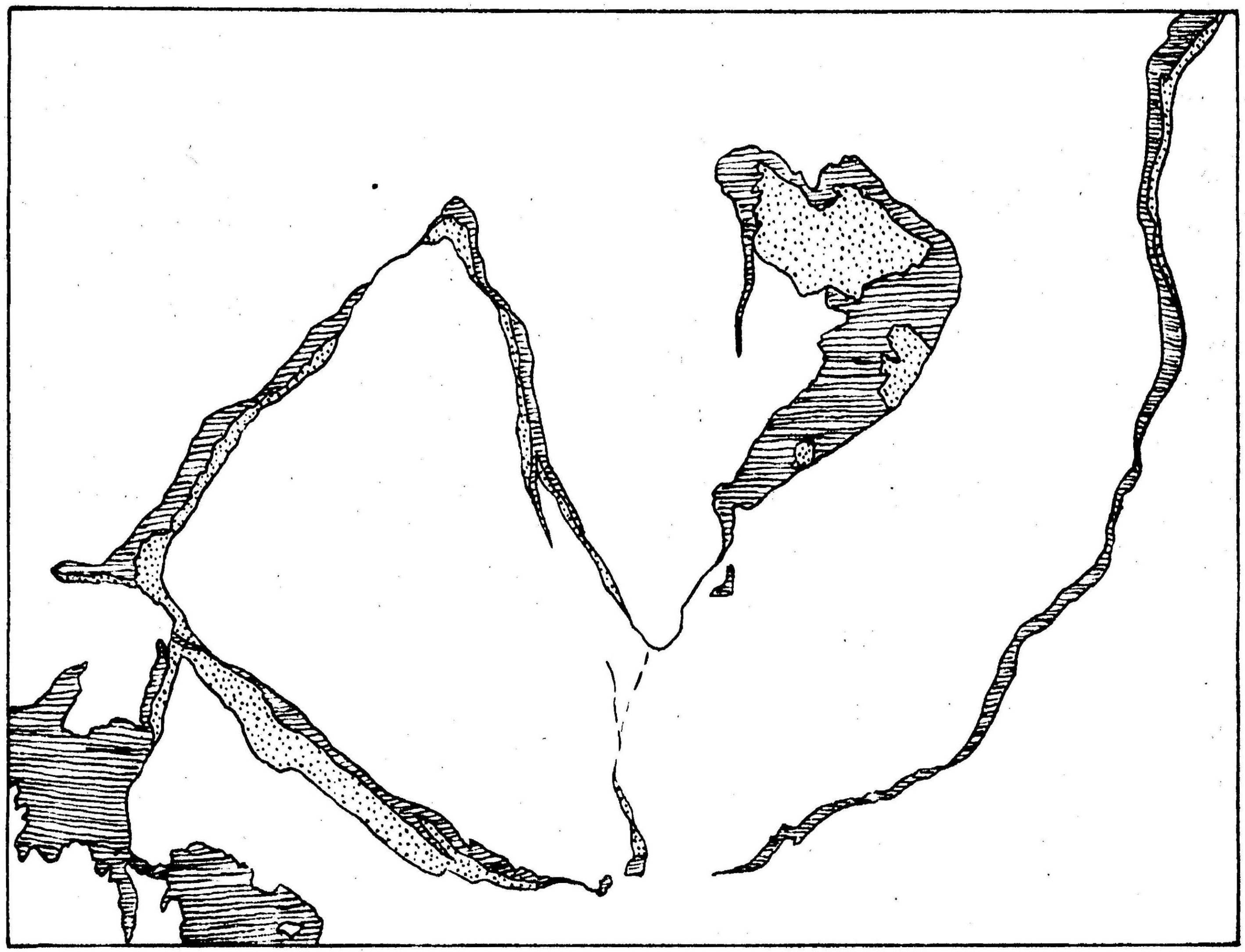


Figure 9 a. Detail of the outcropping barite-limonite boxwork shown in figure 9 b.

Limonite and limonite staining dolomite

Barite

Dolomite

Figure 9 b. Barite and limonite boxwork in dolomite in the open pit north of Missouri Highway No. 8 (horizontal outcrop)

Figure 10 - Patches of barite in the open pit north of Missouri Highway No. 8.

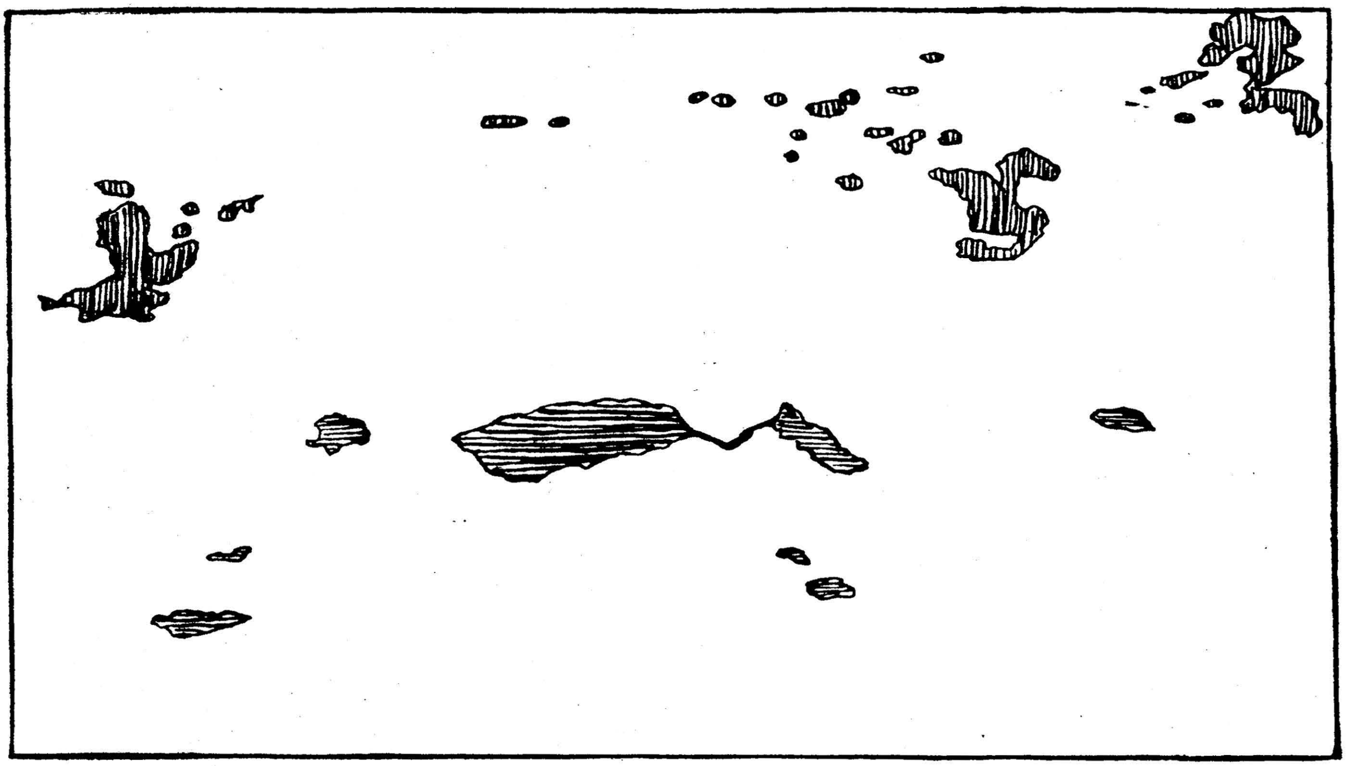


Figure 11a.- Detail of Figure 11b.

Barite

Chert

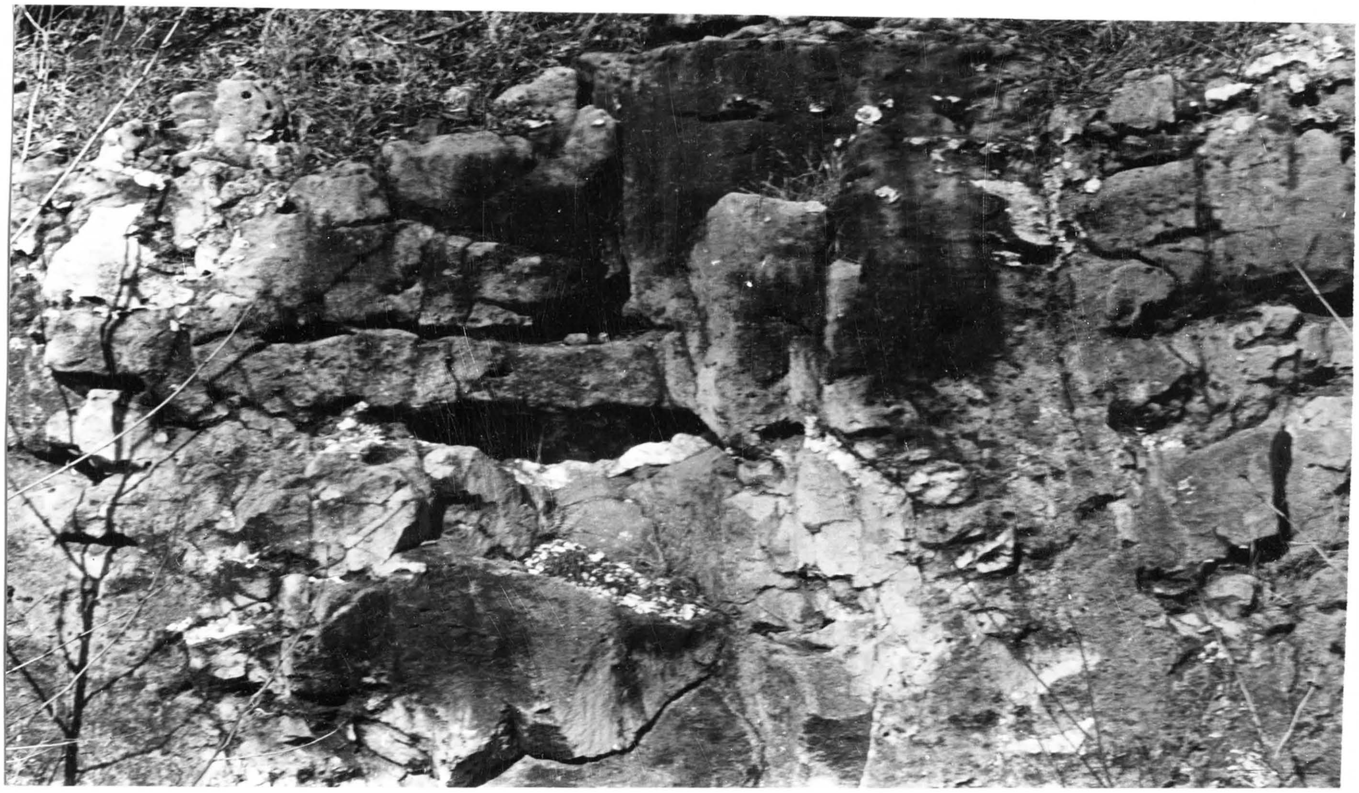


Figure 11 b - Barite and chert nodules in the outcrop along Missouri Highway No. 8.

CHAPTER III

PREVIOUS INTERPRETATIONS

The following three sections contain summaries of the criteria and theories related to the barite genesis, as offered in previous publications both in this country and abroad. The following sequence is observed:

Barite deposits of the United States exclusive of Missouri
Barite deposits of foreign countries
Barite deposits of Missouri

An attempt was made to set up a bibliography of all available papers containing valuable information on the occurrence and origin of barite in sediments. The review of previous work is, however, based on a selection of papers which were thought to be the most important ones from a genetic point of view.

Barite deposits of the United States exclusive of Missouri

In 1907 T. L. WATSON studied the genesis of the barite deposits of Virginia. According to him the barite contained in the Shenandoah limestones (Cambro-Ordovician) was deposited by shallow waters circulating epigenetically in them. The waters had previously leached the barium which WATSON believed present in the same formation, and successively redeposited it as barium sulphate. WATSON offers the following conclusions which are quoted in full length:

1. With two exceptions, the barite deposits are associated with limestone or its residual decay. These exceptions show the occurrence of the barite in crystalline siliceous rocks, more or less remote from limestone masses.
2. The occurrence of the barite in the limestone is partly as a replacement, and partly as vein-like masses filling fractures; and in the residual clays as loose nodular masses irregularly assembled and of different sizes and shapes. In each of these occurrences the barite is crystalline in texture, and is the result of solution and deposition.
3. The barite and associated minerals suggests deposition from reasonably-shallow circulations. The barite is believed to have been largely, if not entirely, derived, in most cases, from the rocks in which the concentrations are now found. (p. 733).

In 1913 F. H. FOHS, studying the barite deposits of Kentucky in Mississippian and Cambro-Silurian limestones, related the source of barium directly to the basic igneous rocks present in the area. The barium, according to this author, is, ". . . the element appearing as a constituent of certain feldspars, biotite, and their alteration products. Barite is not a rock making mineral and is only deposited from rock making solutions." (p. 573).

The barite deposits of the Appalachian area[3] were reviewed in 1915 by T. L. WATSON and J. S. GRASTY. They related the genesis of the barite present in veins of either sedimentary or crystalline rocks, to the barium compounds derived from rocks surrounding the actual deposits by action of shallow circulating water.

C. H. GORDON in 1918 studied extensively the barite

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3. Alabama, Georgia, Kentucky, Maryland, Pennsylvania, North Carolina, South Carolina, Tennessee, and Virginia are comprised in this area.

deposits of East Tennessee. These were described by him as ". . . bed veins or shattered zones in limestone in which the barite occurs as a replacement, or cement filling the interstices in the breccia," or as "residual deposits formed by weathering of the above . . ." (p. 52). Stratigraphically the barite occurs in the dolomite of the Knox formation (Ordovician), which contains a large quantity of chert in nodules or masses.

GORDON, following H. RIES theories (1916), thought that barite could have been formed from deposition from aqueous solutions, and expressed it as follows:

> The source of the barium was evidently in the dolomite and associated limestones, great thicknesses of which have in the course of time been removed by solution (p.56).

Chemical analyses of the Knox dolomite are reported in the same paper showing that barium is present in relatively appreciable amounts as sulphate and oxide.

The same theory of water acting as solvent of the barium in preexisting formations was accepted by J. P. D. HULL in 1919 in his paper "Barite Deposits of Georgia". According to him, these deposits might have been formed by leaching of barium from feldspars and micas of igneous rocks. The barium could have been removed by action of meteoric and thermal waters and transported upward along faults and fractures. Particularly favorable conditions and chemical reactions caused the precipitation of barium as barium sulphate at the contact between the ascending solutions and the Cambrian limestones. The Georgia barite deposits are classified by

HULL as: "(1) veins, (2) replacement, (3) breccia, (4) residual, (5) colluvial, (6) alluvial deposits" (p. 12).

C. L. ROBINSON studied the vein deposits of Central Kentucky in 1931. Three hypotheses were listed by him:

> (1) Meteoric waters leaching the vein materials from the enclosing rock, transporting this material to the fissures and there depositing the load, or by (2) meteoric waters rising by means of artesian conditions, obtaining their load of materials from the underlaying rocks, carrying the vein materials in solution from a deep-seated source, and depositing the load in the higher rocks, or by (3) magmatic solutions derived from some deep-seated basic intrusion, rising along the fissures or fault plane, and depositing the vein minerals present at the last phase of magmatic activity (p. 60).

ROBINSON in a brief discussion of the value of these theories, excluded the first one because of the lack of bedding planes or solution cavities which are present in the other districts of the Mississippi Valley. The possibility of water solutions leaching the material from preexistent formations was discarded because analyses of the limestones of Central Kentucky showed no traces of barium, fluorine, lead, and zinc. The lack of artesian conditions in the district, lead ROBINSON to preclude also the second hypothesis, and to accept the third one.

In 1931 G. I. ADAMS attributed the barite deposits of Alabama to the mesothermal and epithermal type of hypogene deposits. The author stated that ". . . the barium was brought up in emanations from magmas and deposited as veins and replacements, which were formed after the main Applachian structure was developed at the close of the Paleozoic" (p. 776).

The Sweetwater barite deposits of Tennessee were studied by R. A. LAURENCE in 1939. He suggested, with reserve, a deposition from thermal ascending water of meteoric or magmatic orgin.

Barite deposits of foreign countries

Several deposits of barite and associated sulphides have been described in different countries outside of the United States.

O. HOLTHEDAL (1909), studying the Cambro-Silurian system in Norway and its barite inclusions, expressed the opinion that the barite crystals are of secondary origin and have been formed in the sediments by circulating solutions in Silurian or Devonian time.

A. HADDING (1939) worked on the barite occurences in swedish black shales and clayey limestones. He stated that the barite has to be considered strictly syngenetic with the enclosing sediments. The barium, contained in some mud beds, was concentrated in place as barium sulphate.

L. STØRMER (1953) is, however, of the opinion that the barite crystals present in limestones and shales of the Cambro-Silurian of Norway and Sweden could have originated from substitution of sedimentary material by barium in the sediments during diagenesis.

The barite deposits in the sedimentary formations of the Odenwald in Germany were studied by ENGELHARDT (1936), SCHNEIDERHÖHN (1948), and MURAWSKY (1954). W. ENGELHARDT considered a possible origin of deposits of the Odenwald either by hypogene warm solutions or by supergene solutions which had leached the barium from preexistent formations. H. SCHNEIDERHÖHN and H. MURAWSKY, however, thought that barite bearing solutions should definitely have had a hypogene origin.

W. and W. E. PETRASCHEK (1950) recognized syngenetic-sedimentary characteristics in the barite and sulphide deposits of Meggen in Westfal (Germany). The same deposits were studied some years later by E. NICKEL (1956) who suggested a volcanic exhalative origin. The exhalative fluids could have brought up into the sedimentary ooze barium compounds which under anaerobic conditions, precipitated barium sulphate.

The barite deposits of Pessant (France) are, according to E. RAGUIN (1949), related to the structural features of the area. The barium bearing solutions may have come up along the faults and deposited their barium content epigenetically in the Liassic sediments. According to RAGUIN, also all the other occurrences of barite in sediments along the Pyrenees, the Alps and the Central Massive are related to hypogene solutions, introduced into the sediments through channelways provided by the several faults of the region.

The large barite deposits in limestone of the Cuddapah district (South India) were studied by P. B. MURTHY (1950) who referred to their origin as ". . . the mixing of ascending barium-bearing and descending sulphate-bearing waters in the earlier formed fissures."

The barite and celestine deposits of Tarquinia (Italy) were considered by B. CONFORTO (1950). The minerals are contained in a conglomerate of Post-Pliocene age and presumably originated by epigenetic deposition from ascending hydrothermal solutions of low temperature.

Barite deposits of Missouri

In 1908 E. R. BUCKLEY working on the barite and lead-zinc deposits of the Potosi area, and following the ideas of BISHOF about the solubility and the chemistry of barium, wrote:

> The barite of the area under discussion has probably been derived from barium carbonate which is soluble in 4300 times its weight in water, the solubility being increased through the addition of carbonic acid gas. The barium carbonate introduced, in solution, into the Potosi formation was probably precipitated through the mingling of barium carbonate solutions and solutions carrying an alcaline sulphate, perhaps calcium sulphate. The original source of the barium was probably the feldspars of the igneous rocks, from which were derived the materials making up the sedimentary formations of the area. The fact that barite does not occur in the formations beneath the Potosi, although occurring in those above, seem to argue that the barite bearing solutions come from above and that during the period of introduction of the barite, the Potosi was the oldest of the sedimentary formations reached by the downward-circulating barite bearing solutions (p. 247 - 248).

One of the most extensive works published in the first years of this century on the geology of the Missouri barite deposits is that of A. A. STEEL (1909). He considered the barite deposited contemporaneously with the galena, but not with calcite and dolomite. He suggested two types of occurrence of barium in solution: from weathering of overlaying formations or from igneous rocks buried not far below the deposits.

The genesis of the barite in Missouri was extensively studied by W. A. TARR (1918) and the conclusions were published in "The Barite Deposits of Missouri" (1918). The author outlined two hypotheses for the origin of these deposits: "(1) The barium was concentrated from the surrounding rocks and deposited in the veins, caves, etc.; (2) the barite was deposited by deep-seated solutions as veins, replacements, and cave deposits" (p. 75). TARR, in the conclusion of his paper, excluded the first hypothesis for the following reasons:

> (1). . . carbonate rocks, the dominant type in this area, have been shown to contain no barium, save in rare instances where it is not certain that it was not actually introduced into the rocks by later solutions; (2) the waters in such rocks are dominantly carbonate waters which are poor solvents for the barium salts; and (3) the rocks of the region are of very low permeability, save along the divisional planes where the activity of solutions is confined to the immediate walls (p. 85).

He excluded an origin from descending solutions, but accepted as more probable an epigenetic deposition of the barite and associated sulphides by ascending heated waters of igneous origin.

W. M. WEIGEL in 1929 published a complete summary of the barite deposits of Missouri, and also gave his interpretation of their genesis. He did not support the magmatic origin proposed by many geologists because of the structural features of the deposits. The barite, together with chalcedony, chert, and drusy quartz, supposedly contemporary according to WEIGEL, is genetically related to descending waters. Galena, frequently present as crystals enclosed in the barite, is considered to be of earlier deposition.

C. L. DAKE's paper on the geology of the Potosi and Edgehill quadrangles was completed in 1930. The problem of the genesis of the barite was considered, and four possible theories to explain its origin were advanced: "(1), descending cold solutions; (2), ascending cold solutions under artesian head; (3), ascending hot solutions from deep-seated hidden igneous sources; and (4), original deposition in colloidal form, along with disseminated silica, from sea water." (p.204) The complete absence of barite in the residual soil of the Gasconade formation, overlaying the Potosi and Eminence, is, according to DAKE, a strong point against the first hypothesis The presence of an impermeable horizon below the Potosi formation (Davis formation) is one of the evidences against the second and third theories. After the exclusion of three out of four theories, the author emphasized that the barite was syngenetically deposited as colloidal barite from sea water during the formation of the enclosing sediments.

W. A. TARR, who in 1918 had already proposed a magmatic origin for the barite deposits of Missouri, in 1932 after the discovery of a vein of barite in the granite of Iron County, some fifty miles south of Potosi, stated:

> The occurrence of the barite vein in the granite (which undoubtedly also occurs under the sedimentaries in the barite district of Washington County to the north) is confirmatory evidence of the conclusion, previously reached, that the solutions which deposited the barite in the dolomites of Washington County were of magmatic

origin. The solutions depositing the vein and those responsible for the barite deposits to the north were undoubtedly similar, though as the latter deposits were stratigraphically higher the solutions depositing them were undoubtedly cooler. However, although both deposits are of magmatic origin, they may not have been deposited by solutions from the same part of the magma; which would account for the minor differences in mineralization (p.447).

TABLE I

CHRONOLOGICAL LIST OF LITERATURE ON BARITE AND THEORIES OF ORIGIN

Author-Year	Locality	Bedrock	Origin
KEITH (1904)	North Carolina	Granite-Feldspar-Quartzite	epi-hypo: magmatic solution
WATSON (1907)	Virginia	Limestone	epi-super: meteoric water
BUCKLEY (1908)	Missouri	Limestone-Dolomite	epi-super: descending solutions
HAYES-PHALEN (1908)	Georgia	Limestone-Dolomite	epi-super and hypo: percolating of surface waters and thermal spring at depth
HOLTHEDAL (1909)	Norway	Sediments Cambro-Silurian	epi-super: later circulating solution
STEEL (1909)	Missouri	Limestone-Dolomite	epi-super and hypo: ascending or descending solutions
FOHS (1913)	Kentucky	Limestone	epi-hypo: ascending solutions
GRASTY (1913)	Alabama	Dol. Limestone	epi-super and hypo: descending meteoric water, thermal spring
WATSON-GRASTY (1915)	Applachian States	Sedimentary & cryst. rocks	epi-super: leaching from shallow water circulation
RHIES (1916)	General	Sediments	epi-super: leaching from aqueous solutions
TARR (1918)	Missouri	Limestone-Dolomite	epi-hypo: heated water of igneous origin
GORDON (1918)	Tennessee	Dolomite	epi-super: water solutions
HULL (1919)	Georgia	Limestone	epi-hypo: thermal water solutions

TABLE I (continued)

LINDGREN(1919)	General	Sediments	epi-super:meteoric waters
WEIGEL(1929)	Missouri	Limestone-Dolomite	epi-super: descending solutions
DAKE(1930)	Missouri	Limestone-Dolomite	syn-super:colloidal barite from sea water
ADAMS(1931)	Alabama	Limestone-Dolomite	epi-hypo: magmatic emanations
ROBINSON(1931)	Kentucky	Limestone	epi-hypo: magmatic solutions
TARR(1932)	Missouri	Limestone-Dolomite	epi-hypo: magmatic solutions
STUCKEY-DAVIS (1933)	North Carolina	Cryst. rocks	epi-hypo:magmatic solutions
ENGELHARDT (1936)	Germany & General	Dolomites Limestones Sandstones	syn-super:weathering through descending solutions
LAURENCE(1939)	Tennessee	Dolomite	epi-hypo: ascending thermal water
HADDING(1939)	Sweden	Shale-Limestone	syn-? : concentration in place
EMERY-REVELLE (1942)	California	Recent marine sediments	syn-hypo: hot springs rich in barium and sulphate of sea water
SCHNEIDERHÖHN (1948)	Odenwald (Germany)	Sediments	syn-hypo: ascending solutions
RAGUIN (1949)	France	Liassic Sediments	epi-hypo: ascending solutions
CONFORTO (1950)	Italy	Conglomerate	epi-hypo: ascending hydrothermal solutions
MURTHY(1950)	India	Limestone	epi-hypo: ascending barium solutions and descending sulphate solutions

TABLE I (continued)

PETRASCHECK (1950)	Meggen Dep. (Germany)	Sediments	syn-hypo: ascending solutions
STØRMER (1953)	Norway and Sweden	Limestones-Shales	syngenetic substitution (?)
MURAWSKY(1954)	Odenwald (Germany)	Sediments	syn-hypo: ascending solutions
NICKEL (1956)	Meggen Dep. (Germany)	Sediments	syn-hypo: volcanic exhalative solutions
WEEKS, et al. (1957)	Colorado	Sandstones	syn-hypo: volcanic emanations

CHAPTER IV

DETAILED OBSERVATIONS

Definitions of terms used

A study of the geometry of the deposits, of the geochemistry of barium and of some factors of logic, which influenced the final interpretation, is offered in the following pages.

In order to reach a conclusion which is as independent from previous theories as possible, and furthermore, in view of the highly controversial nature of the topic, an attempt is made not to introduce geometric and geochemical terms with genetic connotations. Such sets of terms have been offered by NIGGLI (1948, 1954) with regard to complete rock bodies, and by AMSTUTZ (1956) on individual intergrown grains.

In the literature the terms "vein", "veinlets", "masses", "stringers", and "replacements" are used for barite occurrences in bedrock. According to HUTTON (PLAYFAIR, 1802, p. 67) veins are "traversing the strata". The AGI Glossary (1957) offers various definitions, the scientific ones of which all imply crosscutting relationships. BERINGER-MURAWSKI's Geologisches Wörterbuch (1957) defines veins as small dykes, thus also implying a crosscutting relationship of elongated body through a bedded or homogeneous mass. C. M. RICE (1940) in the "Dictionary of Geological Terms", defines a vein as an "irregular sinuous injection or a tabular body of rock formed by deposition from solutions rich in water or other volatile substances".

For the purpose of a deeper genetic understanding it is thus necessary to create a specific terminology. Terms like "spot", "amoeba-like mass", or "patch" appear to be most appropriate and have the advantage of no genetic connotation.

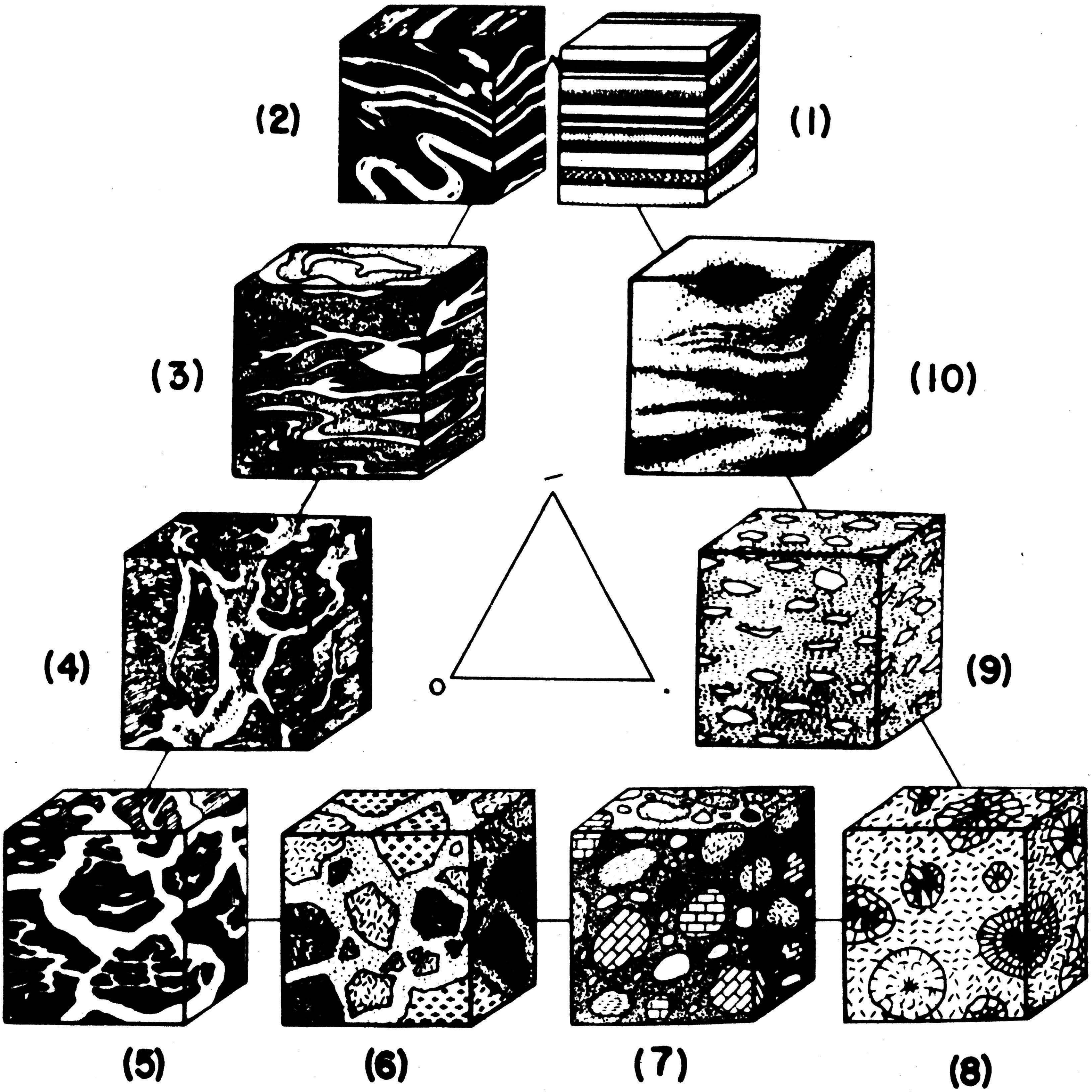
In a few cases it is possible that some connected spots or patches almost form a stringer. There has not been found any reason to use the term "vein", inasmuch as in none of the outcrops could be found a continuation of the deposit in the foot wall or in the hanging wall. NIGGLI's classification of rock fabrics offers such simply geometric connotation-free terms as "phlebite" and "merismite" for the textures observed in the Missouri bedrock barite deposits.

The drawings that are useful for the barite deposits studied are nos. 3, 4, 5, 6, in table 2. This chapter on the detailed observations is divided as follows:

- Geometric observations
  - Barite in coherent bedrock
  - Barite in the matrix of the dolomite breccia
  - Barite in complex arrays
  - Observations on crystal growth
- Geochemistry
  - Geochemistry of barium
  - Geochemical observations
- General rules of logic

TABLE II

THE NIGGLI CLASSIFICATION OF ROCK TEXTURES



<u>Purely geometric nomenclature of rock textures</u>
free of genetic interpretations, for chorismites or chorismatic, polyschematic rocks or mineral deposits (= rocks which consist of two or more textural units).

1 and 2 = Stromatites	7, 8, 9 = Ophthalmites
3 and 4 = Phlebites	(8 = Miarolithite)
5 and 6 = Merismites	10 = Nebulite

Geometric Observations

The occurrence of barite and associated sulphides in the Potosi and Eminence formations can be classified into three principal types, but this subdivision into types is made only because of convenience. The transitions between them are actually completely gradational, as visible both in the outcrops and drill cores.

Barite in coherent bedrock

The term coherent is here used for those portions of the dolomites or other sediments which are not broken up into pieces which are separated by a matrix. Barite in coherent bedrock is present in all the outcrops as irregular phlebitic masses, some centimeters wide and several centimeters long. These masses are usually oriented in a horizontal plane. If the horizontal portions are compared with the vertical ones, leaving out the inclined or highly curved segments, the horizontal portions outnumber the vertical ones by about two to one. This gives the general impression of somewhat bedded nature to the scattered patches of barite.

The same tendency to horizontality is conspicuous where there are large masses of barite in the bedrock. These masses generally have a diameter of 25-35 cm., sometimes one of the two dimensions being much greater than the other. The maximum dimension, in this particular case, is always along the horizontal plane (see Figures 10-11a,11b). This type of barite occurrence is quite widespread. At the margin of the brecciated, or type 2 barite deposits, there are perfect transitions between the two geometric forms.

Type one geometry occurs for example in the upper parts of the drill cores of the Krueger property (logged by the author in the U. S. Bureau of Mines Core Library of Minneapolis).

Barite in the matrix of dolomite breccia

The second geometric type differs from the first one with regard to the inverse role which the barite and the dolomite play. In this case the dolomite is incoherent, whereas the barite and other matrix materials are coherent. As stated above, type one geometry corresponds to no. 3 of the NIGGLI-textures, whereas type two geometry corresponds to type no. 5. Texture no. 4 is transitional (see Table 2).

The lateral extension of one of the outcrops, exhibiting this second type of deposit, is shown in Figure 4. From the same picture the complete lack of barite in the foot wall is seen.

Thin crusts of limonite are often observed at the contact between the barite and the bedrock in the outcrop north of Missouri Highway No. 8. The limonite (see Figure 7, 8a, 8b, 9a, 9b) is also present between dolomite "blocks" where no barite is found, forming the same boxwork pattern as when "cemented" by barite or barite and limonite (see Figure 9a, 9b).

Limonitic boxworks are also seen on exposed horizontal outcrops, parallel to the bedding of the dolomite, being evidence of the boxwork pattern in three dimensions.

The origin of this limonite is discussed later.

In this type of occurrence as well as in the first one, large crystals of galena are frequently associated with the barite and occur always in the center of barite masses. In only one case, out of about twenty where galena was found with barite, did it occur in a vertical portion of the network. In all other cases galena occurred in larger barite masses which are the knots of the network.

A relatively high amount of green shaly material is always present either in the outcrops or in the drill cores studied (in the massive beds overlaying the Krueger property breccia). This shale occupies small fractures, vugs, stylolitic features. Sometimes the shale is associated with the ore minerals and occurs right above them.

An X-ray text was performed by Mr. Krisnaswamy of the Missouri School of Mines and Metallurgy on a sample of this material collected by the author. The results bring to the conclusion that this shale consists of a micaceous mineral belonging to iron-magnesium mixed layer type.

In a few cases muddy calcareous material is present in the upper parts of vertical networks of the breccia, and it is associated mostly with barite and shale (see Figure 12a, 12b).

Barite in complex arrays

By complex arrays is meant a complex rock both in a mineralogical as well as in a geometric way. Geometrically this breccia shows various generations of brecciation.

Previously cemented breccias are broken a second or third time. The mineralogical variation is described later.

Barite associated with lead, zinc, and iron sulphides is present in the dolomitic and cherty breccia representing the mineralized portion of the Krueger property. This breccia consists of angular fragments of dolomite and chert of different shapes and sizes. The size of these fragments varies from about one to ten cm. The color of the medium-grained dolomite is prevalently light-gray, and it changes to pinkish-brown during weathering. The chert is always of a light-gray color. It occurs in the breccia seen in the dump as well as in portions of the outcrop close to the shaft of the property. Barite occurs associated with sphalerite, marcasite, and galena as matrix of this dolomitic, cherty breccia (see Figures 13, 14, 15).

Galena is present as crystals or crystal aggregates inside the barite and never occurs in layers or in shell-like patterns around the fragments of the breccia. The analyses of the drill cores did not show any appreciable amounts of lead.

Marcasite is fairly abundant either as massive, or small grained aggregates consisting of idiomorphic drusy crystals. It occupies thin layers, coating the dolomite fragments of small vugs and holes of the breccia. A botryoidal form is also present. In a few fragments of the breccia, marcasite is present in a disseminated form.

In addition, it was sometimes seen in vugs outside this breccia and then as a rule covered the bottoms of vugs. A detailed discussion of the paragenesis will be given in the next chapter.

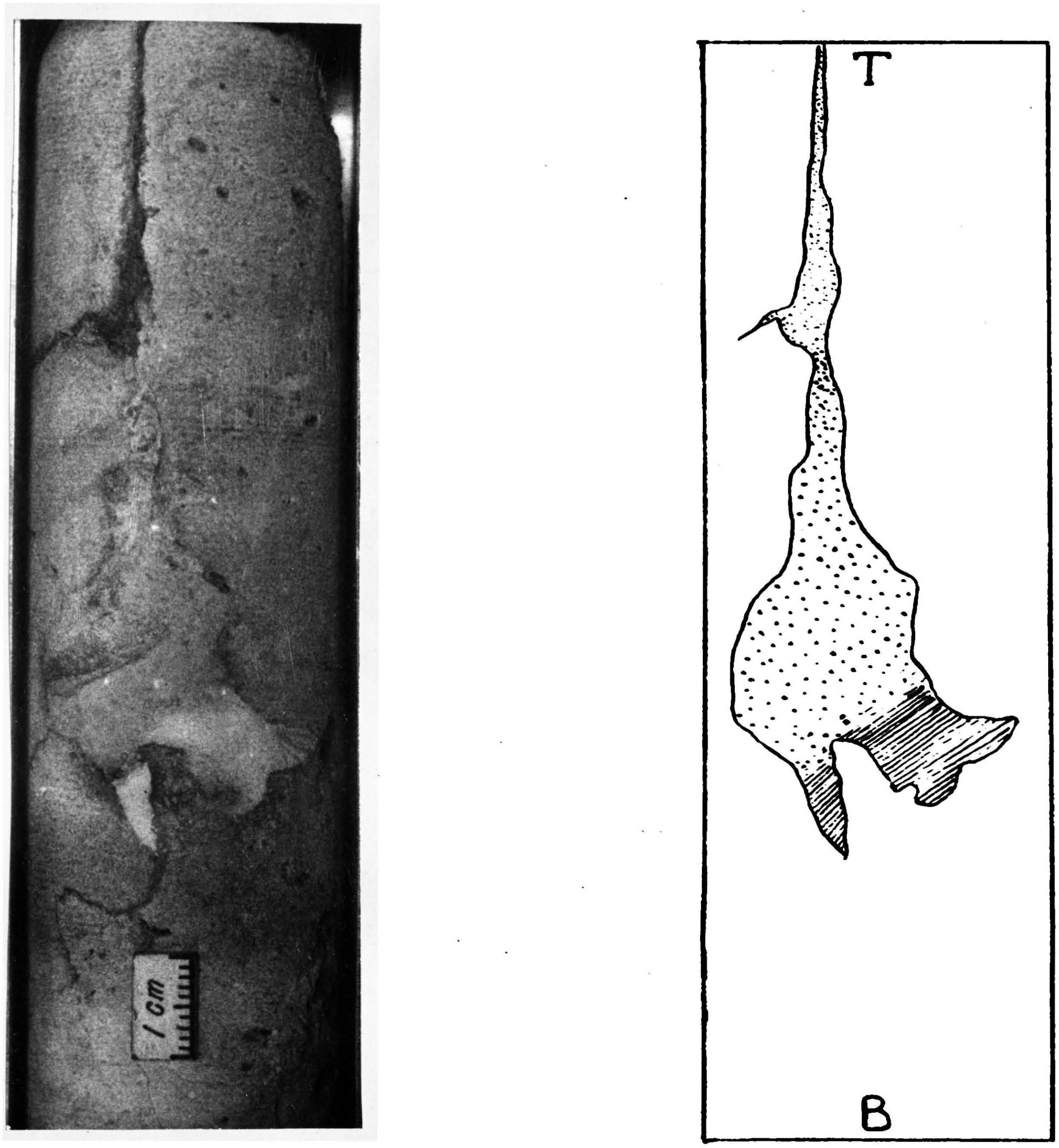
Sphalerite is the most abundant sulphide present. Generally it occurs in a massive form and not as crystals, surrounding the fragments of dolomite and chert. Sometimes it occurs also as small crystal aggregates either in holes of the breccia or as disseminated spots in the dolomite itself. In some specimens and in a few parts of the drill cores studied, sphalerite assumes the typical crustaceous texture ("Schalenblende" in german).

Observations on crystal growth

A wealth of detail observations on the growth of individual crystals and crystal aggregates could be made. Only a few basic ones, with a bearing on the genesis, can be mentioned in this connection. When making observations on the size, the shape and growth texture, as well as the growth directions of the barite crystals the following details were noted: Coarse grained crystal aggregates of barite are present in all three types described above and illustrated in figures 16a, 16b, 17. In some occasions the crystals are of considerable size (up to 15 cm.) and sometimes form starshaped arrays, occasionally ending in a drusy cavity.

The genetic significance of this crystal growth is discussed below. In the drill cores from the Krueger property, in about ten places, small and delicate crystals of barite occupy isolated spots on quartz and chalcedony or dolomite crystals at the bottom of the small vugs (see Figures 18, 19a).

In most cases observed in the drill cores of the property, the distribution of barite and marcasite in the matrix or in the vugs between the dolomite breccia pieces grew from the bottom and reflects thus its strong dependence on the gravity field.



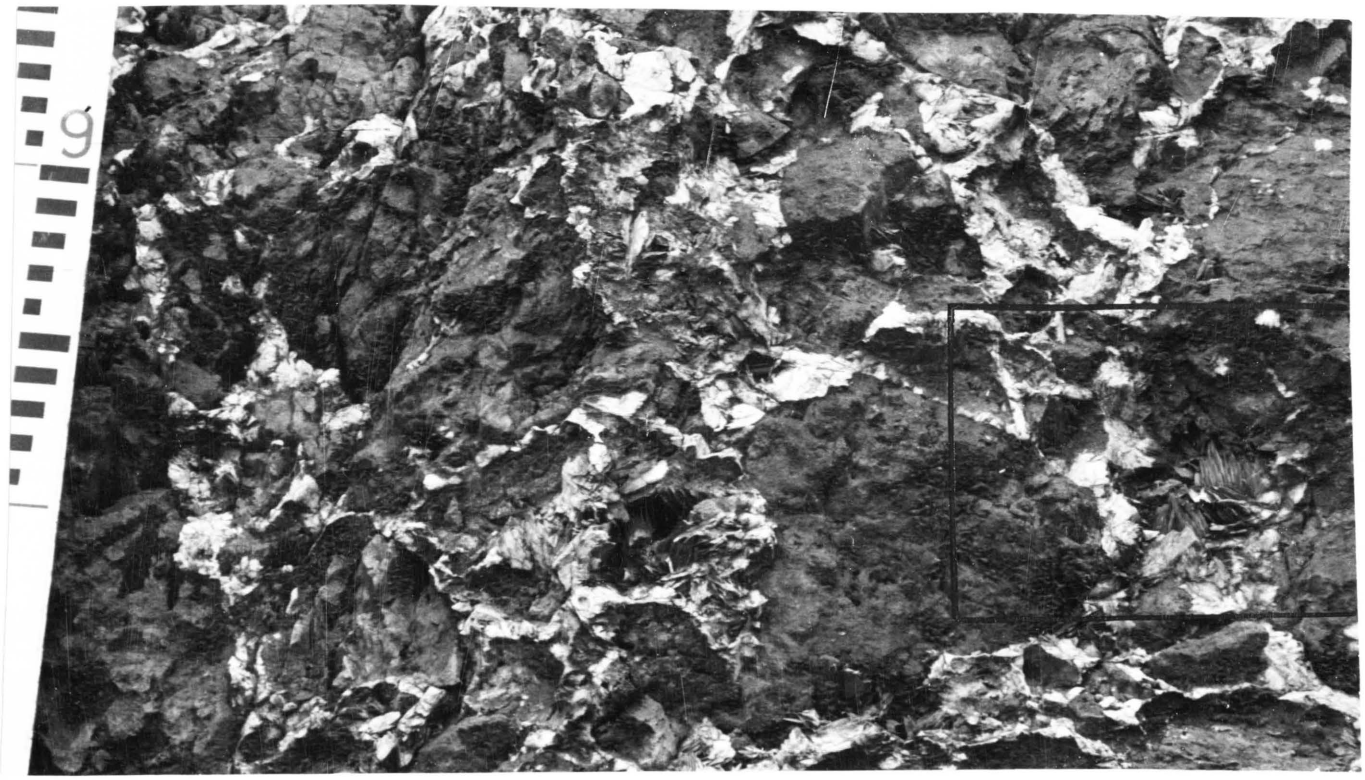
a. b.

Figure 12 a, b - Top-bottom feature in a piece of the drill core of the Krueger Zinc Deposit.
White spot on bottom is barite, next portion (about 6 cm.) is calcareous mud, the uppermost portion (dark fissure filling is shaly material.
Location: hole 38,184 feet depth, U. S. Bureau of Mines Core Library, Minneapolis.

Figure 13 - Barite-sphalerite-marcasite as matrix of the dolomitic breccia of the Krueger Zinc Deposit. Location: Dump south of the pit shown in Figure 2.

Figure 14 - Barite, sphalerite and galena as matrix in the breccia of the Krueger Zinc Deposit. Location: Hole 34,186 feet depth, U. S. Bureau of Mines Core Library, Minneapolis.

Figure 15 - Samples of the dolomitic breccia of the Krueger Zinc Deposit.
In the sample to the right, the sharp edges of the dolomite fragments are visible; at the left a view on a plane cutting almost exclusively through the sulphide matrix is exposed, mostly with marcasite and sphalerite. Both are slightly oxidized to limonite.
Location: Dump south of the pit shown on Figure 2.



Figures 16a, 16 b - Bladed crystals of barite in the outcrop on the Hornsey Brothers Mining Company, southwest of Potosi (Section out of Figures 2 and 3).
One crystal cavity showing centripetal growth of barite is seen in the marked area on Figure 16a and is enlarged on Figure 16b.

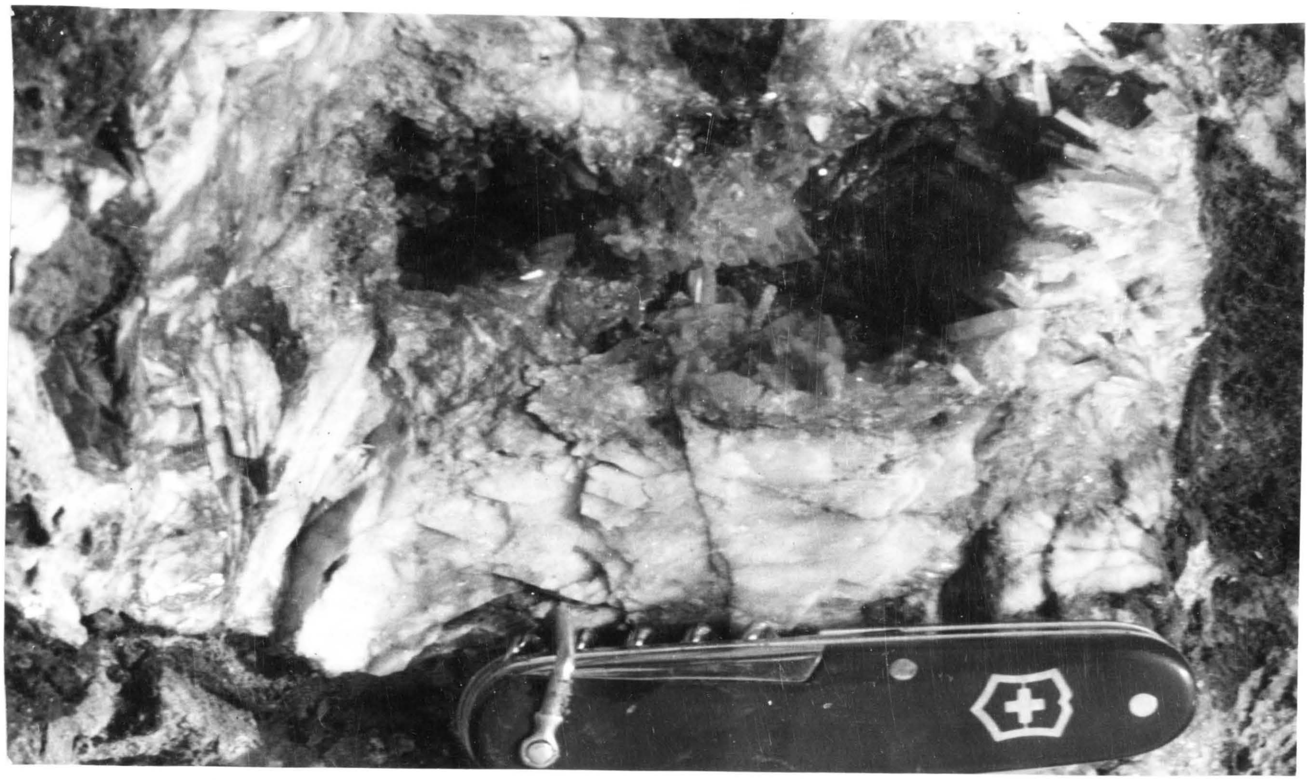
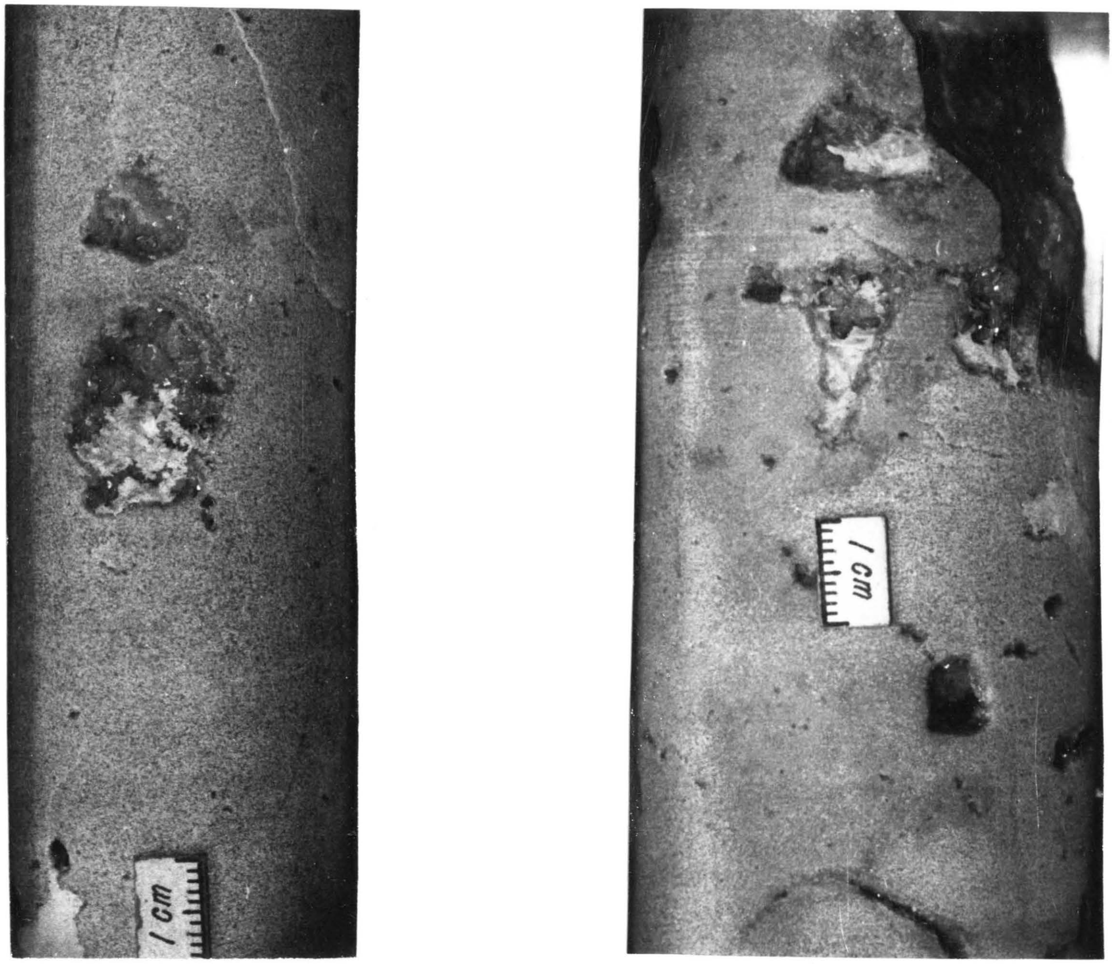


Figure 17 - Crystals of barite in a cavity in the center of a matrix portion of the breccia of the Krueger Zinc Deposit.
Location: Large block on the dump south of the pit.



a. b.

Figures 18a, 18b - Thin crystals of barite at the bottom of small vugs in the drill cores of the Krueger Zinc Deposit.
Location: hole 34,165.5 feet depth, U. S. Bureau of Mines core Library, Minneapolis.

a.

b.

Figures 19a, 19b - Crystals of barite and massive barite associated with marcasite at the bottom of vugs in the drill core of the Krueger Zinc Deposit.
Location: hole 42,156.5 feet depth, U. S. Bureau of Mines Core Library, Minneapolis.

Geochemistry

This section is divided into two subdivisions: the first gives a general review of the geochemistry of barium and barium compounds as advanced by several authorities as ENGELHARDT (1936), SVERDRUP, JOHNSON and FLEMING (1942), EMERY and REVELLE (1942), RANKAMA and SAHAMA (1950), P. NIGGLI (1954), E. NICKEL (1956) and others. The second contains the geochemical observations of the author on the barite deposits of southeastern Missouri.

Geochemistry of barium and barium compounds

Barium belongs to the geochemical group of the rarer elements (see P. NIGGLI, 1954, p. 50-51). Although it is relatively rare, it forms its own minerals, besides occurring in camouflage or substitution positions in major minerals such as K-feldspars. The average content of barium in the earth's crust is about 0.08 per cent and in sea water 0.05 mg/L as reported by GOLDSCHMIDT (1937, Re. SVERDRUP, JOHNSON, and FLEMING, 1942). RANKAMA and SAHAMA (1950) reported a value of barium of 0.05 gr/ton while BORCHERT (1950) mentions a considerably lower quantity. In table 3 is given a value of 10 mg/ton = 0.000 001 % of barium. In the same table the averages of BaO for all the common and many rarer types of rock are given.

Of a different opinion are REVELLE, BRAMLETTE, ARRHENIUS and GOLDBERG in their publication of 1955. These authors do not accept the values given previously and at p. 229 of their paper stated:

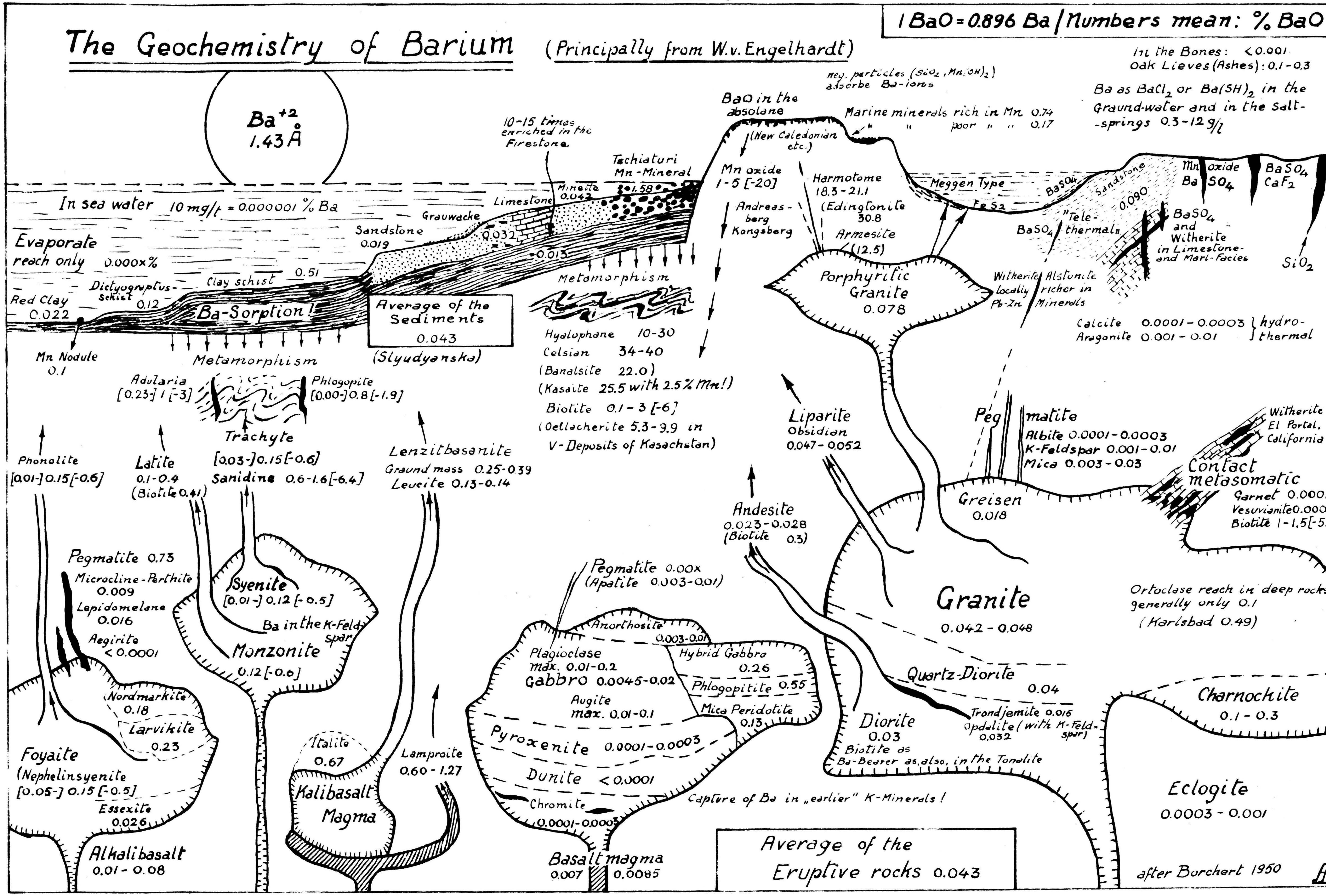
> Strikingly high concentrations of barium are found in siliceous sediments fringing the calcareous-ooze areas. Though barium usually ranges between 0.05 and 0.30 per cent in pelagic sediments, the concentration here rises to 1-2 per cent. Barium has never been detected in sea water, but an upper limit of 0.1 part per million has been established by spectroscopic methods. A possible explanation of the high concentration in the siliceous ooze in that minute amounts of barium in the calcareous skeletons of marine plankton become concentrated when calcium carbonate is dissolved, because of the relatively low solubility of barium sulphate. High-barium concentrations would be expected in areas where the rates of both deposition and dissolution of calcium carbonate is high. The concentration of barium may thus be a measure of the rate of dissolution of calcium carbonate, a variable which has not been previously measurable.

Barium as a substitution element is mostly concealed in rock forming minerals of igneous origin, the highest content being found in rocks of the syenite family where Ba^{++} is contained in the K-feldspars. It was also detected in pyroxenes in granite. AHRENS (1950-1951) reports a BaO-average of 1450 g/ton in granite, and a BaO-average of 213 g/ton diabase. AMSTUTZ (1953) found 1000 g/ton in Permian quartz-porphyries in the Alps and only 300 g/ton in the spilites associated with them.

Potassium bearing minerals are the most favorable for containing barium, because its ionic radius (1.43 kX) enables it to substitute for potassium (ionic radius 1.33 kX). Barium forms its own minerals during the last phase of magmatic differentiation.

Some authors derive barium from weathering solutions, others assume that it was extracted from previously formed igneous rocks by a hypogene solvent action of hydrothermal solutions.

~TABLE 3~



1 BaO = 0.896 Ba / Numbers mean: % BaO
The Geochemistry of Barium
(Principally from W.v. Engelhardt)
In the Bones: < 0.001
Oak Lieves (Ashes): 0.1 - 0.3
Ba as $BaCl_2$ or $Ba(SH)_2$ in the Graund-water and in the salt-springs 0.3 - 12 g/l
Ba^{+2} 1.43 Å
In sea water 10 mg/t = 0.000001 % Ba
Evaporate reach only 0.000x %
Red Clay 0.022
Dictyograptus-Schist 0.12
Clay schist 0.51
Ba-Sorption!
Mn Nodule 0.1
Sandstone 0.019
Grauwacke 0.032
Limestone
Minette 0.042
0.013
10-15 times enriched in the Firestone
Tschiaturi Mn-Mineral 1.58
Average of the Sediments 0.043
(Slyudyanska)
Metamorphism
Metamorphism
Hyalophane 10-30
Celsian 34-40
(Banalsite 22.0)
(Kasaite 25.5 with 2.5% Mn!)
Biotite 0.1 - 3 [-6]
(Oellacherite 5.3 - 9.9 in V-Deposits of Kasachstan)
BaO in the absolane
neg. particles (SiO_2, $Mn(OH)_2$) adsorbe Ba-ions
(New Caledonian etc.)
Marine minerals rich in Mn 0.74
poor " " 0.17
Mn oxide 1 - 5 [-20]
Andreas-berg Kongsberg
Harmotome 18.3 - 21.1
(Edingtonite 30.8
Armesite (12.5)
Meggen Type
FeS_2
$BaSO_4$
Sandstone 0.090
Mn oxide
Ba SO_4
$BaSO_4$ CaF_2
$BaSO_4$ "Tele-thermal"
$BaSO_4$ and Witherite in Limestone- and Marl-Facies
SiO_2
Porphyritic Granite 0.078
Witherite locally Pb-Zn
Alstonite richer in Minerals
Calcite 0.0001 - 0.0003 } hydro-
Aragonite 0.001 - 0.01 } thermal
Adularia [0.23-] 1 [-3]
Phlogopite [0.00-] 0.8 [-1.9]
Trachyte [0.03-] 0.15 [-0.6]
Sanidine 0.6 - 1.6 [-6.4]
Phonolite [0.01-] 0.15 [-0.6]
Latite 0.1 - 0.4 (Biotite 0.41)
Lenzitbasanite
Graund mass 0.25 - 0.39
Leucite 0.13 - 0.14
Liparite Obsidian 0.047 - 0.052
Pegmatite
Albite 0.0001 - 0.0003
K-Feldspar 0.001 - 0.01
Mica 0.003 - 0.03
Witherite El Portal, California
Contact metasomatic
Garnet 0.0001
Vesuvianite 0.0003
Biotite 1 - 1.5 [-5.1]
Greisen 0.018
Andesite 0.023 - 0.028 (Biotite 0.3)
Pegmatite 0.73
Microcline-Perthite 0.009
Lepidomelane 0.016
Aegirite < 0.0001
Syenite [0.01-] 0.12 [-0.5]
Ba in the K-Feldspar
Monzonite 0.12 [-0.6]
Nordmarkite 0.18
Larvikite 0.23
Foyaite (Nephelinsyenite [0.05-] 0.15 [-0.5]
Essexite 0.026
Alkalibasalt 0.01 - 0.08
Italite 0.67
Kalibasalt Magma
Lamproite 0.60 - 1.27
Pegmatite 0.00x (Apatite 0.003 - 0.01)
Anorthosite 0.003 - 0.01
Plagioclase max. 0.01 - 0.2
Gabbro 0.0045 - 0.02
Augite max. 0.01 - 0.1
Hybrid Gabbro 0.26
Phlogopitite 0.55
Mica Peridotite 0.13
Pyroxenite 0.0001 - 0.0003
Dunite < 0.0001
Chromite 0.0001 - 0.0003
Basalt magma 0.007 0.0085
Granite 0.042 - 0.048
Ortoclase reach in deep rocks generally only 0.1 (Karlsbad 0.49)
Quartz-Diorite 0.04
Trondjemite 0.015
Opdalite (with K-Feldspar) 0.032
Diorite 0.03
Biotite as Ba-Bearer as also in the Tonalite
Charnockite 0.1 - 0.3
Capture of Ba in „earlier" K-Minerals!
Eclogite 0.0003 - 0.001
Average of the Eruptive rocks 0.043
after Borchert 1950

In the exogenetic cycle, barium can be found as bicarbonate, chloride, or sulphate obtained by weathering of barium bearing rocks. The bicarbonate and the chloride are the most easily transported in the solutions while the sulphate is only very slightly soluble and only slightly attacked by atmospheric agents. The solubility of the sulphate, however, can be increased if the waters leaching the barium-mineral-bearing rocks contain a small amount of hydrochloric acid or chlorides of the alkali metals (see RANKAMA and SAHAMA, 1950, p. 480).

Several controversial explanations were offered for the precipitation of barium in sediments. ENGELHARDT (1936, Re. RANKAMA and SAHAMA, 1950), RANKAMA and SAHAMA (1950), and others stated that barium precipitates easily during the formation of the clay minerals. Among the different types of clays those which contain barium or barium compounds in greatest quantity are the ones deposited relatively near the coasts in comparison with those at the bottom of the oceans.

This property of accumulation of barium in relatively shallow clays is said to be mostly due to the "adsorption" properties of the clays. In the Hofmeister series, barium is one of the elements which shows a relatively high tendency to "adsorbability" and this property is related to its ionic potential ($\Phi = 1.40$) and its ionic radius (1.43 kX). Here too, the relationship between K and Ba becomes evident.

The enrichment of the clays of the lithoral zone in barium, reduces considerably the quantity of the element still in solution, and consequently only small amounts of barium may be carried to the open oceans. Analyses of several samples show a maximum of 0.022 % of BaO in the red clays as against the 0.047 % of BaO in the near-shore clays.

Limestone, dolomites, and other carbonate sediments usually show a very small amount of barium. This is due to the small quantity of barium available during their formation and, also, according to ENGELHARDT (1936), to the absence of diadochy between barium and calcium.

Barium sulphate concretions have been found in various sediments, and the symmetrical growth-form of barite described as "rosettes" are well known. Barite concretions in recent marine sediments were reported close to the west coast of Ceylon at 1235 meters depth, near the Kai Island in the Dutch East Indies at a depth of 304 meters, and near Catalina Island close to the coast of California at 800-650 meters depth, as stated by SVERDRUP, JOHNSON and FLEMING (1942). EMERY and REVELLE (1942, Re. SVERDRUP, JOHNSON and FLEMING, 1942) believe that the formation of these concretions could be formed by the interaction between barium contained in hot spring waters and the sulphate content in the sea water.

E. NICKEL (1956) studied the possible formation of pyrite and associated barite in the Meggen deposit in Germany in great detail, and published a number of papers on this problem. The possibilities of pyrite and barite formation in a sedimentary basin are shown in Figure 20 which is copied from his last paper on the Meggen deposit. The illustration is reproduced in order to avoid misunderstanding. The conclusions reached by NICKEL are reported in full from p. 134 of his publication:

> Wo sich in Lagerstätten wie Meggen oder Rammelsberg Anzeichen eines starken Temperaturgefälles während der Förderperiode finden, kan man von einen "exhalativen Telescoping" sprechen. In diesen Fällen is auch die z.B. in Santorin beobachtete Folge $FeCl_3$-$FeCO_3$-FeS_2 auf unsere Lagerstätten übertragbar; im Sinne der auch sonst beobachtbaren Erzfolgen (z.B. Lahn-Dill-Gebiete Spateisen folgt auf Hämatit; späte Sulfide in Eisenkarbonatgängen usw.).
> Wahrscheindlich sind in Meggen schon die ersten Lieferungen nicht H_2S-frei gewesen, so dass gemischte Hydroxid-Sulfidfällungen stattfanden. Stetig verschob sich die Lieferung zur H_2S-Seite, wodurch sich die Hydroxide vollstanding in Sulfide unwandelten. Im Schema kommt man von links nach rechts; der niedergeschlagene Schlamm würde dann auch noch nachträglich mit H_2S durchstromt worden sein. Unsere Mainung ist also, dass das solfatarische Stadium zu steril ist, um eine Lagerstätte vom Ausmasse Meggens kurzzeitig und engräumig entstehen zu lassen, und dass man deshalb den im Sinne v. Wolffs fumarolischen Exhalationzyklus hinzunehmen soll. Um den Meggener Verhältnissen gerecht zu werden, müsste man also das Schema der Abb. 1 so verändern, dass die schräge Cl-SO_2-CO_2-Achse senkrecht zu stehen kommt; gerade das wäre dann charakteristisch für exhalatives Telescoping.
>
> Im ganzen gilt, was Schneiderhöhn für die hydrothermalen Lösungen schon 1941 unterstrich: "Man hat oft angenommen, dass die Schwermetalle auch in Form von Alkalidoppelsulfiden in Lösung seien. Das scheint nach neueren Befunden immer mehr die Wahrscheinlichkeit zu-genommen, dass Chloride und Fluoride der Schwermetalle eine grosse Rolle spielen und dass die Gleichgewichtsverhältnisse dieser Lösungen mit der gelösten freien H_2S für die Ausfällung eine ausschlaggebende Bedeutung haben" (p.303). "Zur Beurteilung der Natur der hydrothermalen Lösungen lassen sich die Flüssigkeitseischlüsse verwenden. In allen untersuchten PbS- und ZnS-Proben der verschiedenen hydrothermalen Lagerstätten kommen nur NaCl und etwas $CaCl_2$ in einer ziemlich konzentrierten, wässrigen Lösungen vor" (p.301).
>
> Wir haben uns schon dahingehend geäussert, dass wir uns

alle Absätze entstanden denken nach vorausgegangener inniger Verteilung im Meerwasser. Die nach dem Absatz noch weiter tätigen H_2S-Quellen erzeugen die Bilder primärer Bildungsunruhe, reichern zugleich das Sediment an Schwefel (FeS--FeS_2) und bewirken nun erst, nachdem das Ba ausgetreten ist und als Lösung übersteht bzw. zur Seite gewandert ist, die erhöhte kolloiddiagenetische Agilität des Koagelschlammes, der nun zu der von uns im Versuch reproduzierten Gekrösestruktur kommt und die topochemische Strukturierung erhält. Nach der Oxidation zum Sulfat fällt das Ba als $BaSO_4$ aus.
Es ist denkbar, dass auch die Art der Barytausscheidung durch die späten (in bezug auf das Eisen immer steriler werdenden) H_2S-Ausströmungen beeinflusst ist. In diesem Zusammenhange sind weitere Untersuchungen zum Verständnis der Barytstrukturen im Gange.
Die Mannigfaltigkeit der Strukturen und Texturen im Meggener Lager ist also bedingt durch eine Koagelfällung, durch die ausschliessende Kolloiddiagenese und durch metamorphe Ueberprägungen an schon verfestigten Niederschlägen. Die getrennte Lagerung des Pyrits und des Schwerspates lässt sich auch dan von chemischer Seite her verstehen, wenn man gleichzeitige Förderung von Fe und Ba in den Ablagerungsraum hinein annimmt. Mit Hilfe von Fällungsversuchen wurden die Bedingungen herausgearbeitet, die man den Vorstellungen ueber Erzförderung und Erzabsatz zugrunde legen muss.

Geochemical observations

The chemical environment of deposition of barium and barium compounds - syngenetically during sedimentation, or epigenetically in pores and fractures of the bedrock - is determined by the characteristics of environment of deposition, or of the bedrock and/or possible fluids (groundwater, etc.) in which and/or from which it forms.

Some observations were made in the field and are reported below.

<u>Basic environment</u>: The environment in which the barite, discussed in this thesis was formed, was probably always basic since the host rock consists of carbonates. The water

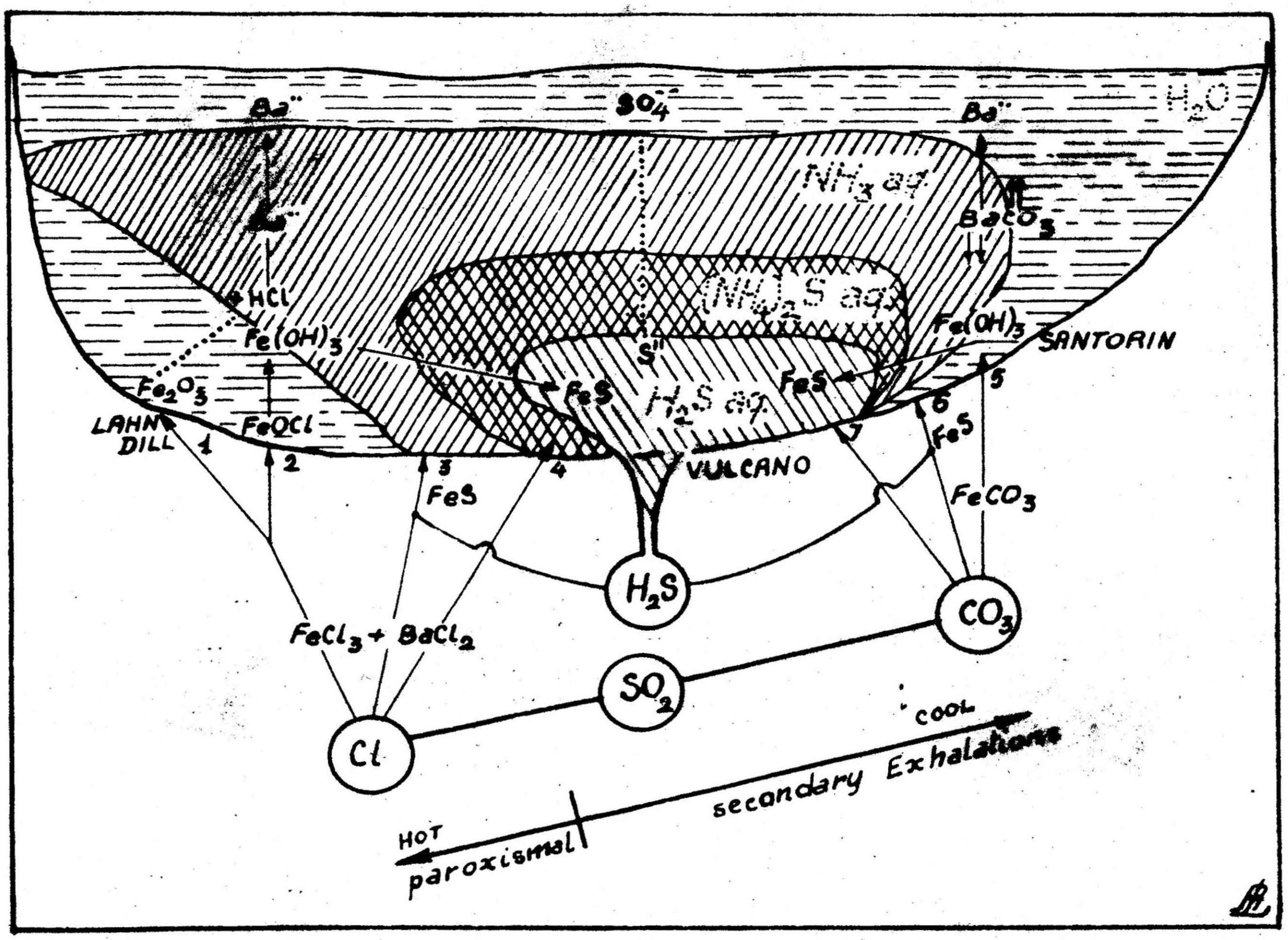


Figure 20 - Scheme of introduction and reactions of marine exhalative iron deposits. (Drawing and translation from NICKEL's paper 1956, p. 102-103).

If in a water basin, which contains partly neutral water, partly hydrogen sulfide water, and partly ammonium sulfide water, (punctuated formulas) springs appear, the following types of reactions take place as causes of chloride emanations (from left to right in the scheme):

1. Discharge of $FeCl_3$ at high temperature into the water. Fe_2O_3 and HCl form according to the Stirnemann experiment. This reaction coupled with the formation of SiO_2 from $SiCl_4$, is assumed to take place for the formation of the Lahn-Dill Ores. Because of required partial pressures for $FeCl_3$, temperature values of at least 300°C have to be supposed.

2. At low temperature (by way of FeOCl) hydroxide forms. The hydrochloric acid has to be neutralized for complete precipitation. For that reason, ammoniacal water is necessary. In presence of hydrogen sulfide, already precipitated hydroxides would be completely transformed into sulfide (arrow to the right!).

3. If one assumes a complete reaction between chlorides and H_2S, which took place already below the surface, colloidal sulfides would be discharged at the effluence into the sea water. "The principal agent in deposits, which acts in such a way, is probably H_2S . It peptizes metal sulfides and can, through the discharge of pressure . . . escape rapidly. The sulfide flocculate out rapidly and form small but rich deposits." (SCHNEIDERHÖHN, 1941, p.274). The HCl which forms is neutralized by NH_3.

4. Finally it is possible that chlorides penetrate into water containing ammonium sulfide, and that in this way, sulfides precipitate there while the freed acid is neutralized.

Reaction-mechanisms as described in paragraphs 2 to 4 are possible for the formation of the pyritic deposits of the Meggen type. The other possibility of formation of larger masses of iron is familiar to us from siderite deposits. Also in the formation of hematite deposits (see above) follows a carbonate phase after an oxidation phase. Such solutions are in a less intimate relation with the magmatic emanations, according to the classification of von WOLFF (1914).
On this basis the axis Cl_2-SO_2-CO_2 in the scheme, by which the sequence Cl-S-CO_3 group is symbolized, was drawn as an inclined ascending line.
Here also are several possible variations:

5. Discharge of iron carbonate in the water causes hydrolysis and precipitation of hydroxide. Secondary action of H_2S is possible (arrow to the left).

6. In the same way as in 3 it can be assumed that a reaction with H_2S takes place already in the discharge channel . . . . In the scheme FeS is always written for the iron sulfides, according to the primary precipitation-product in laboratory-experiments. One has to take in account also FeS, Fe_2S_3, FeS_2. Barium has entered as Ba^{++}-ion in order to show that at the beginning it does not enter into the precipitate but reacts later with SO_4^{--} (which formed meanwhile).
$BaCO_3$ is written only in the right part of the basin: in an alcaline medium the entire barium would precipitate (double arrow pointing to the bottom); in neutral marine water it is only partially precipitated (double arrow pointing to the top).

The individual zones in the ocean water are marked in the schematic drawing in a way which can be expected in lagoon type depositions which are being invaded by H_2S-springs: surficial and marginal neutral water (marked H_2O) surrounding an ammoniacal zone (NH_3 aq.). In proximity to the spring high hydrogen sulfide concentration (H_2S aq.), on the border against the ammoniacal zone, there is a transitional region of ammonium sulfide water $(NH_4)_2S$ aq. .

of the surface circulation is also of a basic composition. The sediments deposited and leached by surficial waters consist of a calcareous and dolomitic rock which cause an increase of $CO_3^=$ in the water. The basicity of the waters makes difficult the solution of barium compounds that may be contained in the formations. As evidence for the absence of solutions capable of dissolving $BaSO_4$ the very large amounts of barite present as insoluble residuum in the soils formed by the decay of the sediments can be mentioned.

Presence of chert: The presence of chert means that silica, either in higher dilute or in a colloidal state, was available and was precipitated either syngenetically or epigenetically (see below). RANKAMA and SAHAMA (1950) report that silica concentrates mostly when the pH is relatively low. It was also observed that the major concentration of silica, both as chert, quartz or chalcedony, is found where sulfides are present.

Grain size of the dolomite: The bedrock dolomite shows a certain relationship between its grain size and its ore mineral content. When dolomite contains a relatively large amount of barite, the grain size is large to medium.

Deposition of limonite: Limonite is deposited in interspaces of the blocks of dolomite in the breccia whether or not barite or other minerals are present. This limonite may form during weathering of the sediments either as concentrations from the adjacent dolomite or as transported limonite from subjacent formations.

Many other observations could be listed. The ones mentioned are, however, believed to serve as a sufficient geochemical basis for a discussion of the nature of the barite and associated sulfide deposition, in the frame of this thesis.

General rules of Logic

Generally, the approach to a natural phenomenon for which a number of more or less dogmatic theories have already been proposed, is influenced by these theories. The genesis of barite deposits is an example. In this paper a solution evolved, through the application of a number of principles, based on assumptions which are considered to be more logical than others.

The author has reached his assumptions on the basis of observations and criteria collected and, as much as possible, has tried not to be influenced by previous theories offered.

The weight, importance or significance of the observations and criteria applied have, however, a relative value. Principles of probability, as logically applied as possible, were also taken in consideration.

On the preceding pages and in the following chapter are illustrated the observations and criteria used, and the conclusions have been reached through their correlation.

It is accepted that in any problem in which the possible solutions can be several, that solution has the highest probability which can be reached by the association of the fewest number of necessary assumptions AMSTUTZ (1959a). For example if the possible solutions to a problem are three and the number of necessary assumptions is so distributed:

Solution A	Solution B	Solution C
3 assumptions	5 Assumptions	7 Assumptions

in terms of probability, the solution A is closer to reality than the other two mentioned, provided the assumptions are of the same weight.

The same principle presented above was used in reaching the conclusions of this study.

CHAPTER V

DISCUSSION ON THE OBSERVATIONS IN VIEW OF THE VARIOUS POSSIBILITIES OF ORIGIN

Definitions of terms used

The discussion of the genesis of the studied deposits is based on a critical review of the observations illustrated in the preceding chapters and on a comparison with the different theories as reported in the literature.
The discussion of the genesis of barite and associated sulphide deposits of the Potosi quadrangle and of the Washington County in general, is divided into two parts:

-- time and sequence of deposition (paragenesis)
-- origin of the ore-bearing fluids

With regard to time and origin, there are two main possibilities of mode of formation, or origin of the ore matter, respectively:

TIME	ORIGIN
Epigenetic	Supergene
Syngenetic	Hypogene

The four possibilities of origin of a rock or mineral deposit are thus:

i. epigenetic supergene
ii. epigenetic hypogene
iii. syngenetic supergene
iv. syngenetic hypogene

A definition of the controversial terms used in discussing genesis of ore deposits is useful for a better understanding of the meaning in which these terms are used. McKINSTRY (1955, p. 656) writes that syngenetic ore deposits are: "deposits formed by processes similar to those which have formed the enclosing rock and in general simultaneously with it," and (p. 638) that epigenetic ore deposits are "deposits of ore introduced into a preexisting rock (Lindgreen). " DESIO (1949, p. 642), BATEMAN (1956, p. 70), and others offer the same definitions. For the purpose of this study the above definitions need additions. The line between syngenetic and epigenetic deposition is drawn after diagenesis of the sediment.

Previous authors have introduced in the literature a series of different terms to indicate the causes which have lead to the deposition of the barite and associated sulphide deposits both in Missouri and in other parts of the Country or abroad (see Table I).

Some terms, which have been most frequently used in papers dealing with the genesis of the barite deposits, are listed below:

i. magmatic solutions
ii. ascending solutions
iii. heated waters of igneous origin
iv. magmatic emanations
v. meteoric waters
vi. leaching from shallow waters
vii. descending solutions
viii. solutions at low temperature at shallow depth
ix. exhalative emanations
x. deposition from sea water

In the present paper the discussion about time and origin is based upon a condensation of the above causes as shown in the following table:

TIME	ORIGIN
Epigenetic	Supergene=ore fluids from later ground water circulation
	Hypogene=deposition from epigenetic hydrothermal fluids by replacement and/or open space filling
Syngenetic	Supergene=barium and associated sulphides from weathering solutions of adjacent granitic and sedimentary rocks
	Hypogene=volcanic exhalative feeding of ore fluids into the ocean

Diagenesis is defined in the following way by SUJKOWSKI(1958):

> All those processes which turn a fresh sediment into a stable rock of some hardness, under conditions of pressure and temperature not widely removed from those existing on the earth's surface.

and AMSTUTZ (personal communication) defines diagenesis as ". . . the process of consolidation of a sediment, embracing the time from its deposition to the time at which it has become a hard sedimentary rock."

Time and Sequence of deposition (paragenesis)

The time of deposition of the barite and associated sulphide deposits of the Potosi quadrangle can be defined on the basis of the various observations mentioned above. An attempt has been made to set up a list of geometric and geochemical criteria, and the conclusions are based on a comparison between these criteria.

For a better correlation these criteria are listed with capital letters and numbers. Each letter refers to the type of criterion mentioned as Gm for geometric and Gc for geochemical.

Geometric criteria

Gm1) The horizontality of the "mineralized" area is visible in all the visited outcrops as well as from the logging of the drill core. Either barite or barite associated with sphalerite, marcasite, and galena, are almost completely confined to a narrow horizon in the sedimentary formation (Figure 5). This feature is typical for sedimentary rock formations and the deposition of the minerals could have taken place in a sedimentary environment, syngenetically with the rock formation itself. It has been suggested, however, by various authors that the horizontality of the deposits may be explained by a replacement of a favorable horizon. The possibility that one horizon in the Potosi and Eminence formations was more favorable than another can hardly be defended. The favorability is an assumption and no reason is offered in the literature why a particular horizon should be more favorable than another. The lack of epigenetic channelways and epigenetic gradients are striking. It is reasonable to use horizontality as a criteria which strengthens a syngenetic origin, just as crosscutting relationships are commonly used as proof for epigenetic origin. Also, a replacement in a large scale involves later movement of solutions, and the presence of channelways in the overlying or underlying formations would be a prerequisite for such an origin (compare AMSTUTZ, 1959 a, d).

Gm2) No channelways of any sort extending below the Potosi were found in proximity of the studied deposits. The only place in which any sort of channelways could be present is in the area of the Krueger property, where the Shirley fault is supposed to be. The brecciation in this place has been, by some authors, related to the fault, and it is assumed by these authors that this fault served as channel for hypogene mineralizing solutions, which spread into the breccia and the adjacent sediments, depositing barite and sulphides.

From the study of the drill cores of the Krueger deposit it is clearly visible that the ore minerals occur not only in the breccia but also in the relatively massive dolomite. As mentioned before, the vertical arrays of barite, marcasite, etc., are all of limited extent and as seen in Figure 8, these small and short vertical bodies, which are often erroneously called veins, usually correspond to, and terminate with vertical walls of breccia fragments. Also the symmetry of the deposit does not show, and does not even suggest any relation to the fault (see Tables 5, 6, 7).

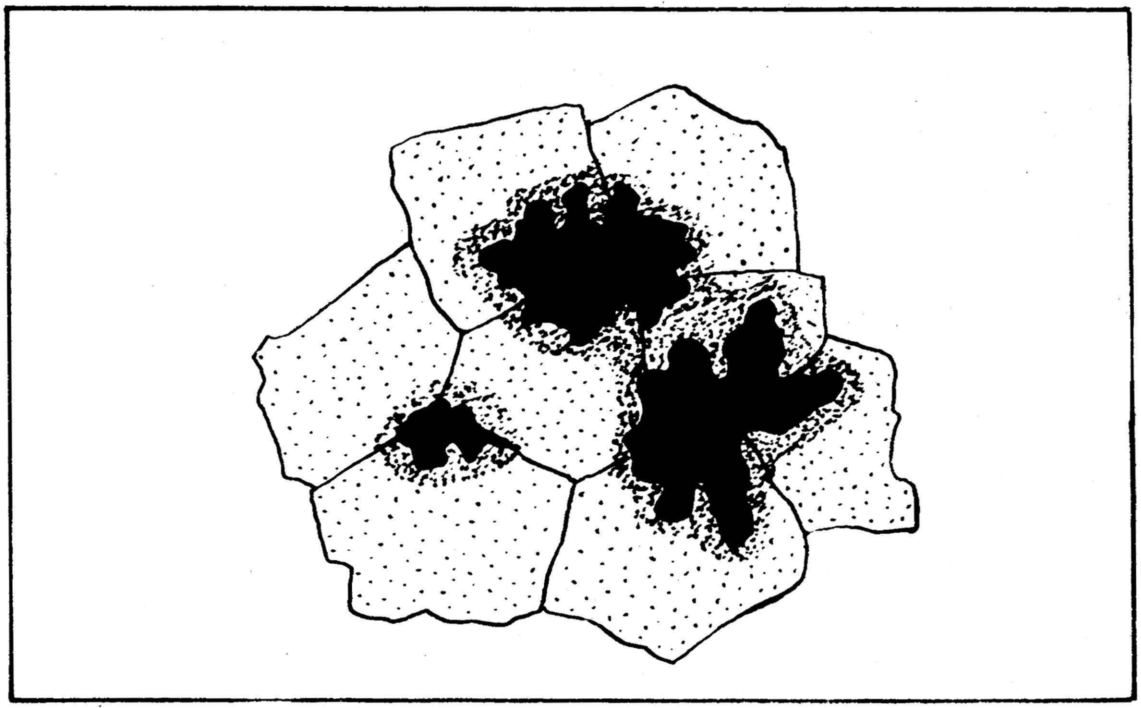
Gm3) Instead of presenting rounded surfaces, the major part of the fragments of the dolomite and chert breccia has sharp edges. This fact could prove the relatively static breakage of the sediments, and the partial rounding of a few fragments can be ascribed to very slight shearing between the fragments themselves. Perhaps the movement leading to brecciation originated from seismic movements. The roundness of a few fragments can, however, support the thesis of the epigenetists who may interpret them as replacement criteria. Roundness may be due to mechanical abrasion of the corners of the breccia fragments. Replacement involves dissolution and thus corrosion, and requires removal of old and deposition of new material from a central point, line or plain, as drawn in Table 4, Figure 1. The following observations show that the roundness is due to chemical action, it must have been a solution and not a replacement action. The large number of cavities present in the breccia and in the more compact dolomitic rock shows always a deposition and nucleation from the walls towards the center of the cavity, which speaks against a replacement process (see Table 4, Figure 2). After Table 4 was drawn it was found by the author that NEWHOUSE (1928) published almost the same drawing in his paper on "Microscopic criteria of replacement". At page 154 he describes his figure as ". . . advance island of one mineral (2) in another (1)."

The defendants of the replacement idea may reply that first a solution of material takes place, and then only deposition. However there is no evidence for such an assumption and also such a process would not be called

Figure 1. Schematic drawing showing the geometric arrangements which may result from replacement. The replacement substitution starts from a "channelway" or from the confluents of various "channelways" and spreads out in a centrifugal way, corroding the adjacent dolomite fragments. This geometry is absent in the studied deposits.

Figure 2. Open space or matrix deposition. Material which may have been introduced syngenetically or epigenetically precipitates and crystallizes in a centripetal way starting on the surfaces of the individual fragments. This geometry is abundant in the studied deposits.

TABLE 4



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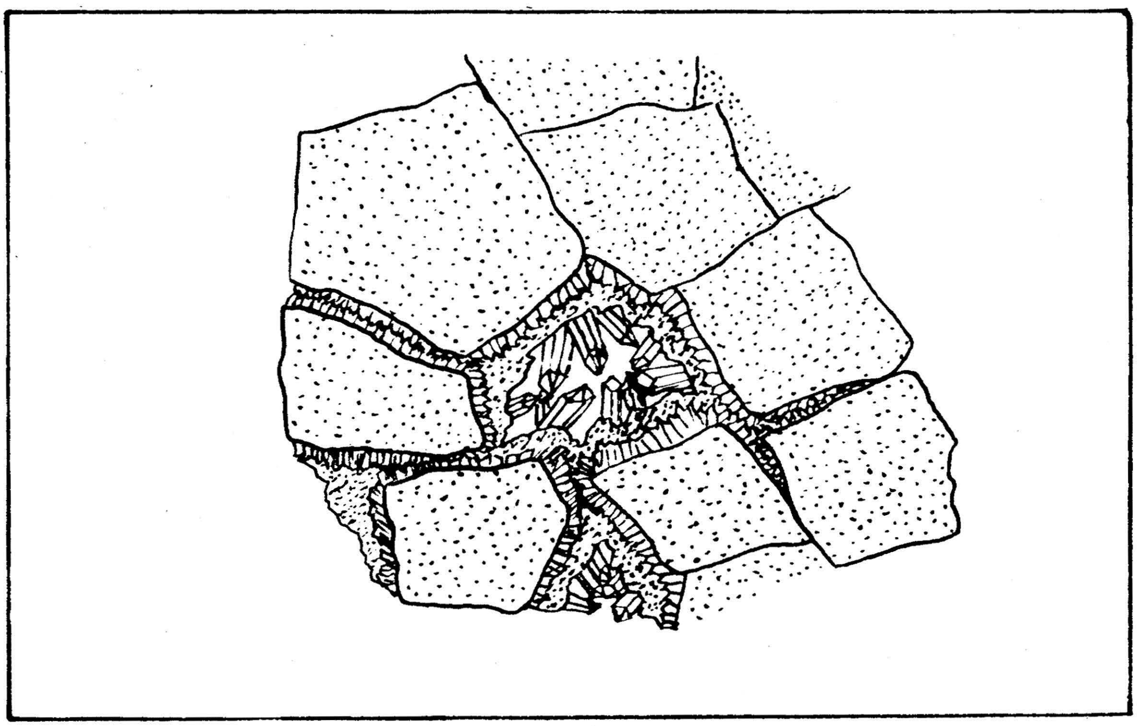


2

replacement. Any replacement theory has to make about twice as many assumptions as the syngenetic explanation.

Gm4) Several top and bottom features are visible scattered along the drill cores studied. Barite, and sometimes sphalerite and marcasite, is frequently found in many cavities of the host rock. These cavities are completely isolated in the dolomitic mass and the heavy minerals are as a rule concentrated and deposited at the bottom, while the walls are covered by light mineral crystals, usually quartz or dolomite (Figure 18). Barite shows sometimes a peculiar form. Delicate crystalline aggregates are concentrated at the bottom of the vugs (Figure 18). A useful account on the mechanism of cavity or geode formation was found in PETTIJOHN (1957, p. 205). He states:

> Nothing is present in the initial cavity except fluid, presumably connate salt solution. Inasmuch as the outer wall of the true geode is chalcedony, the initial deposit must have been a layer of gelatinous silica. The formation of this layer isolated the salt solution. If, in the course of time, the water outside the cell thus created freshen, osmosis will begin and build up internal pressures. This pressure is directed outward against the cell wall. Hence the geode will tend to expand. Expansion may occur at the expense of the surrounding limestone, by solution at the silica-limestone interfaces. Or if the geode forms prior to consolidation, the surrounding lime mud may be simply pushed aside. Expansion continues until the cell volume is much increased and the salt concentration of the containing fluids reduced to such value that the expansive force becomes negligible.

In the case of the Missouri barite a cavity filling origin appears to fit the observations best as shown. The minerals present in these cavities (druses, vugs, geodes) appear to be formed without replacement. PETTIJOHN (1957, p. 205) also states that "the metallic sulfides, if present, are most generally the last-deposited minerals" and this observation is corroborated by the various examples of marcasite and sphalerite occurring in some of the vugs of the studied drill core.

Gm5) Low permeability and porosity of the dolomite are other characteristics which speak against later solutions carrying minerals.

TARR (1918, p. 83), in relation to the porosity and permeability of the Potosi and Eminence stated:

> ". . . there are no determinations of the porosity of the Potosi or the Proctor, but judging by the large openings scattered thruout the rocks it is about 8 to 10 percent. But this porosity does not represent the ability of the water to move thru the rock, for the large openings are disconnected and, therefore, the true permeability of the rocks is that of the dense crystalline dolomite. This must be fully the equivalent of the permeability of granite, or about .5 per cent. This difference between permeability and porosity is not generally recognized and porosities are taken that are commonly too high. Recent experiments made by a graduate student under the writer's direction show that pressures of 1500 pounds per square inch will not force water thru a limestone with a porosity of .5 per cent. A pressure of 2800 pounds per square inch broke the rock but failed to force any water thru it."

Permeability studies which showed negative results both in a quantitative and a qualitative way were carried out by PERRY at the Missouri School of Mines (Master's

Thesis, 1958).

Gm6) Sedimentary differentiation of heavy and light mud is visible in Figure 12. This geometric feature is classical, and is clear evidence for the contemporaneous presence of heavy material - possibly in colloidal state - in the mud which was squeezed into the interspaces of the breccia, and after differential sedimentation, deposited in the sequence now observed. The Figures 12a, 12b shows clearly the sequence of the deposition with barite at the bottom, coarse calcareous material, in the middle, and fine shaly material on top. Top-bottom features of this type were called geo-petal by SANDER (re. AMSTUTZ, 1959 c.). The presence of this feature supports the theory of the formation of the breccia close to, or at the surface while the dolomite of the superjacent sediments was still in an unconsolidated or semi-consolidated state. In this case the possibility of the influence of seismic movements in the formation of the breccia may explain the facts best, since it is known that under relatively strong shocks, applied for short periods of time, a still plastic material can react as solid and break. The oozy sediments on top of the brecciated layers found their way into the open spaces in between the fragments of the breccia and formed the matrix.

Geochemical Criteria

The following geochemical criteria were found to be of interest with regard to the origin of barite deposits.

Gc1) The low content in sea water, $5x10^{-3}$ gr/L, reduces markedly, if not completely, the possibility of concentration and deposition of barium compounds from the water of the oceans. However, this possibility exists, if a gradual increase of barium during geologic times is taken into consideration. It was reported by RANKAMA and SAHAMA (1950, p. 493) and also suggested by AMSTUTZ (1958,a, p. 236) that in early geologic time volcanic exhalations and emanations were more abundant and stronger than today, and it is probable that during these volcanic activities one of the volatile constituents was barium, exhaled and/or dissolved either as chloride or carbonate.

NICKEL (1956) introduced this concept with regard to the genesis of the pyrite and barite deposits of Meggen (Germany) (see Figure 20).

Gc2) Ba^{++} anions combine with SO_4^{--} cations and lead to the precipitation of barium as barium sulfate. When barium is introduced into sea water either as chloride or carbonate, it does not readily precipitate. When H_2S is present in the water, barium usually stays dissociated in the water and reacts only when sulphate cations are available. Figure 20 from NICKEL illustrates clearly the process involved. Barium which enters the sea water as barium chloride or carbonate does not react in acid medium, according to NICKEL, but diffuses as Ba^{++}. Later it combines with SO_4^{--} present in slightly acid or neutral water near the surface, precipitating as barite. Two possibilities arise if $BaCO_3$ is introduced in the water, especially during the last phase of volcanic activity (Figure 20, far right). The first implies the influence of alkaline water. When $BaCO_3$ enters NH_3-rich water the complete precipitation takes place. If $BaCO_3$ enters the neutral zone directly, the precipitation is incomplete and Ba^{++} is available. In this case Ba^{++} combines with SO_4^{--} and precipitates later.

Gc3) Cold solutions containing barium compounds precipitate their metal content under certain chemical conditions at low temperatures. A peculiar example for this type of deposition is given by KUKUK (1951, p. 155, Figure 243). In a water-ditch of a mine in the Ruhr district (Germany) barite was found filling almost completely a wooden box.

Gc4) Barite decrepitates at room temperatures or at relatively low temperatures, as reported by DONS (1956). According to him, this barite may have formed at very low temperature.

The necessity of epigenetic high-temperature hydrothermal solutions containing barium compounds, on the basis of the concepts of DONS, is not warranted. The decrepitation properties of the barite of the Potosi area has not been studied extensively. However a simple experiment carried out by the writer with a few samples shows that the decrepitation starts at about 60° to 90° C. As shown by CORRENS (1949) decrepitation is however only a primitive method and reports rather on the strength of the crystals than on the temperature of formation. The only indication which may be gained is an upper limit of formation.

Gc5) A decrease of pH in sea water causes the precipitation of SiO_2, according to RANKAMA and SAHAMA (1950, p.554). Volcanic exhalations, with their contributions of H_2S and other sulfides and chlorides to sea water, create a more acid environment favorable to the concentration and later precipitation of SiO_2.

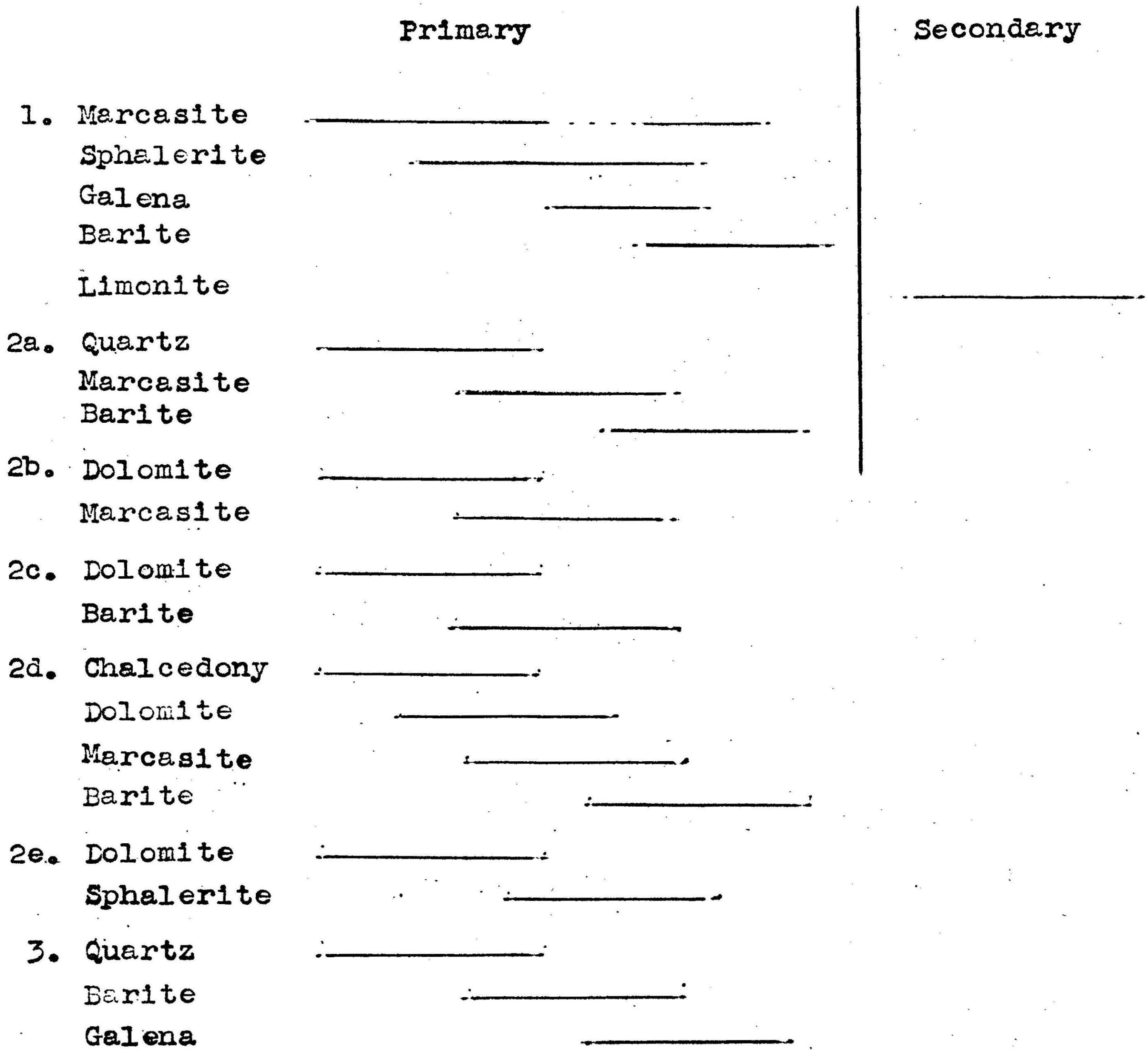
It was observed by the writer that on the Krueger Zinc Deposit, where the sulfides are more abundant, as compared with the barite deposits, silica is also present in more quantity. This concentration of SiO_2 both as chert or quartz or chalcedony, may have taken place because of an increase in acidity of the water of the basin.

Sequence of deposition (paragenesis)

The paragenetic sequence observed in the Krueger deposit is summarized on page 88 and does not include the wallrock.

No. 1 paragenesis is commonly observed in the open pit and dump of the Krueger deposit (for example pictured in Figure 13). No. 2a, 2b, 2c, 2d, 2e sequences were observed in drill cores logged at the Core Library of the U. S. Bureau of Mines in Minneapolis. Paragenesis 2a is

PARAGENETIC SEQUENCE IN THE KRUEGER DEPOSIT
AND IN THE BARITE PITS



pictured in Figure 19a and paragenesis 2d is shown in Figure 19b. A description of the sequence of minerals and the relationships among them is given below.

Marcasite, fairly abundant with zinc sulfide and barite on the Krueger deposit, shows two positions in the paragenetic sequence. The first and more abundant one occurs as a number one generation deposited directly in contact with the dolomitic and cherty fragments of the breccia. The second one occurs in a few places on top of the sphalerite bands. The cause of this second generation of marcasite may be due to a later enrichment of iron sulfide in the solution.

Closely associated with the first generation, or possibly often older than this first crustification on top of the breccia fragments or cavity walls, there is a sort of disseminated marcasite type in these breccia fragments. This dissemination occurs in two distinctly different distribution patterns. One is a homogeneous peppering of the dolomite with tiny grains of marcasite. The lack of a gradient of concentration does not suggest a later penetration into the fragments, either by a filling of pores or a replacement mechanism. It rather suggests an original formation.

The second pattern of distribution shows a marked drop of the amount of marcasite from the rim of the fragments towards the inside. Here it might be assumed that a slight replacement has taken place. These zones of higher marcasite content measure however only a fraction of a millimeter or at the most one or two millimeters. The inside of these breccia fragments is usually devoid of marcasite.

Chalcopyrite was reported by TARR (1918, p. 55). No sure indications of chalcopyrite were seen during this study, although marcasite coatings or stainings often show chalcopyrite colors.

Sphalerite is the most abundant sulfide present in the Krueger deposit. It occurs as small dark-brownish to dark-ruby crystals scattered along the dolomitic formation, and as the principal mineral in the matrix of the breccia. Sphalerite shows frequently the typical form of "banded sphalerite" (Schalenblende of the german literature). The origin of this type of texture may be ascribed to colloidal precipitation which, according to DI COLBERTALDO (1954, p.10), takes place readily in presence of lead and iron sulfides. It was observed in several samples that sphalerite assumes the characteristic banded texture when it is deposited over layers of marcasite as first generation deposited on top of the dolomite or chert fragments as described above. On top of this banded sphalerite, and in other occurrences, sphalerite occurs almost always as drusy overgrowths on the bands, or on dolomite, etc.

Galena is a rare constituent in the Krueger deposit. When present, it shows sometimes idiomorphic crystals. It is always associated with barite and generally was deposited earlier. Only in a few questionable cases it deposited at the same time as barite.

Barite is, with galena, the last mineral of the para-genetic sequence. It occurs in large crystals which grow in a centripetal way towards the middle of the cavities. They sometimes terminate as well formed bladed crystals. These bladed crystals can be seen in the whole outcrop and are frequently found also in the residual soils. Light delicate crystals are also present in some open spaces of the breccia. These occurrences, and some small barite filled fractures cutting across first generation marcasite, suggest the possibility of a second generation barite.

Limonite in thin layers constituting boxwork-like secondary coating around the fragments of the brecciated dolomite, are common in both deposits, the Krueger deposit and the barite pits. The limonite was deposited much later than the other minerals. The iron of the limonite may originate from the decomposition of marcasite (mostly in the Krueger deposit) or as secondary product from supergene leaching of iron in the dolomite.

Quartz occurs frequently as coating on the wall of the cavities in some vugs in the dolomite constituting host rock for the ore minerals. Also dolomite is sometimes present in a crystalline form and associated with marcasite and barite.

Quartz: Silica was apparently always the first material deposited if available. It occurs as "chalcedony" and "drusy quartz". Chert is present as wall rock throughout the Potosi and Eminence, and is considered one of the main characteristics for the identification of these formations. As mentioned before it was found in the area studied that chert is more abundant where sulfides are present. Chalcedony is very frequently associated with drusy quartz. The chalcedony form of silica is deposited first in the sequence and with its characteristic banded texture it coats the walls of the many cavities present in the dolomite. The internal layer of chalcedony is usually coated with small and delicate quartz crystals ("come-quartz"). Frequently small crystals of marcasite and barite occur on top of this drusy quartz. If marcasite and barite are found together, marcasite is always earlier.

Dolomite as small crystals is sometimes present in cavities of the dolomitic rock. Some of these crystals were coated later by small and delicate crystals of barite (paragenetic sequence 2c). In the cavities in which dolomite crystals are found with marcasite, the latter mineral coats the first one (sequence 2b). If dolomite and sphalerite occur together (sequence 2e), sphalerite is clearly later.

The paragenetic sequence observed in the barite pits is simple. The only minerals occurring are, listed in the sequence of deposition (paragenetic sequence no. 3 in the table): silica, barite, and galena. Limonite, the secondary alteration product, is mentioned above.

Conclusion on the time of deposition

Considering the various criteria mentioned before in this chapter containing the discussion of genetic criteria, and from a careful comparison of them, it appears reasonable to assume that the deposition of the ore minerals and marcasite took place syngenetically. For example the enclosing sediments were broken up on the ocean bottom not too long after and partly during diagenesis; and in the area of the ore deposits there happen to be an accumulation of "sedimentary ore fluids" available for cementation of the breccia.

The geometric and geochemical characteristics of the minerals involved in the process are proved to support such a theory. The assumptions which are <u>necessary</u> to support a syngenetic origin, seem to be fewer than those <u>necessary</u> to prove later epigenetic processes as shown below:

1. Assumption necessary for syngenetic origin:
   a. Ba^{++} and SO_4^{--} were available in the sedimentary environment.
   b. Ba^{++} and SO_4^{--} were accumulated locally in the places where the deposits formed.

2. Assumptions necessary for epigenetic origin:
   a. Ba^{++} and SO_4^{--} containing fluids were formed at depth (hypogene) or in ground water streams (supergene)
   b. Channelways (porosity, permeability, etc.) for these accumulated Ba^{++} and SO_4^{--} containing fluids were

available (from "unknown depth" or from distant weathered areas).

c. These fluids or presumably preceding fluids were able to upset the stability of the dolomite and dissolve it.

d. Cavities were present to begin with.

e. Pathways for the dissolved material have to lead out of the place of deposition in order to permit the replaced material to go out.

f. The new material reaches at the particular place the conditions for precipitation (saturation, required Eh, pH values, etc.), in the cavities created by the dissolution or in preexisting spaces.

In the next section the origin of the ore bearing fluids will be discussed.

Source of the ore bearing fluids

The four possibilities offered in the introduction of the chapter are here discussed:

Epigenetic supergene origin. The possibility that later ground water circulation can have leached barium compounds from preexistent formations can hardly be defended. Several factors oppose this theory, as shown in the chapter on the geochemistry of barium.

The low solubility of barium compounds in ground or surface waters is one of these criteria. Even today barite is practically unaltered, despite the relatively high content of organic acids of these waters. The solubility is said to increase, however, with the presence of alkaline compounds in the water.

Among the barium compounds, carbonate and chloride are the most soluble and the presence of such compounds in the overlaying sediments of the examined area should be expected if any epigenetic origin could be correct. The average calculated in several analyses of overlaying rocks shows, however, that barium is scarcely or not at all present in the formations mentioned.

Permeability of the rocks traversed by the migrating solutions and of the rocks actually host for barium minerals must also be considered. The rock formation of the Eminence and Potosi is usually of dolomitic composition and its permeability is very low, as was shown by TARR (1918, p.83), OHLE (1951) and PERRY (1958). In such a case, only joints and fractures can be considered capable of acting as pathways for the mineral bearing solutions. It was already mentioned that no evidence for this could be found in the studied deposits.

The chemical composition of the waters which eroded the overlaying formations, as well as other factors mentioned above, is opposed to a later supergene origin of the ore bearing fluids.

Epigenetic hypogene origin. An epigenetic hypogene origin of the ore bearing fluids was suggested by several authors for the barite deposits of southeastern Missouri as well as for other localities of the United States and abroad.

A later hydrothermal fluid, however, needs for deposition of its mineral content several geometric and geochemical conditions which are not fulfilled in the Potosi and Eminence formations.

It is useful, here, to summarize once more the several factors that have to be considered for such an origin.

The lack of channelways is one of the factors mentioned, and the open spaces supposed to be present in the formations before the arrival of the ore fluid, were proved not to be able to provide the space for the large amount of ore mineral deposited. To mention only one geometric criteria against the assumption of open spaces, there are many fragments of dolomite and chert which are literally suspended in barite or other ore minerals or in gangue matrix and are thus not supported.

A high grade replacement process was also taken into consideration and to support its possible occurrence the law of replacement of equal volumes was introduced. Such a law cannot be applied because no evidences for replacement processes were found in the studied deposits. If replacement is accepted, a space has to be provided for the material carried away. This and other criteria are lacking.

A diffusion process has also been proposed as a cause of deposition of the ore minerals. Conditions at which barium carrying fluids can diffuse without deposition through the formations have to be inside of the stability field of these traversed formations. It is reasonable to assume, in this case, that a fluid containing barium and diffusing by BROWN's diffusion principle (1948), should precipitate its barium content into the underlaying formations (frequently shales) and not primarily, in the dolomitic rocks of the Potosi and Eminence.

Another way of introducing later hypogene epigenetic fluids into the sediments from an intrusive source, particularly into carbonate rocks was described for example by BATEMAN (1956, p. 89). This probability can be excluded in the area examined, however, because the sediments containing ore minerals as well as the deposits themselves are horizontally bedded. Moreover, the absence of up-dip channelways does not support the concept of a contact metasomatic deposit, nor is "across bedding" deposition observed.

From the concepts illustrated above, the writer believes that an epigenetic hypogene origin of the ore bearing fluids is highly improbable, if not impossible.

Syngenetic supergene origin. Barium and associated sulfides could have been carried in solution from weathering of adjacent granitic and sedimentary rocks, transported to the water of the basin of sedimentation, and later concentrated in the unconsolidated sediments of the bottom, where syngenetic brecciation may have played an important role in providing low zones where heavy barium solutions could accumulate.

As stated by ENGELHARDT (1936), barium does not precipitate easily under the normal environment for deposition of carbonate rocks. Conditions of local concentration or unusual local sources thus, could have caused the deposits. Some of the factors which speak against a supergene origin are discussed in section 1.

It is questionable whether the igneous rocks in the region are a sufficient source of barium, zinc, and lead. Only by assuming a factor leading to a strong concentration in space and time of weathered Ba^{++}, Zn^{++}, and Pb^{++} could this theory of origin become a probable one.

Syngenetic hypogene origin. Volcanic exhalative enrichment of ore fluids, in the sedimentary basin, is the fourth possible type of origin. The source of barium may be found, in this case, in the volatile part of the magma which formed the shallow igneous rocks in the area.

All the minerals present in the deposits are well known in the epithermal stage of magmatic differentiation, and this fact supports the suggested origin of the ore fluids.

During the later phase of magmatic activity, volcanic exhalations are very frequent, and it has been said that during early geologic times this volcanic activity was stronger than today (RANKAMA and SAHAMA, 1950, AMSTUTZ, 1958). The gradual degassing of the earth is a well known concept of geology (BARTH, 1952).

On the basis of this assumption and in view of the evidences previously discussed, a volcanic exhalation can be assumed to be the source for barium. Moderate volcanic activity is shown to be present all through the Paleozoic exposed in Missouri, (KIDWELL, ALLEN, BUCHER, KELLER; Re. AMSTUTZ, 1958a, 236).

CHAPTER VI

GENERAL CONCLUSIONS

A syngenetic hypogene origin from volcanic exhalations is proposed as the most probable one for the barite deposits of the Potosi quadrangle. This theory is supported by several lines of evidences as offered throughout this thesis.

Several authors as for example BUCKLEY (1908), STEEL (1909), TARR (1918, 1932), and others, advanced both an epigenetic supergene or hypogene theory for the origin of the Missouri barite. The criteria mentioned by them to support those modes of origin do not fit the geometric and geochemical evidences collected by the writer and discussed in detail in the previous chapters.

Among the criteria previously mentioned, the most important ones against a possible epigenetic origin of the considered ore deposits, are here summarized:

- Horizontality of the mineral deposit.
- Absence of channelways extending below the Potosi formation.
- Lack of "mineralization" in the faults of the area.
- Presence of several top and bottom features characteristic of contemporaneous deposition on the surface. For example: sedimentary differentiation of heavy and light mud visible in several places.
- Prevalently sharp boundaries of the fragments of the dolomitic breccia.
- Lack of replacement criteria.
- The ore and "gangue" minerals can form at surface temperatures.

Furthermore the necessary assumptions needed for an epigenetic origin were shown to be more complex and of a larger number in comparison with the ones necessary to support the syngenetic point of view.

The epigenetic theories are thus eliminated and the following two syngenetic possibilities remain to be discussed:

- syngenetic supergene
- syngenetic hypogene

A supergene origin from erosion on land, and subsequent deposition in the form of colloidal barite in a sedimentary basin, requires certain special conditions. A supergene deposition through colloidal barite in sea water was already suggested by DAKE (1930) for the barite deposits of Missouri. The difficulties encountered in the assumption of a supergene source were mentioned above.

Although the syngenetic-supergene theory can not be dismissed, a hypogene source of barium appears to involve less assumptions. Several criteria leading to a hypogene syngenetic origin were discussed in detail in the previous chapters.

The presence of the brecciation in the dolomitic sediments could be explained as a result of seismic movements. These may have been responsible for volcanic activity and consequently the exhalation of magmatic fluids discharged and chemically precipitated by a mechanism similar to the one described in detail by NICKEL (1956). The distribution of volcanic material, diatremes, polygonal and other tectonic fractures through almost all the Paleozoic, shows that vertical tectonic movements were relatively strong and broadly distributed. Associated with it there was some volcanic activity as mentioned.

This mode of origin has been proposed and explained on the basis of many details for numerous deposits of the same type in this and other countries, for example by AMSTUTZ, BORCHERT, GRUNER, LINDGREN, MAUCHER, NIGGLI, OFTTEDAHL, PROCTOR, RAMDOHR, SCHNEIDERHÖHN, TAUPITZ, and others.

It is here offered as a working hypothesis, on the basis of the criteria described that for the barite deposits of the Potosi quadrangle syngenetic hypogene origin and mode of formation has the highest degree of probability.

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VITA

Attilio Ligasacchi was born on 13 September 1928 in Milano, Italy. He completed the Elementary School in Milano, attended the Istituto Tecnico Inferiore (Junior High School) from 1939 to 1943 and the Liceo Scientifico (Senior High School) in Milano from 1943 to 1947 and received a "Diploma di Maturita Scientifica" in June 1947.

He entered the Engineering School of Milano in 1947 and studied three years towards a degree in Mechanical Engineering. In 1950 he enrolled in the Department of Geology of the University of Milano and in November 1954 received the degree of Dottore in Scienze Geologiche.

In February 1955 he entered the Military School of Lecce for general officers training and in July 1955 was admitted to the Military School for Artillery officers in Foligno. In January 1956 he was appointed 2nd Lieutenant in a Regiment of Mountain Artillery, being discharged with honors in August 1956.

From September 1956 until August 1957 he was employed by the Societa Minerali Radioattivi Energia Nucleare (SO. MI. R.E.N.) and conducted geological surveys and mine prospecting for radioactive ores both in the south and north Italy.

He came to the United States and enrolled in the graduate School of the Missouri School of Mines and Metallurgy in September 1957. From February 1958 until January 1959 he held a research fellowship and from February 1959 until the present a graduate assistantship.