GEOCHEMICAL PROSPECTING IN WALLROCK ADJACENT TO VEIN DEPOSITS: ROSICLARE, ILLINOIS

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by

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ABSTRACT

This study was conducted in the Rosiclare district of the Illinois-Kentucky fluorspar region. A total of 48 rock samples were collected from the St. Louis limestone formation and the Lower Fredonia limestone member of the Ste. Genevieve formation and colorimetric analyses were run to determine their lead, zinc, and manganese content. The samples were taken in traverses approximately perpendicular to the mineralized veins so that the dispersion patterns of ore solutions which penetrated the rock could be studied. The results show that the sole sources of the lead and zinc content of the wallrock are the mineralizing solutions while the manganese concentrations of the formations appear unrelated to the veins. It was found that lead penetrated the wallrock to an average distance of 24 feet; penetration of the zinc averaged 50 feet. The dispersion curves for lead and zinc appear consistent and well developed enough to be utilized in geochemical prospecting.

ACKNOWLEDGMENTS

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The spectrographic analysis was run by S. T. Bass, agricultural research chemist, and his contribution has been greatly appreciated.

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INTRODUCTION

The purpose of this study is to examine wallrock adjacent to mineralized veins for trace element anomalies. If such anomalies can be shown to be distinct enough from the surrounding, and otherwise similar, rock, support will be given to the relatively recently introduced method of geochemical prospecting. The area selected is the Rosiclare Fluorspar District in southeastern Illinois. Here, Mississippian sedimentary rocks are cut by well-defined veins which serve ideally for the purpose.

Preliminary spectrographic analyses indicate which trace elements are present in suitable concentrations for determination by colorimetric methods. The latter are based on the use of chemical procedures that result in solutions with color intensity proportional to their metal content. Colorimeter comparisons with standard solutions enable the concentrations of the various metals to be determined in each sample, and so their distribution in relation to the veins can be studied.

CHAPTER I

GEOLOGY OF THE AREA

Location

The Rosiclare fluorspar district lies in the southwest corner of Hardin County in southeastern Illinois. It extends through the northwestern edge of the town of Rosiclare and occupies the eastern half of Sec. 29, T12S, R8E, the central part of Sec. 32, T12S, R8E, and the western half of Sec. 5, T13S, R8E.

Mining History

During the early history of mining in the Rosiclare district, galena was the mineral sought and the accompanying fluorspar was discarded as waste. It was not until the early 1870's, more than 30 years after the first discovery of lead ore in 1839, that the area began shipping fluorspar (Weller, J. M., 1952). About 1880, the emphasis shifted from lead to fluorspar due to the declining market prices for lead and to the increasing demands for fluorspar.

Prior to 1905, major production was from the numerous small individually owned mines scattered along the several faults extending through the area. Since that time, however, the district has been controlled by three companies:

(1) Aluminum Company of America, formerly known as Aluminum Ore Company, and present owner of the old Franklin Fluorspar Company's properties, (2) Rosiclare Lead and Fluorspar Mining Company, and (3) Hillside Fluorspar Mines. Of these three, only the Aluminum Company of America is still in operation.

Stratigraphy

The following formations are those either cropping out in the Rosiclare districts or encountered in the mine workings.

- Mississippian System
  - Chester series
    - Elvira group
      - Vienna-Menard limestone and shale
      - Tar Springs sandstone and shale
    - Homberg group
      - Glen Dean limestone and shale
      - Hardinsburg sandstone
      - Golconda shale and limestone
      - Cypress sandstone
    - New Design group
      - Paint Creek shaly sandstone
      - Bethel sandstone
      - Renault limestone and shale
  - Iowa series
    - Meramec group
      - Ste. Genevieve formation
        - Levias limestone
        - Rosiclare sandstone
        - Fredonia limestone
      - St. Louis limestone

Detailed descriptions of these formations may be found in several publications of the Illinois State Geological Survey including Bulletins 41 and 76, and Reports of Investigations 61 and 71. Therefore, for the most part, stratigraphy will be dealt with briefly and only the Fredonia and St. Louis limestones, from which the samples were taken, will be considered at greater length.

Vienna-Menard. This normally consists of two formations separated by the Waltersburg sandstone, which, in this area, is poorly represented. The lower part is a black carbonaceous shale and is overlain by interbedded limestone and shale. The upper and thicker part, corresponding to the Menard, is a greenish to gray, calcareous shale alternating with limestone layers up to 3 feet thick. The total thickness of the formation is approximately 100 feet.

Tar Springs. The Tar Springs sandstone is made up of a lower zone of massive, fine-grained, light gray sandstone overlain by as much as 40 feet of interbedded dark, sandy shale and sandstone. The uppermost part is thin-bedded and shaly with some fairly massive fine-grained sandstone. A 2 to 6 inch coal seam marks the top of the 100 to 150 foot thick formation.

Glen Dean. The Glen Dean consists of about 60 feet of interbedded limestone and shale. The shale is generally dark gray and varies from argillaceous to siliceous and calcareous. It is present in beds up to 2 feet thick near the base but higher up is found only as thin partings between the medium to dark gray, massive limestone beds.

Hardinsburg. This formation is a fine-grained, light-colored sandstone ranging up to 100 feet in thickness. The lower part is the more massive while the upper beds contain some dark gray sandy shale.

Golconda. The Golconda closely resembles the Glen Dean but is thicker, varying from 125 to 180 feet. Like the Glen Dean, the stratigraphically higher portions contain less shale and more limestone. The most prominent bed consists of 10 feet of limestone and occurs near the top.

Cypress. This is a fine-grained, light gray sandstone with darker gray streaks and some dark shaly partings. Its thickness is about 80 feet.

Paint Creek. The major part of the Paint Creek formation is a very fine-grained, gray to dark gray, even-bedded sandstone with dark shaly partings. Below these lies 5 to 10 feet of interbedded dark gray sandy shale and thin light very fine-grained sandstone. The topmost beds are composed of similar strata and are capped by several feet of calcareous shale and shaly limestone, making a total thickness for the formation of about 65 feet.

Bethel. The Bethel is a fine-grained, light to dark gray sandstone appearing somewhat speckled. It closely resembles and is very difficult to distinguish from the Cypress formation. The thickness is commonly about 85 feet.

Renault. This formation, varying in thickness from 60 to 80 feet, is primarily made up of a gray crystalline to finely granular, often oolitic, limestone with a few scattered shaly beds. The lower part has several of these shales up to 5 feet thick.

Levias. The Levias, Rosiclare, and Fredonia are technically members of the Ste. Genevieve formation but are often considered as having the rank of formations. The Levias is from 30 to 40 feet thick and is almost entirely a gray, fine to coarsely crystalline, oolitic limestone. A few feet of dark, calcareous shale may be present in the upper portion.

Rosiclare. This is a greenish to light gray, calcareous, fine-grained sandstone varying from 15 to 20 feet in thickness. The lower part of this sandstone is slightly oolitic and is underlain by a thin basal bed of greenish sandy shale.

Fredonia. The average thickness of the Fredonia in this area is 115 feet. To the northwest, the thickness reaches 200 feet and an 8 to 15 foot bed known as the Spar Mountain sandstone divides the limestone into the upper and lower Fredonia. After deposition of these strata, erosion in the Rosiclare district removed at least 75 feet (Tippie, 1945) leaving only the Lower Fredonia.

The basal section of this formation is a buff to light brown, partly oolitic, massive limestone. Above this, the beds vary from blue-gray to gray and almost white in color, most of them being distinctly lighter than the underlying St. Louis limestone. The texture may be anywhere from coarse-grained to dense and compact with conchoidal or splintery fracture.

The outstanding feature of the Fredonia formation is the abundance of oolites. Some of the beds in the upper zones are so rich in the light-colored oolites as to appear almost white in color. The lower strata contain lesser amounts.

In some areas, the upper part of the formation contains thin beds of calcareous shales but in the Rosiclare district these are represented by nothing more than shale partings. Other layers may be petroliferous and stained with black bituminous matter.

Many beds, particularly in the lower portions, have much chert in them. This chert, however, differs from the more abundant chert of the St. Louis formation in that it occurs in plate-like masses, much more regular and smooth in outline.

St. Louis. The thickness of the St. Louis is approximately 350 feet throughout most of southern Illinois but reaches at least 500 feet in the Rosiclare district. Here, it is composed of hard, tough limestone deposited in even beds from a few inches to several feet thick which grade conformably into both the underlying and overlying limestone formations.

The characteristic color of the upper strata is bluish-gray or gray although some of the more crystalline beds are lighter. The lower portions, however, are darker and the bottom 200 feet appear almost black. Thin beds of shaly limestone are present in these dark zones and also occur in the central beds above.

Much of the limestone is almost lithographic in texture; the rest is coarser and crystalline. Beds approaching lithographic texture are brittle and break with a conchoidal or splintery fracture. Oolites are much less common than in the Fredonia and seem to be confined to the upper parts.

Chert occurs as lenticular or irregular masses parallel to the bedding planes and is more abundant in the top part of the formation. It is "clearly of secondary origin" (Weller, S., 1920). The major source of the limestone-replacing-silica was probably unconsolidated surface deposits from which the silica was leached by circulating ground-waters. Other silica may have originally been present in disseminated form throughout the limestone.

Structure

<u>Structure of the Illinois-Kentucky Fluorspar Area</u>. This region is unique in that it consists of an intensely faulted zone lying in the middle of a great province of nearly horizontal, almost fault-free rocks. The location comprises parts of Hardin, Pope, and Johnson Counties in Illinois and Livingston, Crittenden, and Caldwell Counties in Kentucky. Minor faulting extends as far east as Hopkinsville, Kentucky and southward into northwestern Tennessee.

If the Mississippian-Pennsylvanian contact is followed through southeastern Illinois (Fig. 1), the semi-circular trace produced suggests a dome-like structure which extends from this area, the northwest boundary, southeastward into Kentucky. Peridotite dikes are exposed over a 25 mile by 15 mile northwest-southeast trending zone but are not found in the surrounding undisturbed province. If they are associated with some underlying igneous intrusion then this intrusion may be the cause of the domal uplift (Weller, S., 1920). Tensional forces connected with the introduction of magma into the underlying rock, and the subsequent forcing up of the strata, would have caused lines of weakness which have developed into fault zones.

Later, faulting occurred due to a settling of the dome's central portion. Several factors may have contributed to this settling and it is probable that all of them played a part. Contraction due to cooling most certainly took place but probably was of secondary importance to the spreading out of molten magma into surrounding rock as a result of the weight of overlying sediments. S. Weller (1920) suggests that a third cause may have been the "withdrawal of some portion of the molten material into the cavities from which it had been extruded in the first place."

This later faulting, resulting from the subsidence of the dome, tends to produce normal faults with the downthrown blocks toward the dome's center. The pattern of this faulting may be very complicated and generally consists of short faults of irregular direction which surround small blocks of broken wallrock of various shapes. Faults formed during the first period of faulting are inclined to be longer and either parallel or divergent at low angles. Displacements of some faults may be as great as 1500 feet.

That portion of the dome which occurs in Illinois may be divided into 3 parts: two areas of predominately Mississippian rocks, one to the northwest and the other to the southeast, and a third dividing belt of downthrown Mississippian and Pennsylvanian strata (Fig. 1).

Of the three subdivisions of the dome, the only one considered here is the central downthrown block of which the Rosiclare district is a part. This block represents the major part of the collapse of the dome's center and within it are to be found the majority of the region's faults. It runs from near the mouth of the Saline River southwest to the vicinity of Rosiclare and has a uniform width of 5 miles.

The rocks exposed in this central belt are younger than those on either side. As shown in Figure 1, Pennsylvanian outcrops extend southwestwardly into this zone 15 to 25 miles beyond the normal Mississippian-Pennsylvanian boundary. The northwest and southeast edges of the belt are marked by well-defined faults. However, displacements were not simply along these margins but along many faults, all trending roughly parallel to the edges. The belt is split longitudinally into two, and, for part of the distance, three arches. Of these, the southeast and central arches are more completely collapsed and more deeply depressed. Faults farthest to the northwest are the most sharply defined and have the greatest individual displacements. Some of the southeasterly ones consist of series of step-like faults. The general direction of the displacements

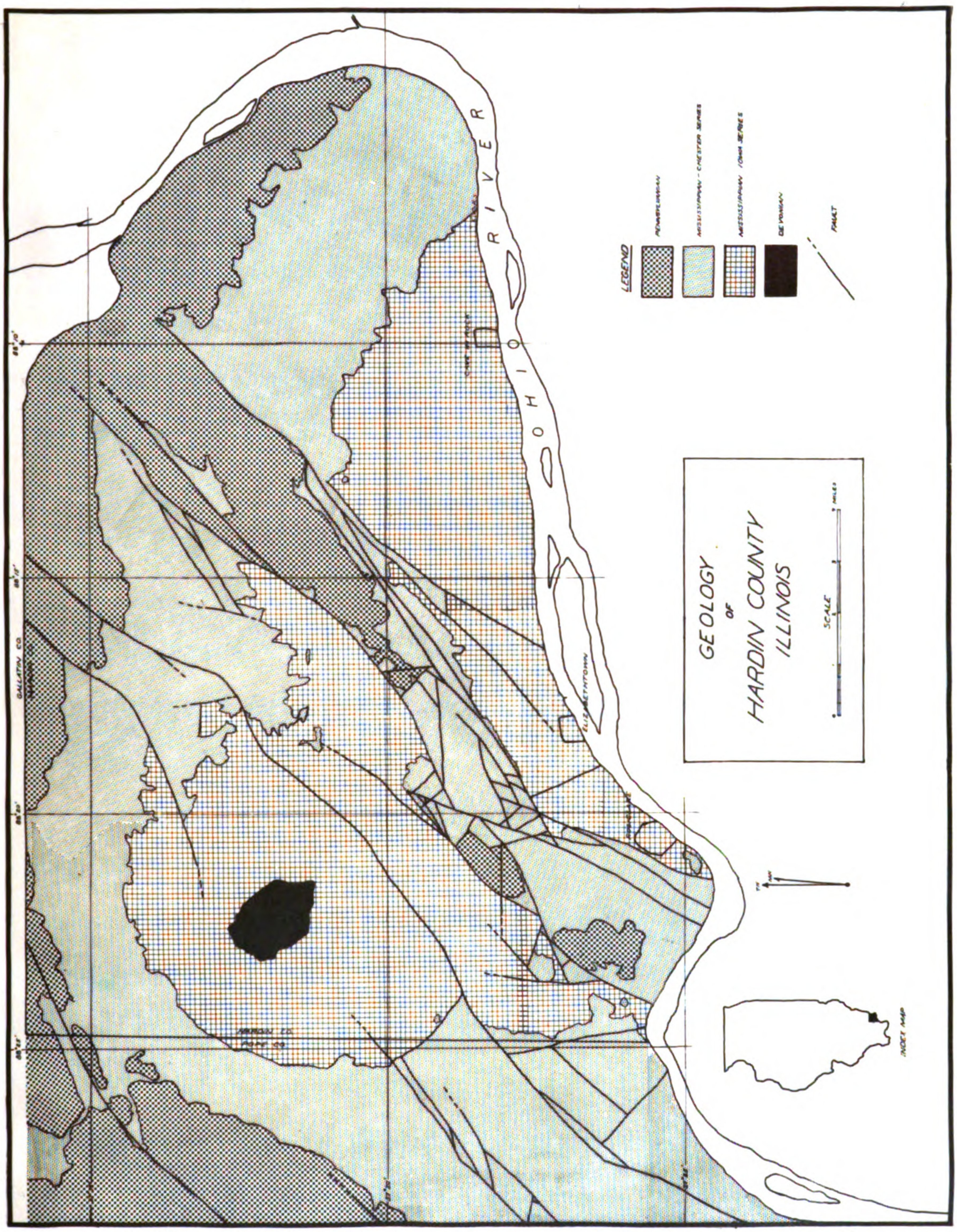

GEOLOGY
OF
HARDIN COUNTY
ILLINOIS
SCALE
MILES
LEGEND
PENNSYLVANIAN
MISSISSIPPIAN - CHESTER SERIES
MISSISSIPPIAN IOWA SERIES
DEVONIAN
FAULT
OHIO RIVER
ELIZABETHTOWN
GALLATIN CO.
HARDIN CO.
HARDIN CO.
POPE CO.
INDEX MAP

Figure 1

is towards the center of the downfaulted zone. The strike of the more important faults southwest of Elizabethtown is N25°E while to the northeast it becomes N50°E. The point where this change in strike takes place is much cross-faulted.

The general strike of the beds in Hardin County is northeast. It swings to the north in Pope County and southeastern Hardin County and continues in this direction into Kentucky. Where undisturbed by faulting, the formations dip gently toward the center of the Illinois basin which is to the north.

Structure of the Rosiclare Fluorspar District. The Rosiclare district lies at the extreme southwestern end of this central downfaulted belt.

The strata throughout most of the area are horizontal or only slightly inclined. Some steeply dipping beds are found near fault zones.

All but a very few of the faults present are normal. Most of them dip from 70° to 90° although some dip as low as 45°; those with the lower dips are usually downthrown in the opposite direction from the nearby more steeply dipping ones. The major faults are subparallel to each other, striking from 20° to 30° east of north but curving to the south as they approach the Ohio River. The only prominent exception is the Hillside fault which strikes north-south. Although the major faults are roughly parallel, they are, in detail, undulatory and often change direction sharply for short distances. A fault may split in two and then the branches come back together again. The enclosed block is usually wedge-shaped and may be downdropped relative to the strata on either one or both sides. These wedge-shaped blocks may also be much broken by irregular transverse faulting.

The rock type which is involved in the faulting is important in determining the character of the fault. Some shattering may occur in hard and strong formations like the Ste. Genevieve and St. Louis limestones but the faulting will be concentrated along a comparatively few, clean-broken planes. These stronger walls preserve the opening better than do weaker walls. Where a fault runs through sandstone, the rock is often silicified, either by recrystallization of the sandstone or by the introduction of silica solutions along the fault planes. Thus the outcrops of faults in sandstone may be characterized by prominent ridges and ledges. Where less resistant formations are faulted, a compound fracture may result with a crushed zone several hundred feet wide. Often, this also may be identified at the surface by depressions. These weak rocks, such as shales, are more likely to be sheared and torn to form more numerous and complex faults. Soft shales may be forced into the faults and dragged upward or downward along fault planes to form a gouge filling. Thus, shales may be detrimental to the preservation of fault openings and to the occurrence of mineral deposits.

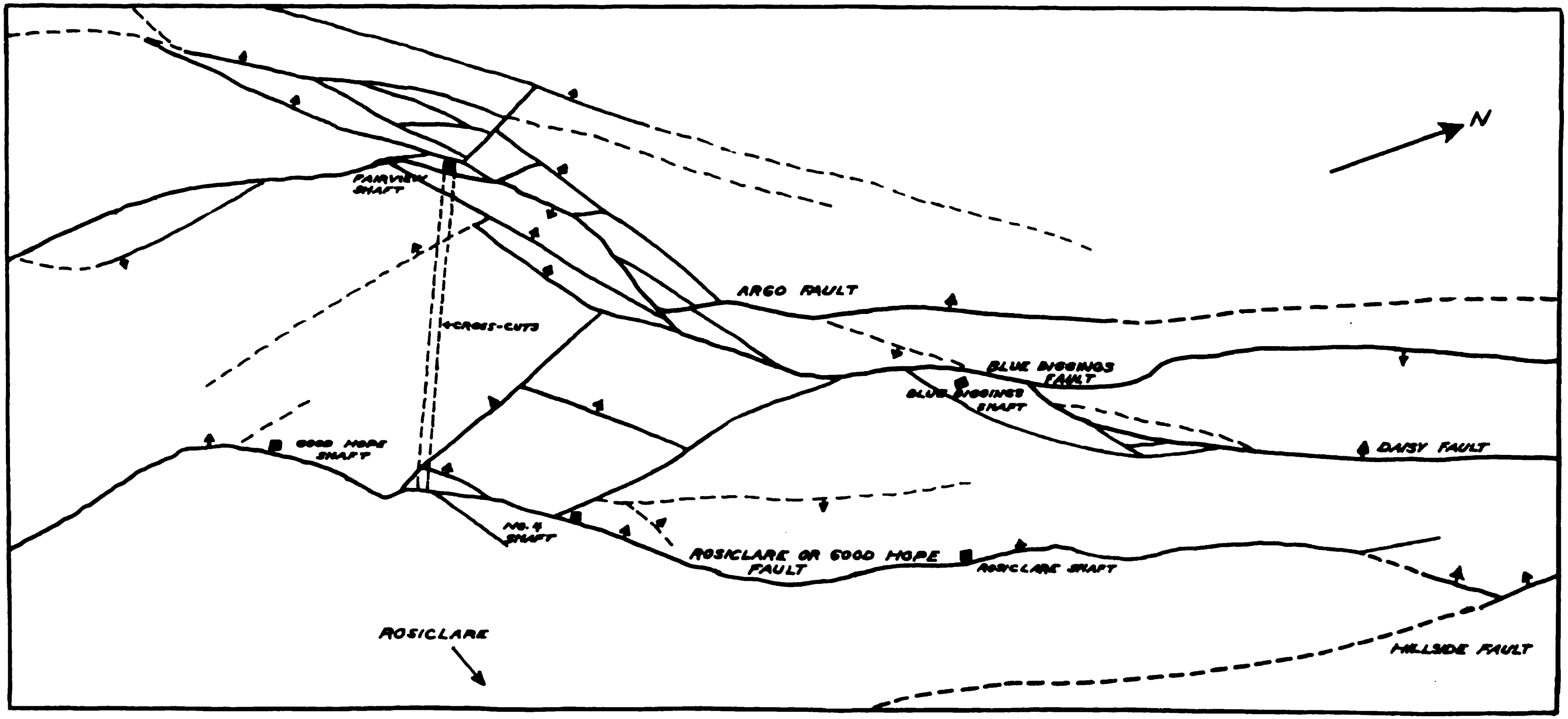
Underground, faults are often conspicuous due to the presence of slickensided surfaces, some very good examples of which are found within the mines at Rosiclare. Evidence of post-mineral cross-faulting is common but appears to be of no major importance. It occurs in the form of minor fractures with minor displacements. Peridotite dikes are found here and there within the mines and are, in all cases, post-faulting and pre-mineralization in age. So far, little study has been made of them.

Following are brief descriptions of each of the major faults in the Rosiclare district (Fig. 2):

Rosiclare Fault. The total mineral production from this fault has far exceeded any other group of faults in the entire region. It joins the Hillside fault at the center of NE 1/4, Sec. 29, T12S, R8E and extends southwestwardly through the Rosiclare mine where it is known as the Good Hope fault. At Rosiclare, the displacement is from 200 to 250 feet. At the outcrop the downthrown northwest side consists of Cypress sandstone and lies against the Bethel sandstone of the southeast side. The fault is very nearly vertical and at some places is overturned.

Blue Diggings Fault. This fault extends from its junction with the Rosiclare fault, about a mile north of Rosiclare, southwestwardly to near the Ohio River. At Rosiclare, it is separated from the Rosiclare fault by a little less than a half mile and joins it at depth. It is the only major fault

Figure 2


N
FAIRVIEW SHAFT
CROSS-CUTS
ARGO FAULT
BLUE DIGGINGS FAULT
BLUE DIGGINGS SHAFT
DAISY FAULT
GOOD HOPE SHAFT
NO. 4 SHAFT
ROSICLARE OR GOOD HOPE FAULT
ROSICLARE SHAFT
ROSICLARE
HILLSIDE FAULT

in the area dipping to the southeast and this dip is also the lowest, varying from 65° to as low as 45°. The vertical displacement varies from 75 to 150 feet. At Rosiclare, Cypress sandstone outcrops on both sides.

Daisy Fault. The Daisy fault crosses the northern part of Sec. 32, T12S, R8E. At the south end it splits, joining the Blue Diggings fault and, a quarter mile to the north, the west branch of the Hillside fault. The north end joins the Rosiclare fault. Maximum vertical displacement is 325 feet.

Argo. This small fault branches off the Blue Diggings fault to the north. Its location is in the SW 1/4, Sec. 32, T12S, R8E, making it the westerly-most mineralized vein in the Rosiclare District. It is nearly vertical and is locally overturned. The downthrow is about 75 feet to the northwest.

Hillside Fault. The Hillside fault extends north and south near the center of the NW 1/4, Sec. 29, T12S, R8E and appears to split at both ends. It joins the Rosiclare fault to the south and one branch is believed to join the Daisy fault to the north. The strike is north-south and the downthrow is about 200 feet to the west.

Geology of the Fluorspar Deposits

Description. Fluorspar in the Rosiclare District occurs in the form of veins filling cavities resulting from an earlier period of faulting. The thickness varies from a mere film to over 30 feet. The average mineralized veins of importance reach a width of 5 to 15 feet in places. Veins with widths of less than 2 feet are generally uneconomical to mine.

The fluorspar, or spar as it is more commonly known, is found distributed through calcite in more or less irregular bands roughly paralleling the vein walls. Calcite was deposited before the spar and at almost all points along the vein is present between it and the wallrock. Replacement of the wallrock has played very little or no part in the deposition of vein material and so the veins are bounded by sharp, often slickensided contacts. Rock fragments broken from the walls and enclosed within the veins are likewise sharp-bounded and are angular.

The fluorspar occurs as thin lenses joined vertically and horizontally to form tabular masses roughly parallel to vein walls with a series of pinches and swells. An individual lens may terminate gradually or abruptly in any direction by passing into uneconomical ore or by pinching due to the vein walls drawing together. Some of the larger ore bodies have their greatest dimension vertically and are known as ore shoots.

Relation to Stratigraphy. The greatest occurrence of spar is opposite walls of competent formations, such as the Ste. Genevieve and the St. Louis limestones. This type of rock has the ability to break in fewer planes and to preserve openings for longer periods of time. Aside from this, the rock type seems to be of no importance in determining where spar is to be found. The chemistry of the wallrock would play little or no part since replacement of this material is not the major ore-depositing process.

The solidification of the ore-carrying solutions probably took place near the surface and so the youngest rocks of the region were the ones surrounding the mineralized veins. The deepest known spar is 800-900 feet below the present surface and occurs on the Blue Diggings fault. Calcite has been found in drill cores from greater depths and the possibility exists of spar extending further but so far this has not been proven. Almost without exception, the age of the vein-enclosing formations is Mississippian. Weller, Grogan, and Tippie (1952) mention that ore occurs in Devonian rocks at the old Rose Mine but this is believed to be the only case. Veins are found in Pennsylvanian beds in outlying areas but not in the Rosiclare district.

Relation to Structure. Economic deposits of spar are related to faulting in several ways. First of all, the amount of displacement is important. Faults of moderate displacement--from 50 to 500 feet--seem to be the most heavily mineralized. Faults of lesser displacement do not form large openings apparently because of insufficient irregularities in the walls. Faults of greater displacement cause shattering and grinding and fill openings with soft gouge or broken blocks of harder rock. However, there are exceptions.

The mineralized veins occur in normal faults which are mostly vertical or steeply dipping and are occasionally overturned. Mineralization is often particularly great at the junction of major faults. At such points, fracturing is extensive and apparently provides environments suitable for deposition. Minor cross-faults are present but unimportant in regards to vein formation. Movement and readjustment which has taken place along the veins subsequent to mineralization has no bearing on localization of the ore.

Mineralogy and Paragenesis. Following are brief descriptions of each of the minerals present within the veins:

Fluorite (commonly called fluorspar or spar). Parts of the fluorspar deposits here are among the purest known in the world and assay as high or higher than 98% CaF_2. However, most of it is intimately associated with calcite and other minerals and must be milled. The spar occurs in great masses or in beautiful crystals and crystal groups. It is very brittle and during mining breaks along cleavage planes into angular pieces. It is mostly colorless to white or faintly yellowish, but may be various shades of purple, amber, green, and blue.

Calcite. This mineral makes up the greatest portion of vein material and is found in massive bulk or as small well-formed rhombohedral crystals lining cavities. It is generally milky white and coarse in texture. Calcite was the first mineral deposited and was replaced, in part, by fluorspar. In some areas, calcite also has been the last mineral deposited as evidenced by its occurrence as snow-like encrustations on older crystals in vugs or cavities.

Galena. If all the mines in the area are considered, galena is the most abundant of the sulfides. It is found as grains disseminated through the veins and in small veinlets closely paralleling the main vein but often traversing bands of spar. These veinlets are rarely over an inch wide and do not extend for any appreciable distance. Their walls are not typical of fissure fillings but, instead, show a cubical outline against the fluorspar. Thus, they are interpreted by Bastin (1931) as replacement veinlets along zones of minor fracturing. Galena also occurs in open cavities as crystals with well-developed cubical and octahedral faces.

Sphalerite. Sphalerite is generally slightly less widespread than galena but in certain areas, such as the Blue Diggings vein, it is more abundant. Its occurrence is similar to that of galena; it is found as small masses, grains and veinlets enclosed in the fluorspar. Well developed crystal forms line the inner surface of many cavities.

Quartz. The vein quartz is glassy, clear, and crystalline. It is not abundant enough to be identified in a hand specimen of vein material but is to be found in almost any thin section.

Other Minerals. Chalcopyrite may occur locally with galena and sphalerite. Barite is disseminated in small amounts through the spar and occasionally may occur as a well-formed crystal in a veinlet cavity. Pyrite has been found inconspicuously disseminated in the wallrocks and vein matter. Malachite is often observed as a green staining in the walls and results from the local alteration of chalcopyrite. Bain (1905) reports having found stibnite in the Fairview mine but this is not supported by S. Weller (1920), E. S. Bastin (1931), nor J. M. Weller (1952).

As mentioned previously, calcite was the first mineral to be deposited. The amount present varies considerably but very few parts of the mine are without it altogether. It mostly occurs along both walls of the vein with the spar and other later minerals being deposited in the center.

Fluorspar followed calcite, replacing it and filling the cavities that were still present. Replacement seems to be of major importance and every stage of this process is in evidence.

The sulfides were deposited after the spar and are believed to be roughly contemporaneous with each other. Some sulfide mineralization may have occurred before the fluorspar as is shown by galena and sphalerite disseminated through and entirely surrounded by spar. In general, however, the sulfides were deposited along fractures or "slip planes" within the spar.

There does not seem to be any well-defined stages in the introduction of the various sulfides. In some cases, galena appears to be first, in others, sphalerite preceeds it and in still others, they must have been deposited simultaneously. In regard to occurrence, some sections of the vein contain only one of these minerals but more commonly both are found together.

Quartz is locally abundant within the vein material as well as in the adjoining wallrock. The introduction of this mineral began with small amounts preceeding some of the fluorspar and continued until after deposition of the sulfides and thus, its range of deposition covers a greater length of time than any of these other minerals. In a study of the occurrence of silica in the Blue Diggings vein, William Oesterling (1951) used thin sections of vein material to show that quartz has replaced calcite and has been replaced in turn by fluorspar. Rock in the area of the faults has also been affected. Silica, either carried by mineralizing solutions or by ground water, has replaced the calcite cementing material of nearby sandstones and limestones and has silicified them. This silicification has been observed to be particularly characteristic of hanging walls.

Second generations of both calcite and fluorite are found in the veins. However, these occur only in small amount and are of little or no importance. No indication has been found of extensive secondary enrichment of sulfide minerals.

Origin of the Deposits. The Rosiclare fluorspar deposits are clearly of igneous origin. Some of the characteristics of the deposits that support this are as follows:

1. The dome structure of the area and the accompanying dikes are evidences of igneous activity.

2. The presence of fragmental acidic igneous material in Hicks Dome and other locations in addition to the basic

dikes indicate a period of igneous activity intense and complete enough to include magmatic differentiation.

3. The occurrence of fluorine in such large amounts and concentrated form is best explained by the process of magmatic differentiation.

4. A relationship between the fluorspar deposits and the dikes is indicated by the presence in the dikes of an unusual abundance of fluorine-bearing apatite and phlogopite. An analysis of the Mix dike near Golconda showed 0.13% fluorine.

5. The localization of the fluorspar in apparently deep-reaching faults is suggestive of an igneous origin. Also, had the mineralization been due to laterally flowing solutions instead, it is more likely that all faults in the area, rather than a select few, would have been mineralized.

6. The extensive replacement of calcite by fluorspar suggests period of intense mineralization. This is also supported by the deposition of fluorspar, galena, sphalerite, et cetera, in a fairly well-defined sequence.

7. The relative insolubility of calcium fluoride is contrary to any theory dependent on the gathering of disseminated fluorine from widespread areas by the action of circulating ground waters.

Only a little is known of the characteristics of the mineralizing solutions. The ore-carrying medium has been established as being liquid by the presence of liquid inclusions in the fluorspar crystals. Studies to determine the temperature of formation have been conducted in bedded replacement deposits of the Cave-in-Rock district. The measured temperature range here is from 83° to 167° C. Weller, Grogan, and Tippie (1952) state that such a temperature is

> well below the critical temperature of pure water and is such that a pressure of less than 10 atmospheres would be sufficient to keep the liquid from boiling, whereas the pressure on the bedded deposits at the time of their formation was probably in the range of 160 to 235 atmospheres, corresponding to depths of approximately 3,000 feet.

The fluorine is generally believed to have been carried as hydrofluoric acid. Such a solution would have been highly reactive when first issued from its source but must have been neutralized to a great extent after traveling past hundreds or thousands of feet of highly acid-soluble limestone.

CHAPTER II

PRINCIPLES OF GEOCHEMISTRY

Geochemical Prospecting

The use of geochemical methods in prospecting is based on the principle that an ore body disperses elements into, or leaches elements from, the surrounding rock to form a characteristic distribution pattern. This pattern may cover a much larger area than the ore body itself and can be used as a guide in finding ore. Such areas contain a greater or less concentration of an element or elements than the surrounding rock and are known as anomalies or "geochemical halos." Halos may be classified into two types--primary and secondary.

Primary halos are those deposited by the actual ore solutions themselves. This study deals with wallrock halos surrounding mineralized veins and presents a good example of primary halos. Little is known about the mechanics of primary dispersion into the wallrock but it is assumed that it takes the form of "intricate systems of very small stringers of the common vein-forming minerals" (Hawkes, 1954). These stringers are, for the most part, too small to be seen with the naked eye and can only be detected by chemical analysis.

Secondary halos or anomalies are the result of weathering of primary deposits and of the subsequent dispersal of weathered products and are usually classified according to the material in which the anomaly is developed. The media in which geochemical prospecting can be carried on include bedrock, residual soil, alluvium, water, and plants. The chemical analysis of plants is known as biogeochemical prospecting, whereas, if the plants are only observed for increased or decreased rates of growth, the method is known as geobotanical prospecting. A special kind of secondary anomaly is the superimposed halo that results from metals being dissolved and transported up into an overlying cover of foreign origin such as glacial drift.

Before geochemical prospecting is applied to an area, one or more indicator elements must be chosen to be used in detecting the anomalies. This indicator should be an element whose chemical analysis is easily made and whose concentration is sharply different from the normal background of the country rock. Often, the valuable constituents of the ore deposit are used as the indicators. Elements used in the past include tin, lead, zinc, copper, boron, nickel, tungsten, molybdenum, gallium, cobalt, chromium, arsenic, antimony, sulfur, and manganese (Wackowski, 1952).

Examples of successful geochemical prospecting programs may be found in U.S.G.S. Bulletin 1000-A, by J. W. Harbaugh (see bibliography). This source lists all prospecting programs of this type through June, 1952.

Factors Influencing Trace Element Occurrence

Trace elements are the elements uncommon in the earth's crust and include all but oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. Clarke and Washington (1924) state that they are "generally found in very small amounts, rarely more than 2 percent for any one, or as much as 5 percent for all of them in any one rock."

Concerning their manner of occurrence, trace elements may be divided into two groups. One group tends to form independent minerals and includes such elements as sulfur, phosphorus, fluorine, carbon, and others. The second group rarely forms independent minerals but instead is included in the structure of other minerals. Included in the latter group are manganese, barium, strontium, chromium, and vanadium. Other elements, such as lead, zinc, and boron, belong to both groups.

Minerals are seldom pure compounds and Mason (1952, p. 75) makes the statement that "substitution of one element by another is the rule rather than the exception." The substituted element is generally randomly dispersed in the host. This substitution is the most important factor influencing the geochemistry of trace elements. Even lead, which occurs quite commonly in the independent mineral galena, occurs in a larger aggregate quantity in feldspars by replacement of the potassium ion (Rankama and Sahama; 1950, p. 104).

If ions of different elements are found in a mineral and are capable of occupying the same structural position, they are said to be diadochic and the substitution of one for another is known as diadochic replacement or diadochy. Diadochy refers only to a particular crystal structure and two elements may be diadochic in one mineral and not in another. Several requirements must be met before diadochic replacement can occur. The factors involved are ionic size, temperature of crystallization or substitution, electrostatic charge, ionization potential, and characteristics of the crystal structure. Other factors include the co-ordination number of the atom, the bond type, and the concept of electrostatic neutrality.

The ionic radius of the mutually replacing ions must be sufficiently close to allow the replacing ion to fit into the crystal structure. A crystal lattice will permit itself to be distorted only to a limited amount and ions exceeding the maximum size or less than the minimum are unable to enter and be retained. According to Goldschmidt (1954), the radii of the two ions must not vary by more than 10 to 15% of the radius of the larger ion. However, he emphasizes that there are exceptions to the rule.

The temperature at which crystallization and substitution takes place influences the relative degree of diadochy. At higher temperatures, tolerances in the crystal lattice are increased and diadochy may occur between ions whose radii vary by more than the permitted maximum. At lower temperatures, tolerances are decreased and the maximum permitted variance of ionic radii is correspondingly lowered.

The electrostatic charge or valence of replacing and replaced ions is the same in the ideal case but it is very common for an ion to substitute for another ion of either lower or higher valence. A good example is the already mentioned replacement of univalent potassium by divalent lead in potassium feldspars. Generally, substitution is rare where the difference in valence between the ions is more than one.

> The ionization potential is the voltage which gives to a free electron just sufficient energy to ionize the atom or molecule, that is, to drive an electron completely out, leaving a positive ion. . . . (Daniels and Alberty, 1955, p. 549)

The ionization potentials of diadochic ions are usually, but not always, similar. Polarization of an ion results from the electric field set up by neighboring ions and acts upon the ion in question by distorting its shape and the distribution of its electrical charge density. Polarization and its effects increase when ions have low co-ordination numbers and a resulting lack of symmetry. The ionization potential roughly measures the polarization; thus, the greater the ionization potential, the stronger will be the ion's attraction for the electrons of neighboring ions and the greater will be its polarization.

The co-ordination number is "the number of nearest neighbors around one central atom" (Goldschmidt, 1954, p. 83). Thus, each atom or ion has one or more co-ordination numbers depending on with what other elements it is combined. The ratio of atomic or ionic radii plays an important part so that a large atom or ion, when surrounded by small ions, will have a large co-ordination number. The importance of co-ordination numbers in the geochemical occurrence of elements is illustrated by the relationship between aluminum and ferric iron. Ferric iron commonly replaces aluminum in minerals where aluminum has a co-ordination number of six or eight as in the garnets and spinels and in the pyroxenes, amphiboles, and micas. However, aluminum is very rarely replaced by ferric iron where it is tetrahedrally co-ordinated as in the feldspars.

Metallic, homopolar, and ionic bonds are never mixed in identical positions in a crystal lattice. Certain elements have a preference for one bond type and this may influence diadochic replacement.

During diadochic replacement, the electrostatic neutrality of the structure must be maintained. If the two ions do not have similar charges the neutrality may be re-established by any of 3 methods. One is by the simultaneous substitution of another ion. If a divalent ion replaces a univalent ion then at the same time a univalent ion must replace a divalent ion somewhere within the structure. The second method is by adding another ion to the structure but not in an actual lattice position. All crystal structures have defects in them and are found to contain stray ions occupying spaces between structural positions. The third method of neutralizing the electrostatic charge is to leave a structural position vacant. As explained above, crystals are not perfect and so in all probability any given crystal will have missing ions somewhere in its latticework.

From the standpoint of electrostatic charge, diadochic replacement can be divided into 3 types. One takes place when the ions have the same charge and is known as camouflage. An example is the replacement of trivalent aluminum by trivalent ferric iron. Another occurs when an ion replaces one with a lower valence. Once the new ion is situated within the structure, a stronger crystal bond is formed because of the higher charge. The replacing ion is said to be captured. An illustration is the capturing of lead in potassium minerals. The third type of diadochy is called admission and occurs when an element replaces another of higher valence. This decrease in bond attraction weakens the structure. An example is the substitution of lithium for magnesium in silicates.

Goldschmidt's Classification of Elements. Goldschmidt (1954) has worked out a classification of the elements with respect to their geochemical behavior. In it he divides the elements into three groups--siderophile, chalcophile, and lithophile.

The siderophile group includes those elements having a strong affinity to the iron-nickel core or the earth's center (siderosphere). Included are gold, germanium, carbon, molybdenum, iron, nickel, cobalt, tin, platinum, and phosphorus. Chalcophile elements are closely associated with sulfur and are enriched in the hypothetical central sulfide-oxide shell or chalcosphere. In this group are, among others, lead, zinc, copper, sulfur, silver, cadmium, mercury, gallium, indium, arsenic, antimony, bismuth, and iron. The lithophile elements are enriched in the outer silicate crust or lithosphere and show a strong affinity for oxygen. They include lithium, sodium, potassium, beryllium, magnesium, calcium, strontium, barium, lead, zinc, boron, aluminum, gallium, carbon, silicon, titanium, vanadium, phosphorus, oxygen, tungsten, manganese, hydrogen, fluorine, chlorine, bromine, and iodine.

Geochemistry of Fluorine

Concentration in the Earth's Crust. The first estimation of the concentration of fluorine in the earth's crust was made in 1920 by F. W. Clark (1924). With little chemical data to go on he concluded the amount to be 200 parts per million of earth material. In 1924, Clarke and H. S. Washington raised this to 300 ppm. They went on the assumption that apatite is the chief fluorine-carrier in igneous rocks. By finding the total apatite and using the fluorine:P_2O_5 ratio for apatite of 1:10 they arrived at this figure. In 1934, E. S. Shepherd used a different approach and came up with 400 ppm. The latest estimation is the 800 ppm made by B. Wasserstein in 1946. At that time he completed a spectrographic analysis of rock specimens from South Africa from which he traced the source of fluorine in underground waters. Using this figure of 800 ppm, fluorine is the twelfth most abundant element in the earth. It is surpassed only by oxygen, silicon, aluminum, iron, calcium, sodium, potassium, magnesium, titanium, phosphorus, and manganese.

Occurrence in Minerals. Fluorine is present in mineral structures as a univalent ion with an ionic radius of 1.33 kX. It is thus similar in size to OH^- (1.33kX) and to O^{2-} (1.32 kX). The similarity of size and charge of fluorine and hydroxyl ions accounts for the common occurrence of fluorine in silicate minerals containing OH^- radicals in their structures. Silicates which usually include some fluorine ions are the micas, hornblende, and tourmaline.

The most important independent fluorine minerals are fluorite (CaF_2) and cryolite (Na_3AlF_6). Fluorine-carrying minerals of no importance other than as mineralogical curiosities include sellaite (MgF_2), fluellite ($AlF_3.H_2O$), yttrofluorite (Ca,YF_{2-3}), tysonite (LaF_3), avogadrite (KBF_4), malladrite (Na_2SiF_6), and villiaumite (NaF).

Occurrence in Igneous Rocks. Apatite is of importance in transporting fluorine from its igneous source but is not the chief carrier in all igneous rocks as was believed earlier. Clarke and Washington's $F:P_2O_5$ ratio of 1:10 holds true for basic rocks but there seems to be no relationship to P_2O_5 in acidic rocks and fluorine may even exceed the phosphorus. In these acidic rocks, it appears more likely that fluorine is fixed mainly in hornblende and biotite.

Fluorine tends to concentrate in the last stages of crystallization and is most concentrated during the pegmatitic stage. In studying a genetically related petrographic province, Wasserstein found that marginal granites containing the usual pegmatites had 0.1-0.3% fluorine while the centers of the eroded batholith had only 0.05% or less. The Bushveld felsites contain 0.04% fluorine while the associated granites have 0.1%

Pegmatites of acid rocks and their accompanying contact metamorphic rocks have been known to contain topaz and amblygonite enriched in fluorine. Pneumatolytic rocks generally include fluorine-bearing micas, such as lepidolite, phlogopite, and zinnwaldite. Micas have been analyzed that contained as much as 2% fluorine.

Occurrence in Thermal Waters and Fumeroles. Acidic hot springs and fumeroles are closely associated with magmatic emanations and contain an unusually high concentration of fluorine. If the magmatic waters are diluted by meteoric waters and sufficiently subjected to reaction with wallrock they become alkaline and the content of fluorine may be reduced to as low as that of river water. Large amounts of gaseous fluorine escape from fumeroles. Zies (1938) estimates that in 1919 the Valley of 10,000 Smokes in Alaska liberated 200,000 tons of hydrofluoric acid.

Occurrence in Marine Environments. Studies have been conducted in finding the ratios of the halogens present in sea water today as compared with the amounts that have been delivered to the seas by weathering. This ratio for chlorine is 33,275 times higher than is the ratio for fluorine. Bromine is 27,500 times higher and iodine is 140 times higher.

These figures mean that for the amount that has entered the sea, much less fluorine is left than any of the other halogens and the rate of precipitation must be greater. The exact mechanics of precipitation are unknown but phosphorus-bearing rocks have variable composition but are, in general, similar to fluorapatite. Tests made on North African phosphates showed the percentage of fluorine to be as high as 3.5%.. It is likely that fluorine is precipitated over widespread regions but is quickly redissolved if phosphorus is not also being precipitated. Thus, the spotty occurrence of fluorine in marine sediments is explained as taking place in areas where fluorine and phosphorus are co-precipitated.

Geochemistry of Lead

Abundance. The following estimations of the average amount of lead found in igneous rocks are considered the most reliable: 20 ppm by Clarke and Washington (1924), 16 ppm by Hevesy (1932) (Goldschmidt, 1954, p. 398), and 14 ppm by Sandell and Goldich (1943). All of these are in general agreement and the figure of 16 ppm by Hevesy is that accepted by Rankama and Sahama (1952, p. 729). Spectrographic data on shales by Goldschmidt (1954, p. 398) indicate an average of 20 ppm. The limestones tested contained less lead--between 5 and 10 ppm.

Geochemical Properties. Lead in the upper lithosphere exhibits both chalcophile and lithophile characteristics. The former is generally the case at low temperatures while at medium and higher temperatures lead occurs almost exclusively in oxygen-bearing compounds.

Lead is grouped with germanium and tin in the periodic table but their manners of occurrence are completely different in igneous rocks. Lead forms bivalent and quadrivalent ions with the bivalent ion being the more important and having a radius of 1.32 kX. Similar and closely associated ions are strontium (1.27 kX) and potassium (1.33 kX). Pb^{2+}, like Sr^{2+}, partially replaces Ca^{2+} (1.06 kX) and is particularly common in apatite, being found in concentrations up to 50 ppm. It also partially replaces this same ion in monoclinic pyroxenes formed at high temperatures. The only other common occurrence of lead in basic rocks is as galena.

Lead is much more abundant in the silicic or acidic igneous rocks. This is mainly due to its close relationship with the univalent potassium ion. In the evolution of magmatic rocks, potassium, lead, and silica are all concentrated in the residual magmas. The diadochic replacement of potassium by lead is most frequent in the potassium feldspars. Lead is able to form a feldspar structure and a stable artificial lead feldspar has actually been prepared. Pegmatities of granite and nepheline syenite often contain lead in the form of galena. Also, volcanic exhalations are known to include galena and other lead minerals.

The most important lead minerals are galena (PbS), cerussite ($PbCO_3$), anglesite ($PbSO_4$), and pyromorphite $Pb_5Cl(PO_4)_3$.

The last three along with other sulfate, carbonate, and chloride minerals of lead are usually found as alteration products of galena in the superficial parts of lead-ore bodies.

Lead is also the product of radioactive decay of such elements as thorium and uranium and generally accompanies them when they are in their primary minerals.

<u>Geochemical Cycle</u>. Under conditions of oxidation, lead is extracted from its minerals and transported in the form of soluble stable compounds. However, it is not nearly as mobile as some other elements, for example, zinc. Galena is often altered to $PbSO_4$, probably through the intermediate formation of divalent lead ions and ions of sulphuric acid. Even more likely, if dissolved CO_2 is present, is the formation of $PbCO_3$. Many other soluble or slightly soluble lead compounds occur in the zone of oxidation, the various anions being supplied by circulating ground waters or by the breaking up of other minerals already present in the vicinity.

Under reducing conditions, lead is almost universally precipitated as PbS or galena. This is a frequent occurrence under marine conditions of black mud deposition and explains the abundance of lead in black shales. Marine animals also assist in extracting lead from sea waters and calcareous shells have been found to have a concentration of as much as 52 ppm (Goldschmidt, 1954, p. 403).

Geochemistry of Zinc

Abundance. Many estimates have been made of the concentration of zinc in igneous rocks. The most recent and the one accepted by Rankama and Sahama is that of 132 ppm made by Lundegardh in 1947 (Rankama and Sahama, 1950, p. 708). Lundegardh, along with Palmqvist, also did analytical work on sediments and sedimentary rocks and came up with the following data (Rankama and Sahama, 1950, p. 713):

Material	Zn (ppm)
Sandstones	20
Clays	80-230
Shales	200-1,000
Limestones	50

Geochemical Properties. The behavior of zinc is determined primarily by the similarities between divalent zinc (0.83 kX) and metals of the magnesium-iron group, especially iron. The important ions of this group and their ionic radii are Mg^{2+}(0.78 kX), Ni^{2+}(0.78 kX), Co^{2+}(0.82 kX), Fe^{2+}(0.83 kX), and Mn^{2+}(0.91 kX). Within the upper lithosphere, zinc, like lead, exhibits both chalcophile and lithophile characteristics. This, and the above-mentioned relationship between zinc and the magnesium-iron group, is shown by the mutual replacement of zinc, cobalt, ferrous iron, and manganese in both oxygen compounds and in the sulfides.

In regard to the relative distribution of zinc in the series of differentiated magmatic rocks, opinions are variable. Sandell and Goldich (1943) found the concentration of zinc to

be similar to the amounts of magnesium and iron present and therefore to be more concentrated in basic igneous rocks. However, Rankama and Sahama (1952, p. 710) state that

> During the magmatic differentiation, zinc and cadmium, together with many other elements, remain largely in the residual melts and solutions throughout the main stage of crystallization and the pegmatitic stage.

This is based on Lundegardh's findings that the highest amounts of zinc occur in the more acidic products of differentiation. Rankama and Sahama suggest that the differences may be due to regional variations but it seems more likely that the distribution of zinc in igneous rocks is due to a combination of two factors: (1) the tendency to follow magnesium and iron in their modes of occurrence, and (2) to concentrate in the latter stages of differentiation because of the high volatility of some of the zinc compounds. The data of Lundegardh show that the highest content of zinc of the acidic rocks is in the ferromagnesium minerals such as biotite and this tends to support the above theory.

The most important zinc minerals are sphalerite and wurtzite (ZnS), zincite (ZnO), smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4), and hemimorphite $Zn_4(OH)_2Si_2O_7 \cdot H_2O$. Two other minerals, generally occurring in metamorphic rocks, are gahnite ($ZnAl_2O_4$) and franklinite $(Zn,Mn)Fe_2O_4$.

Zinc in large quantities often occurs in hydrothermal deposits. Ore deposits result from deposition of ore solutions in open spaces and from metasomatic replacement of limestone and other carbonate rocks with which the solutions come into contact.

Geochemical Cycle. Under conditions of oxidation, zinc is altered to various soluble salts and as such is extremely mobile. The most frequent products of oxidation are zinc sulphate, zinc carbonate, hemimorphite and numerous phosphates, arsenates, and vanadates.

Zinc is one of the most abundant heavy metals in sea water and, therefore, much of this element is precipitated on the ocean floor and incorporated into the accumulating sediments. This is particularly true under stagnant, reducing conditions where muds and shales are formed. Little is known about the occurrence of zinc in calcareous sediments but it is believed that small amounts are commonly precipitated along with them since crystals of sphalerite are often found as the product of diagenetic recrystallization of limestones (Goldschmidt, 1954, p. 265). The precipitation of zinc through the action of marine organisms occurs in amounts exceeding that of any other heavy metal. I. and W. Noddack (1939) (Goldschmidt, 1954, p. 266), found concentrations ranging from 65 ppm in a sea urchin shell to 1,550 ppm in the dry matter of a jelly fish.

Geochemistry of Manganese

Abundance. The average manganese composition of igneous rocks is listed by Clarke and Washington (1924) as being 860 ppm. In 1934, Hevesy and others raised this to 980 ppm

(Goldschmidt, 1954, p. 621). Analyses of sediments and sedimentary rocks by various workers show the following results (Rankama and Sahama, 1950, p. 652):

Material	Mn (ppm)
Limestones	385
Shales	890
Red clays	1770
Siderites	2800
Sandstones	trace

Geochemical Properties. Manganese is a strongly lithophile element, occurring mainly in silicates and oxides. Its chemical properties are closely related to those of iron and to the other members of the iron family. Its occurrence in igneous rocks follows that of iron with the MnO:FeO ratio remaining constant except in the late magmatic differentiates, such as pegmatities and pneumatolytic rocks. In these latter rocks, the ratio increases quite sharply. As a result of the similarity of manganese to iron concentrations during the main stages of magmatic crystallization, manganese tends to become less abundant toward the acidic end of the series. However, the trend is reversed at the very end of the series and pegmatites are often found to contain a number of oxide, phosphate, and silicate minerals rich in this element.

Independent manganese minerals are rarely found in igneous rocks and it is almost always concealed in the structure of other minerals. In so occurring, it is usually in the form of Mn^{+2} ions with a radius of 0.91 kX. This bivalent ion is similar in size and charge to and is able to replace the following ions: Fe^{2+}(0.83 kX), Mg^{2+}(0.78 kX), Zn^{2+}(0.83 kX), and Ca^{2+}(1.06 kX). The replacement of the divalent iron or ferrous ion is by far the most important. This exchange is frequent in dark silicates which have hydroxyl groups in their structures. Biotite is a good example and contains up to 1% manganese. Other common host minerals are tourmaline with up to 2%, augite with up to 0.4%, and hornblende with up to 0.3% manganese. The replacement of calcium by manganese is less frequent but does take place in apatite. However, manganese is unable to replace the same element in either the feldspars or feldspathoids.

Rhodochrosite ($MnCO_3$) and manganese-rich siderite (manganosiderite) are often deposited by hydrothermal solutions. If such solutions make contact with oxygen-bearing ground waters, manganese may also be deposited as the dioxide or complex hydrate.

Geochemical Cycle. Manganese is soluble in waters containing dissolved carbon dioxide and is carried mainly as the bicarbonate, $Mn(HCO_3)_2$. Less often, it is carried as $MnSO_4$. Manganese best remains in solution under reducing conditions. Therefore, humic compounds are important in its transportation. If they are not present and dissolved oxygen is, the divalent manganese is oxidized to the quadrivalent ion and precipitation as $Mn(OH)_4$ is likely to occur. These conditions are often met as manganese is introduced into the shallow near-shore waters of the sea and so the manganese content of ocean waters is generally low. The element is also precipitated when carbon dioxide is removed from the bicarbonate solution by the action of bacteria or by oxidation. Marine carbonate sediments may be enriched in manganese by replacement of divalent calcium ions during or just after precipitation. MnO_2 is formed under conditions of deep-sea sedimentation and, to a lesser extent, so is rhodochrosite.

CHAPTER III

THE TRANSPORTATION AND DEPOSITION OF MINERAL SOLUTIONS IN WALLROCK

The Circulation of Solutions in Wallrock

Permeability tests indicate that no rocks, with the possible exception of volcanic glasses, are completely impermeable. Therefore, some leakage into the adjoining wallrock will occur from the main body of an ore solution in a cavity. The amount will depend upon the rock permeability, viscosity of the fluid, the differential pressure, and the thickness of the rock from its contact with the ore solutions to the nearest flow outlet (Ohle, 1951).

The original introduction of solution into the wallrock results from the pressure gradient between the unsaturated wallrock and the cavity filled with ore solutions under high pressure.

The path that these earliest solutions take is through the many tiny cracks and fractures associated with the formation of the faults. In the case of limestones, as at Rosiclare, some of the beds prove more favorable than others in their ease in being dissolved and consequently are enlarged to become established channelways. The exact form that these channelways take is unknown but is generally conceived to be as numerous microscopic or submicroscopic interconnected pore spaces. Precipitation and reaction with the wallrock occur along the channelways to form relatively impermeable walls which serve to confine further solutions to their channels. This condition may continue until deposition of the solutions' contents has decreased the porosity to below that of surrounding, and originally less favorable, zones. Constant minor fracturing often accompanies the intrusion of hot, magmatically-derived liquids under high pressure and provides opportunities for the breaking of old confining walls and the formation of new channels.

Factors Influencing the Rate of Circulation.

Porosity and Permeability. The porosity of a rock is the measure of the pore spaces and is expressed quantitatively as the percentage of interstices to the total volume of rock. The permeability measures the ability of the rock to allow the passage of a fluid. It is defined as the "volume of a fluid of unit viscosity passing through a unit cross section of the material one centimeter thick under unit pressure gradient in unit time" (Rove, 1947). These two properties of rocks are closely related but the relationship is not necessarily linear. Rocks with high porosity may be very low in permeability if the pore spaces are not connected. The size of the pore spaces is also important. Shales may have high porosity but the smaller and more numerous pore spaces have a greater total surface area which increases the effect of various retarding physical forces and results in a decreased rate of flow through the rock.

Ore solutions characteristically seek out certain beds of rock while ignoring others and often the difference between the two types of beds cannot be detected even with a microscope. The principle factor determining a bed's ability to offer channels for circulation solutions is its permeability. Little is known of why two adjacent strata of the same formation would differ in porosity and permeability. Some possible explanations are suggested below.

Within a limestone formation the magnesium content may vary from bed to bed either because of differing conditions existing during deposition or because of varying amounts of alteration by circulating solutions. These solutions may have occurred at any time after deposition, causing unequal dolomitization. During subsequent alteration and recrystallization by high temperature, high pressure and circulating solutions, the pure limestone and the dolomitzied limestone will react differently. Coarsening of the grain is a common result of this recrystallization and if such is the case, the new pores, although reduced in number, will be larger, smoother, and straighter. All of these characteristics increase the porosity of the pure limestone beds and would make them the more favorable channelways.

Limestone beds could also conceivably vary in the orientation of their calcite crystals. If this were so, the thermal expansion of the crystals that takes place at the higher temperatures met when the formation is covered by later deposits would affect the porosity and permeability to different extents in beds of various composition. The crystal expansion occurs in a zone under great confining pressure and so any enlargement of crystals will take place at the expense of pore spaces. If the calcite crystals were all lying with their "c" axes parallel to each other, very little, if any, pore space would be left. The most favorable situation for the preservation of porosity would be for the crystals to have a heterogeneous orientation.

Chemical reactibility may play a part in determining the relative permeability of two beds in severals ways. First, zones of mineralization are found in beds of favorable chemical reactibility and in general, this mineralization tends to decrease permeability. An exception is in the case of strict volume for volume replacement with no other accompanying precipitation. Under these conditions, permeability remains the same. Secondly, beds whose chemical character make them susceptible to being dissolved will show an increase in permeability. This is the primary reason for increases in permeability during mineralization; a less important cause being the fracturing that takes place due to crystallizing forces.

Size of Openings. William Holser (1947) has classified rock openings available for mineral transporation into the following four sizes.

1. Supercapillary. This size of opening is necessary where large volumes of solution are dealt with. Movement of fluids may be by either streamline or turbulent flow depending on velocity and opening size.

2. Capillary. In these, fluid movement again takes place but only by streamline flow. Also occurring in this sized opening is capillary flow in which no external pressure differential is needed.

3. Grain boundary. Grain boundary openings include the submicroscopic breaks within a single crystal as well as the boundaries between adjacent crystals. Fluids are not able to flow through these openings; instead, all movement takes place by diffusion of ions and molecules.

4. Intra-lattice. These openings are generally not considered seriously as having any geological importance but will nevertheless be mentioned. Fluids, of course, cannot pass through. Movement is by diffusion of ions which enter a crystal and progress through the structure by jumping from one lattice position to another.

In regards to influencing the rate of circulation (permeability), the larger the opening size is, the faster will be the rate. This same relationship does not necessarily hold true, however, to the intensity of mineralization. Later it will be shown that the smaller channelways often offer the most favorable conditions for deposition. Below are listed several other properties which may or may not influence a rock's permeability and consequently its ability to allow the passage of circulating solutions.

Clay Swelling. Many clay minerals found scattered throughout limestone or other rock formations absorb quantities of water and expand as they do so. This expansion, like that of the thermal expansion of crystals, is at the expense of pore space and so results in the decrease of porosity and permeability. Since almost all limestones contain some silt or clay, as is shown by studies of insoluble residues, this could be an important criterion of permeability.

Adsorption. Adsorption is the adhesion of a thin layer of molecules of the solution or of its solutes to the surfaces of rock particles with which it is in contact. The thickness of this layer will depend upon the surface energy of the liquid and also on the size of the opening. In small openings the layer is not as thick but its relative effect is greater. This is a major reason for rocks with small pore spaces being less permeable even though their porosity is as great.

Surface Tension. An experiment by J. C. Calhoun and S. T. Yuster (Ohle, 1951) using liquids of varying surface tension indicates that this property has no effect on solution flow.

Concentration. That permeability increases slightly as concentration of the solutions increases is shown by Grunberg and Nissan (Ohle, 1951).

pH. The pH of a solution also affects its permeability. Calhoun and Yuster (Ohle, 1951) found that the minimum permeability occurred at the neutral point and that both acid and basic solutions were more favorable for increased rates of flow.

Ionic Concentration. Calhoun and Yuster also performed permeability tests while varying the ionic concentration or electrical conductivity but were able to find no connection between the established conditions and the results.

Temperature. Temperature shows a very clear relationship to permeability as is illustrated by the work of Grunberg and Nissan (Ohle, 1951). They reported that there was a decrease of 0.8 millidarcy for every degree Centigrade rise in temperature.

Some of the above factors, such as concentration and pH, will have a very minor effect, while others, such as clay swelling and adsorption, might well be listed with the earlier mentioned causes for two similar appearing beds having widely differing suitabilities for providing solution channelways.

Transportation of Metals in the Solutions

The transportation and emplacement of metallic ions within wall rock is carried on by a combination of two processes. They are as follows:

1. Circulation of solutions carrying metals in the form of solutes and as dispersed colloidal particles, and
2. Diffusion of metallic ions through the noncirculating solutions that saturate the pore spaces.

The mechanics of the first process have already been discussed and it is of most importance in the cases where there has been significant flow of solutions to the replacement front. The second process is the more important of the two in situations where only minor amounts of the metals are introduced and flow is limited or non-existent such as within the wallrock being studied.

The initial solutions from the main zone of ore deposition fill the available pore spaces after a relatively short time and, as a general rule, subsequent circulation is limited. However, as long as any precipitation or reaction is taking place in the interior of the wallrock the metal concentration gradient will be preserved and metallic ions will diffuse down this gradient through the stationary solvent.

The rate of diffusion is dependent on this concentration gradient and on the diffusion coefficients of the ions involved. The latter increase with rising temperature and concentration and with decreasing ionic radius. Other factors include the sizes of pore spaces, the electrical force fields present, which greatly affect the movement of ions and other charged particles, and such processes as adsorption or chemical reaction between the wallrock and solution which decrease metal ions available for diffusion.

Ability of Solutions to Transport Metals. The quantity of metal ions, and their accompanying anions, that can be carried in solution is determined by the solubility product constants. In the situation being studied, the anions are sulfide ions. Thus, for any given temperature and pressure, when the product of the metal ion and sulfide ion concentrations reaches the solubility product constant, precipitation results. The solubility product constant is, therefore, the limiting factor in the transportation of dissolved metals in solution.

However, two conditions can occur to raise this metallic concentration. In acid solutions, excess hydrogen ions are present which combine with sulfur to form H_2S. This reduces the available sulfur and increases the metal's solubility. The other possibility is "the repression of the metal ion by formation of complex ions of the type MeS_n^{2n-2}" (Garrels, 1944).

Garrels experimented with the solubilities of metal sulfides in dilute solutions and reached several conclusions. He found that positive ions have no effect on metal concentrations but that negative ions, such as fluorine and the halogens repress it to as low as 10% of the total metal in solution. The result of this would be the solutions' ability to carry up to 10 times as much metal.

However, Garrels believes that dilute solutions, even with the above increases in carrying capacity, are unable to transport the amounts of metal necessary for the formation of large ore deposits. In the case of dilute and weakly acid solutions, he gives the following illustration:

> If a cube two-thirds of a mile on a side were filled with a solution carrying 0.1 mol of bivalent sulfur per liter,

> and 0.1 normal in acid at 400° C., not more than 1 mol of copper [64 grams] could be dissolved before precipitation would occur. Or, to put this illustration as a dynamic, rather than as a static picture, a volume of dilute solution equal to that of the Mediterranean sea must have passed between the walls of every vein which contains a few tons of copper ore. (Garrels, 1944)

He likewise discredits the theory of dilute, weakly alkaline solutions being the transporting agents because of limitations such as the inability of alkali sulfide solutions to carry more than minute amounts of iron.

It is apparent that highly acid or alkaline solutions would be neutralized by reaction with wallrock after a short period of exposure. This would seem to be particularly true where the wallrock is limestone or dolomite. Once neutral, the change toward alkalinity would be at a slower rate as the solution is now closer to equilibrium with its environment. In fact, it seems doubtful that it would ever reach alkalinity while carrying fluorine (believed to be in the form of hydrofluoric acid).

After discarding the various theories of transportation of metals in a dissolved state, Garrels suggests "that the dominant role is played by a colloidal phase." Thus, the major part of the metal sulfide is carried in a highly dispersed solid phase which is in equilibrium with its saturated solution. The dissolved ions are the ones which take part in precipitation and replacement and the extraction of them sets up a concentration gradient which is satisfied by metals of the dispersed phase being dissolved and migrating to the precipitation or replacement front. Therefore, even though the colloids are not as mobile as the dissolved ions in the smaller openings, they are stored in the larger channels and are available as soon as needed.

The colloidal or dispersed solid phase theory of metal transportation does not change any of the mechanics of precipitation or of reaction with the wallrock. This is still accredited to the solution phase. It does, however, greatly increase the carrying capacity of vein solutions and makes possible the formation of large hydrothermal deposits from reasonable quantities of these solutions.

In the wallrock that this report is concerned with, the metals are present only as traces and colloids may or may not have played a part in their deposition. It is likely that colloids entered the vein walls for a short distance and were available to keep the solution saturated but for the small amounts being deposited they were not absolutely required. The value of the colloidal theory in metal transportation is in explaining how the major portions of the veins were supplied.

Effects of Size of Opening on Metal Migration.

1. Supercapillary. This sized opening permits solutions to transport metals in dissolved form or in dispersed phases of colloidal size and even larger.

2. Capillary. In larger capillary openings under ideal conditions, some fluid flow occurs and with it metals may be carried either in solution or as colloids. Ordinarily, however,

solvent transportation plays a very minor role and diffusion is most important. This process has already been described.

The movement of colloids either by flow or by diffusion also occurs, but to a lesser degree. The increase in size of colloid particles over that of ions and molecules decreases their mobility and hence their rate of diffusion. Diffusing colloids are further hampered by their susceptibility to adsorption and to precipitation by electrolytes dissolved from the rocks.

3. Grain boundary. It has already been mentioned that all movement of ions and molecules through these openings takes place by diffusion. The openings are very small and are characterized by having the molecular forces of the opposite walls overlapping. This creates an energy barrier so that, for diffusion to occur, thermal or other energy must be supplied. Diffusion is governed by the concentration gradient and by the diffusion coefficient, just as before, but the diffusion coefficient is different than it would be under other conditions.

4. Intra-lattice. As in the above case, the diffusion coefficient in intra-lattice diffusion varies considerably from that of more normal diffusion. It may take either of two forms: the Frenkel type, in which the ions or atoms move from one interstitial position to another, or the Schottky type which involves the movement of an ion or atom into a vacant lattice position, leaving a vacancy or hole at its former site (Holser, 1947).

Deposition of Metals by Precipitation and Reaction

Several factors work together in determing either the rate of precipitation from solution or the rate and equilibrium point of reaction between solution and wallrock. Included among these factors are temperature, pressure, concentration of solvent, relative abundance and rate of supply, reactions within the solution, character of the rock, and the area of interface where the reaction or precipitation is taking place.

Causes of Precipitation and Reaction.

Changes in pH. This is recognized as an important cause of precipitation and can take place by either of two means. First, and probably most important, is by contact with reactive wallrock. This is best typified by the neutralizing of acid solutions by reactive rocks, such as limestone and dolomite. The second method is by dilution from the mingling of an acid or alkaline ore solution with meteoric waters. This also has the effect of neutralization.

Van't Hoff's Law. This law states that "a solution in equilibrium undergoes that change at lowered temperature which is accompanied by liberation of heat" (Bain, 1936). In other words, when a solution at equilibrium enters a cooler zone in which its temperature is lowered, it will undergo a reaction that will liberate heat and restore the temperature necessary for equilibrium. Such a reaction may involve precipitation.

Le Chatelier's Law. If the pressure on a solution at equilibrium is allowed to decrease, a reaction will occur within the solution which is accompanied by an increase in volume; the reverse is also true.. Since the sum of the volumes of solute and solvent is, in almost all cases, greater than the volume of the solution, precipitation is a common way of effecting this volume increase.

Bernouilli's Principle. Bernouilli's principle states that "pressure on the moving solution varies inversely as the square of the velocity" (Bain, 1936). Thus, as a solution enters smaller channels and its velocity is slowed down, the pressure decreases and it follows from Le Chatelier's law that precipitation is the likely result.

Nernst's Law. According to this law, "the solubility of a salt is decreased by the presence in solution of another salt that has a common ion" (Batement, 1950, p. 30). This is explained by the increased concentration of that ion with the consequence that the solubility product constant may be exceeded. Such an occurrence may result from the intermingling of the magmatic solution either with other magmatic solutions or with meteoric waters.

Types of Mineral Deposition. Two processes, direct precipitation and metasomatism, will be discussed; after which two others of much lesser importance will be briefly mentioned.

Direct Precipitation. This form of mineral deposition probably occurs to a greater extent in rocks such as sandstone rather than in the more reactive rocks of the limestone-dolomite type.

The causes of precipitation may be changes in temperature, pressure, or pH of solution, the addition of solutes beyond the saturation point, or contact with wallrock favoring deposition.

In the case of the precipitation of sulfides, the order of deposition is determined partly by the Schuermann's series. In this series, "the sulfide of any metal will be precipitated at the expense of any sulfide above it in the table" (Newhouse, 1928).

In studying Lindgren's observed order of mineral deposition, Newhouse attempted to explain it by physical and chemical properties of the minerals. He found that certain characteristics did support and parallel Lindgren's list including the Schuermann's series (based on solubilities) and the heat of formations of the minerals. However, he gives very little evidence to back up some of his conclusions.

Metasomatism. Metasomatic replacement is "a process of essentially simultaneous capillary solution and deposition by which new minerals are substituted for earlier minerals or rocks" (Bateman, 1950, pp. 30-31). The replacing mineral and the replaced mineral or rock do not have to have a common ion.

Metasomatism may be the most important method in the formation of hydrothermal ore deposits and is also important in supergene ore deposition. The replacement may take place due to the action of hot vapors and gases, or by hot or cold meteoric solutions.

This form of mineral replacement differs from ordinary chemical replacement in being volume for volume rather than ion for ion. In the replacement of calcite by sulfides, with which we are concerned, the major volume of each of the minerals is occupied by oxygen and sulfur ions respectively. The exchange of these large ions is the most difficult part of the replacement and has the greatest effect on the structure of the host mineral. After this is accomplished, the exchange of metal ions simply takes place by diffusion between the larger ions.

The following two equations are samples of the sulfide replacement of calcite and the latter is equated for volume for volume substitution (Ridge, 1949):

$$Zn^{+2} + S^{-2} + CaCO_3 = ZnS + Ca^{+2} + CO_3^{-2}$$

$$31\ Zn^{+2} + 31S^{-2} + 20CaCO_3 = 31ZnS + 20Ca^{+2} + 20CO_3^{-2}$$

A limiting factor in metasomatic replacement is the size of ions that must be introduced into the crystal structure of the mineral being replaced. In the case of the above replacement, the sulfur ion has an ionic radius of 1.74 A., and is about 1½ times as large as the oxygen ion it is replacing. However, this size difference is within the allowable limits because it is "small enough in comparison with the packing factors of the minerals involved to permit the postulated diffusion" (Ridge, 1949). The packing index is the ratio of ion volume to unit cell volume and the relatively low packing index of calcite (4.0) allows the large sulfur ion to diffuse through the structure.

These two processes are responsible for the great majority of mineral deposits. Others, such as adsoprtion and base exchange, account for only minor amounts of ore. The former is illustrated by the adsorption of copper from solutions by kaolin to form chrysocolla. The latter is accomplished by an exchange of cations between solids and liquids.

CHAPTER IV

METHODS OF ANALYSIS

Sample Collecting

The mine workings at Rosiclare are located along two major veins, the Blue Diggings and the Good Hope (or Rosiclare), which dip towards each other and are connected by cross-cuts at the 500 foot and 700 foot levels. The upper cross-cut is roughly 1700 feet long while the lower is about 1500 feet long.

The samples were taken at varying distances from the veins toward the midpoints of each of the cross-cuts. Three traverses were made, each containing 16 samples; traverse A was taken from the Blue Diggings end of the cross-cut at the 500 foot level, traverse B from the Blue Diggings end at the 700 foot level, and traverse C from the Good Hope end at the 500 foot level. The original plan was to include a fourth traverse from the Good Hope end of the cross-cut at the 700 foot level, but this was impossible due to flooding. The distances of samples from the vein are found in Table I.

The first step in collecting the samples was to stretch a tape along the cross-cut wall and mark off the desired distances with crayon. Then, the sample, weighing $\frac{1}{2}$ to 1 pound, was chipped out with a pick. Care was used to prevent altered material from being included and, in most cases, the outer 2

TABLE I

Sample No.	Distance from Vein
1	3 inches
2	6 inches
3	9 inches
4	1 foot 0 inches
5	1 foot 3 inches
6	1 foot 6 inches
7	2 feet 0 inches
8	3 feet 0 inches
9	4 feet 0 inches
10	6 feet 0 inches
11	8 feet 0 inches
12	12 feet 0 inches
13	16 feet 0 inches
14	25 feet 0 inches
15	50 feet 0 inches
16	100 feet 0 inches

or 3 inches of rock was discarded before taking the actual sample. Whenever possible, the samples were taken from the same stratigraphic bed. However, when it was obvious that small veinlets of fluorspar and associated minerals were present, the sample would be taken either above or below. The sample, once chipped out of the wall, was then placed in a clean paper bag and labeled.

Sample Preparation

In preparing the samples for analysis, they had to be ground fine enough to facilitate solution in acid. In doing this, it was essential that a method be used which would result in as little contamination of the sample as possible. The method chosen was as follows: first, the samples were washed and a portion of each was selected which was free from weathering and from mineral-carrying veinlets. This section

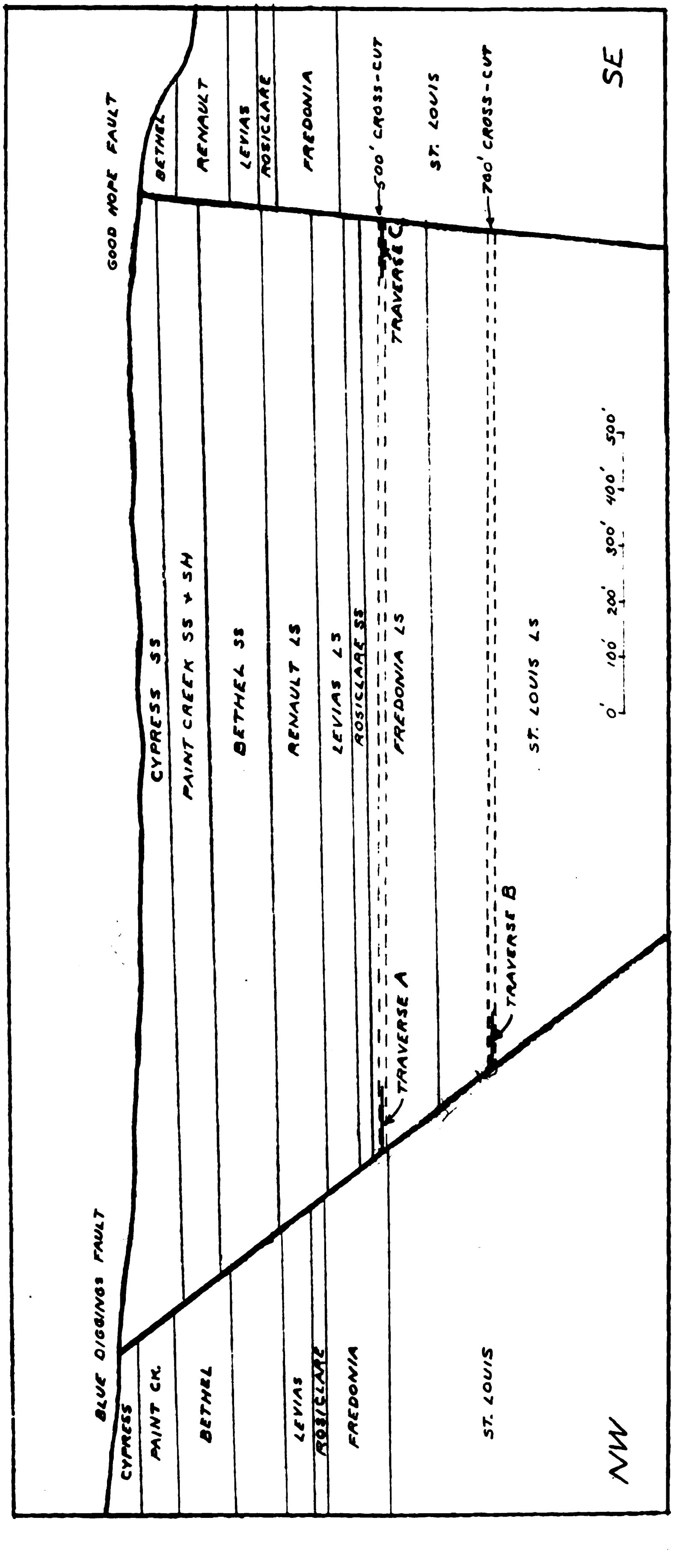


Fig. 3.

CROSS-SECTION SHOWING LOCATION OF TRAVERSES of the rock was then carefully broken up by the sharp edges of a vice. Chips which had been untouched by the vice were separated and placed in a clean mortar to be ground into fine powder. After grinding, the powder was poured into clean glass vials and each vial was labeled. About 4 to 5 grams of each sample was prepared in this way.

Spectrographic Analysis

In order to determine the best indicator elements to be used in the colorimetric tests, random samples from each of the traverses were combined and a qualitative spectrographic analysis was run on them. The results showed that several elements were present in sufficient quantity for colorimetric analysis and, of these, lead, zinc, and manganese were chosen as being best for the purposes of this study. Certain others, such as calcium and magnesium, owed their abundance to the country rock and were of no use to us, while still others, such as strontium and barium, have no suitable colorimetric tests. The quantitative analysis for fluorine is based on volumetric methods and was beyond the scope of this work.

Colorimetric Analysis

Once it was determined what elements were to be used as indicators, the ground samples were dissolved in acid until only a silica residue remained. Then, colorimetric methods were applied to determine the quantities of each indicator.

Colorimetric tests are based on the formation of a specific color when a certain chemical reagent is added to a solution containing the element being tested for. Metal complexes result whose concentration determines the intensity of color. Through the use of a colorimeter, the color of the samples can be compared with similarly treated solutions containing known concentrations. The latter are called standards.

In the course of analysing a sample, chemical reagents must be added to prevent the color-providing reagent from combining with other elements which are in the solution. These, and additional sources, may introduce small quantities of the element to be tested for. These are accounted for by running a solution containing no sample through all the analysis steps. This blank is tested on the colorimeter to determine how much of the particular element must be subtracted from the sample amounts.

Throughout the tests, great care was taken to prevent the introduction of impurities. Use of blanks compensates in part but is not sufficient when the amount of impurities is a high percentage of the total concentration. The concentrations of lead, zinc, and manganese are measured in parts per million and impurities must be kept well below this amount if the results are to be valid. The water used was first distilled and then purified by passing through a "de-ionizer" and all of the reagents were of a grade suitable for colorimetric work. Glassware and other equipment was cleaned before use by soaking in a cleaning solution of sulfuric acid and potassium dichromate and washing in distilled and purified water. The filter paper was of the lowest ash content obtainable. Other precautions that could not be followed were that no facilities were available for the distillation of liquid reagents such as carbon tetrachloride or chloroform, nor for the recrystallization of solid reagents. The general smoothness and consistency of the curves would indicate that contamination was at a minimum.

The chemical procedures used were taken from Sandell (1944) and need not be redescribed here.

CHAPTER V

RESULTS

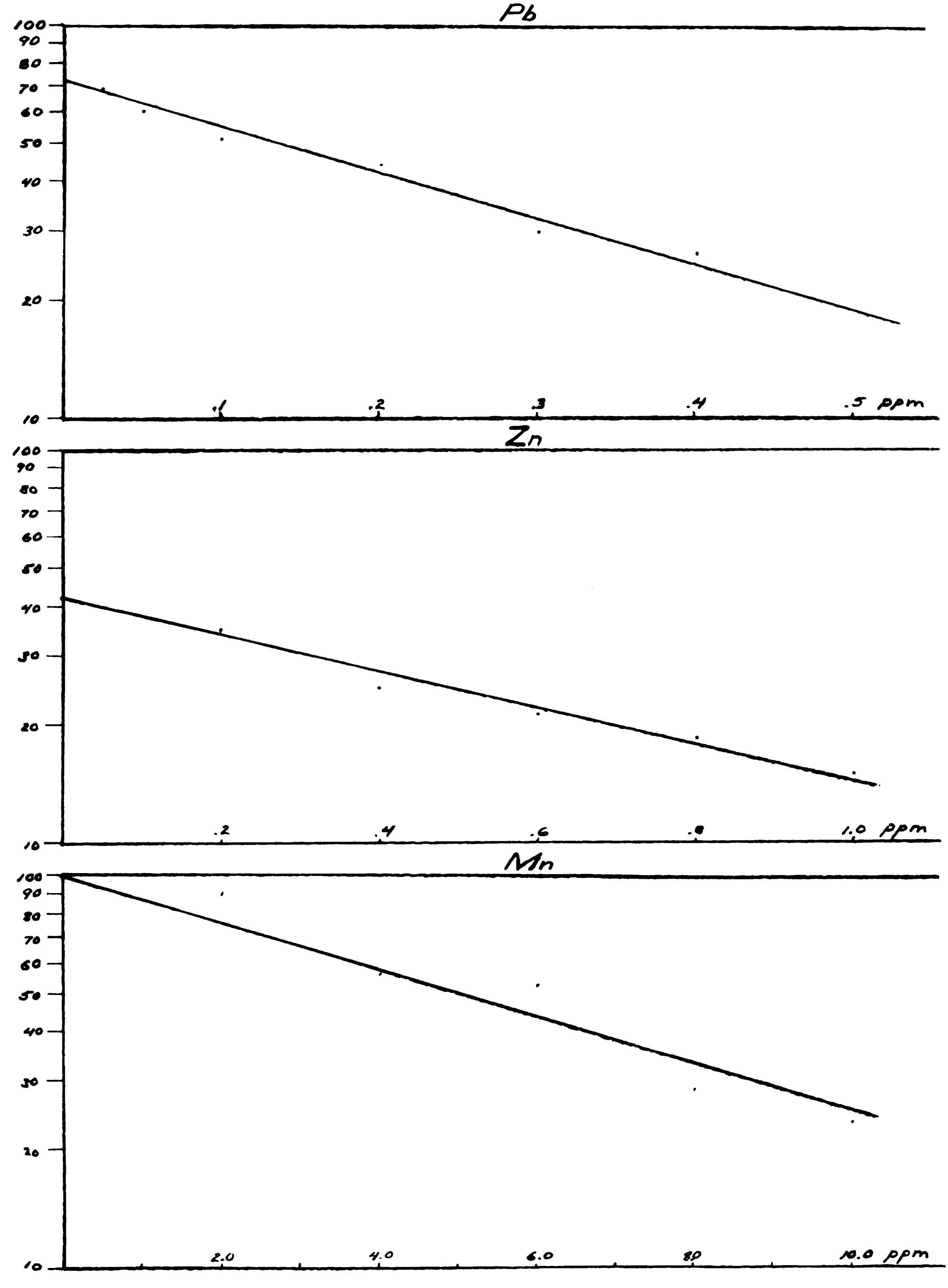
Methods of Presenting Data

Standards. Before sample concentrations can be determined, standard curves must be set up. This is done by plotting, on semi-log paper, the log of the transmittancy of the standards against the linear function of the concentrations. The transmittancy is measured as a percentage of the transmittancy of distilled water.

The tests used for each of the three elements follow the relationship set down by the Beer-Lambert law, and so the standard curves are, in each of the cases, straight lines. However, in measuring the transmittancies of a series of standards, it is highly unlikely that all of the individual solutions will fall on a straight line. Thus, it was necessary first to plot the points on graph paper and then to interpolate a straight line between these points to represent the average.

A blank was run along with each series of standards and its transmittancy was plotted as having a concentration of zero.. One or more blanks were also included with each group of samples and if the transmittancy reading varied from that plotted on the standard graph, an adjustment was made. This was done by drawing a line parallel to the straight line representing the

Fig. 4. STANDARD CURVES



standard curve and having it intersect the line of zero concentration at the reading for the new blank. By use of this new curve, the concentration of each of the samples of the group could be determined from its transmittancy reading.

Sample Concentrations. After the lead, zinc, and manganese concentrations of all 48 samples were derived in this way, the data was put in table form (see Table II).

From this data were also drawn curves showing the relationships between the distance of the samples from the vein and the concentrations in ppm. This was done on semi-log paper with the distances being in logarithmic functions and the concentrations in linear functions. Each traverse is shown on a separate graph and has the concentrations of the three elements plotted on it.

Interpretation of the Results

Lead and Zinc. The background concentrations for lead and zinc appear to be zero. If this is so, then either lead and zinc were not present in the limestone before mineralization or leaching has since removed them. As the metals introduced by the veins are still present, the former seems more likely.

The introduction of metals from the main bodies of ore solutions has left genetic halos, or anomalies, surrounding the veins and standing out well above the zero background concentration. Each anomaly tends to decrease quite rapidly away from the vein.

TABLE II

METAL CONCENTRATIONS OF SAMPLES

Traverse A				Traverse B				Traverse C			
	Elements (ppm)				Elements (ppm)				Elements (ppm)		
Sample No.	Pb	Zn	Mn	Sample No.	Pb	Zn	Mn	Sample No.	Pb	Zn	Mn
1	51	100	1.8	1	19	42	1.8	1	16	53	5.3
2	50	99	2.2	2	12	38	1.0	2	16	53	1.3
3	60	99	1.4	3	18	40	0.9	3	19	42	1.6
4	60	96	2.0	4	20	32	0.8	4	20	25	5.7
5	58	88	2.6	5	8	30	1.5	5	14	24	3.9
6	54	88	4.0	6	4	22	1.9	6	7	8	3.7
7	54	57	1.6	7	6	20	2.3	7	7	30	2.0
8	18	57	2.8	8	1	8	1.0	8	10	28	1.7
9	10	42	1.6	9	0	9	1.2	9	4	28	3.7
10	6	49	1.8	10	0	10	2.2	10	3	34	4.5
11	0	28	2.3	11	1	11	0.9	11	0	28	0.7
12	12	23	2.0	12	3	19	1.9	12	2	28	0.6
13	14	16	1.1	13	0	4	2.4	13	5	30	0.6
14	0	15	2.8	14	0	18	0.4	14	2	21	1.3
15	0	0	2.4	15	0	0	1.0	15	0	9	1.5
16	0	0	2.2	16	0	0	1.0	16	0	0	1.1

The extent of the penetration of zinc into the wallrock is greater than that of lead and indicates its greater mobility. If the maximum distance of penetration from the vein is considered to be half way between the last position in which it occurs and the first position in which the concentration reads zero, then the average penetration of zinc for the three traverses is 50 feet and the average for lead is 24 feet.

Besides being displaced further outward, zinc also occurs in greater amounts than lead. The average zinc content of the 48 samples is 33 ppm while that of lead is only 14 ppm. The lower mobility of lead probably had little or nothing to do with the lower concentrations found in the wallrock directly adjacent to the vein and so it appears that zinc occurred in greater amounts within the ore solutions. Contemporary solutions may have contained more zinc than lead or the relative amounts may have been about the same but with zinc being deposited over a greater interval of time.

The concentrations of lead and zinc found in a particular formation are influenced by that formation. The two traverses made on the 500 foot level (Lower Fredonia) showed lead and zinc concentrations to average 18 ppm and 40 ppm respectively, while the single traverse taken from the 700 foot level (St. Louis) showed the concentrations of the same metals to be only 6 ppm and 19 ppm.

The individual curves shown on the graphs differ slightly from each other and none are perfectly smooth but smooth curves are not to be expected. Each has high and low points which are out of place but these can be explained by unavoidable sampling and analytical errors alone. Many additional factors are involved, some of which are cited in the conclusions.

Manganese. The manganese occurring in the samples has a different origin. It was obviously not introduced by the veins because there are no noticeable increases in concentration near such points. Therefore, it must have been incorporated into the limestone at the time of deposition. The concentrations are usually low and the cause for this is not understood. It may be that these particular formations contain less than normal amounts of manganese. The chemical procedures seem to be satisfactory since the standard solutions responded as they should have.

The average manganese concentration for the 48 samples is 2 ppm. The average for the two traverses made on the 500 foot level is slightly higher, being 2.3 ppm as compared to 1.4 ppm for the traverse from the lower level.

Conclusions

The intrusion of ore solutions under pressure forced small amounts of the contained metals into the adjoining wallrock. This initial introduction resulted from the pressure gradient that existed between the unsaturated wallrock and the veins carrying the solutions. In all probability, this gradient was quite high at first but was soon greatly reduced or

Fig. 5. TRAVERSE A

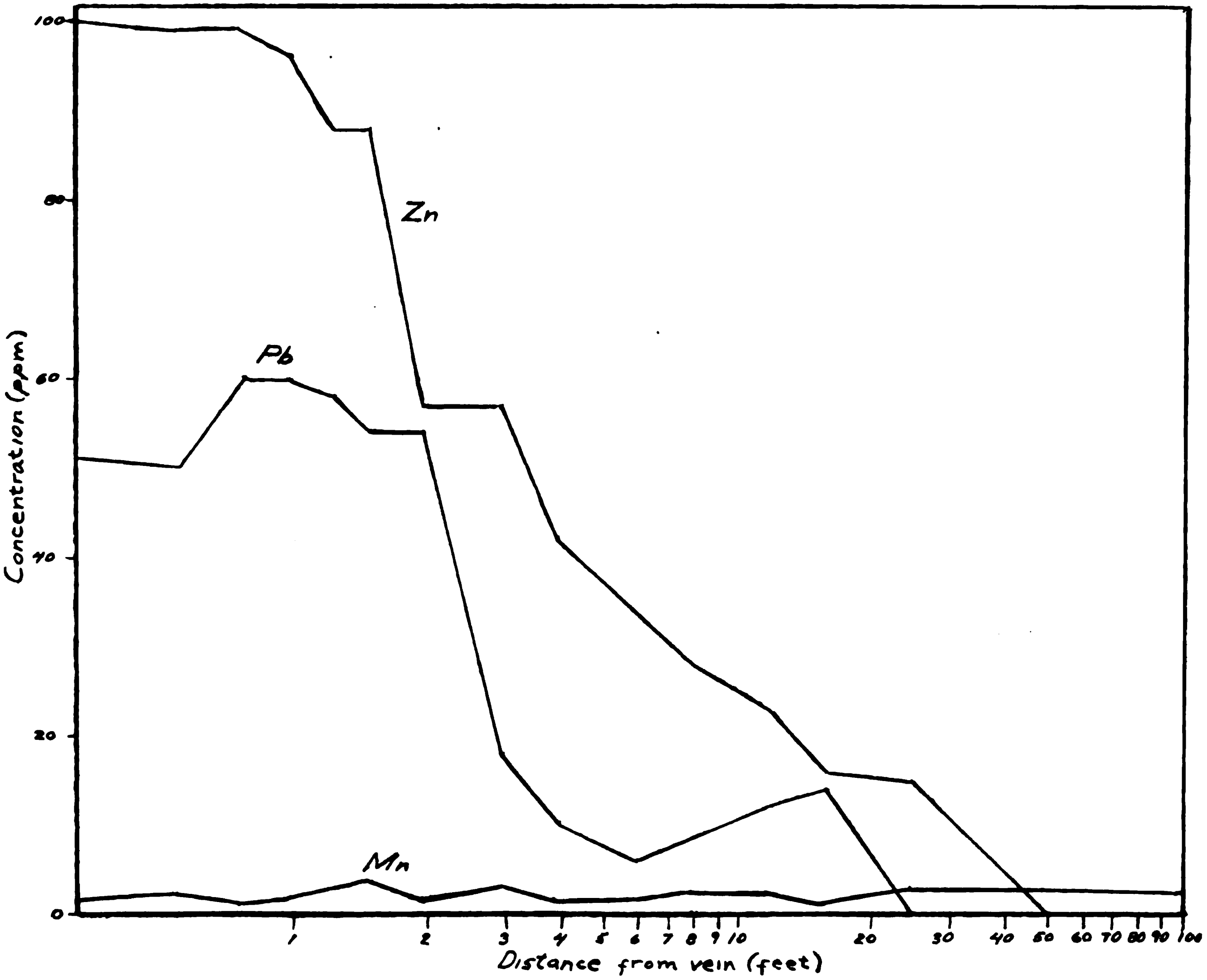


Fig. 6. TRAVERSE B

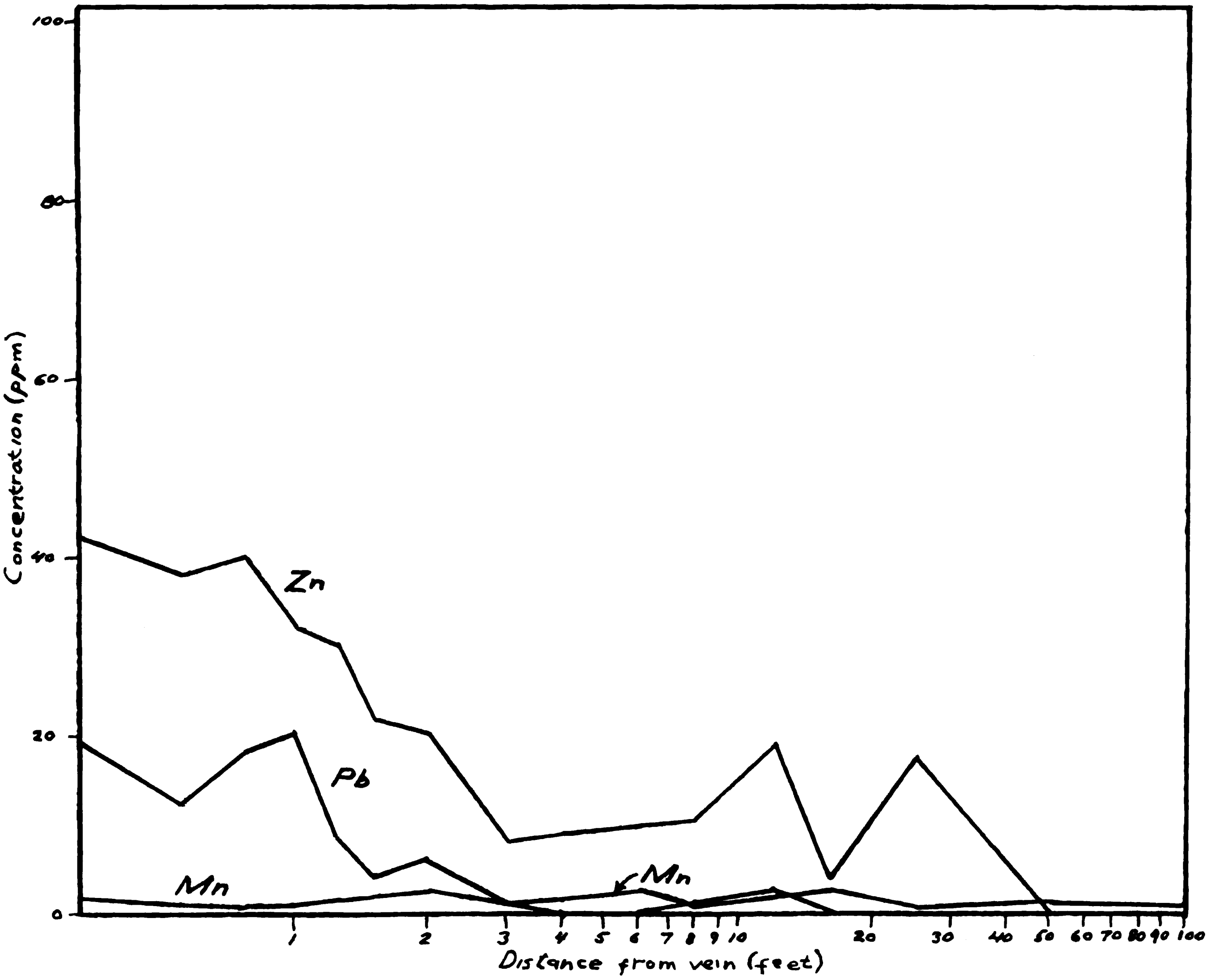
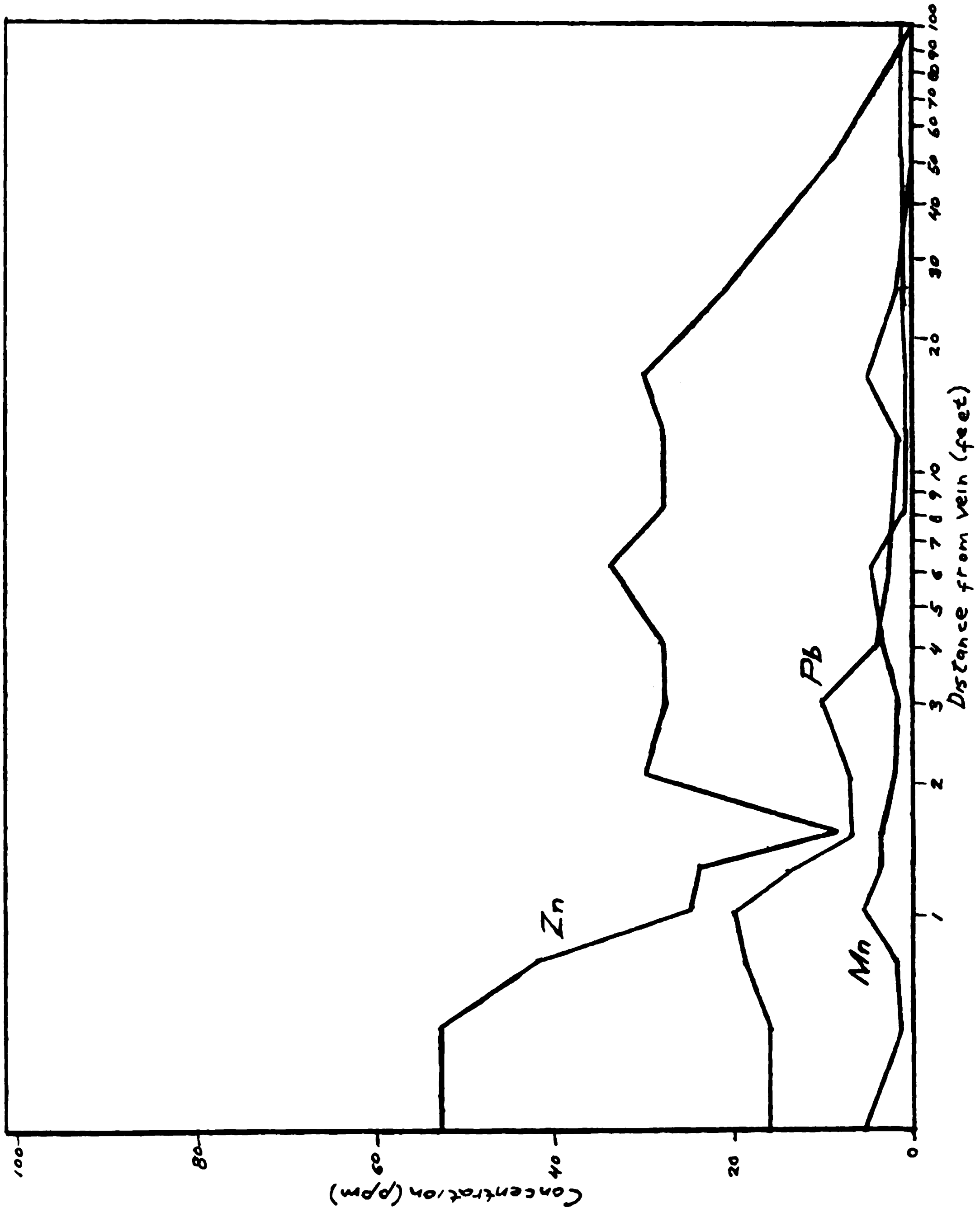


Fig. 7. TRAVERSE C



eliminated due to the almost immediate filling of the connected pore spaces.

The shallow depth to which metals penetrated the rock is shown by the dispersion curves and is strongly suggestive of limited circulation. Following this brief period of introduction of solutions in body, emplacement of metals was carried on by diffusion. This process was able to last as long as precipitation and chemical reaction within the wallrock renewed the concentration gradients.

It is probable that colloids provided the major means of metal transportation within the solutions. However, they were not able to move, in mass, to the final positions of deposition but, instead, remained in the larger channelways and served as stockpiles from which metal ions dissolved and diffused into the smaller openings. Evidence to support the above can only be gained from experiments under artificial conditions as the nature of colloids is such that the final deposit gives no clues as to whether or not they played a part.

The present distribution of metals in the wallrock very likely has been affected by secondary dispersion resulting from the dissolving of these elements by ground waters. Rock adjacent to the veins has high metal concentrations relative to rock farther away but these concentrations are very low when compared to the veins themselves. Weathering processes would tend to reduce this anomaly between the vein and the nearby wallrock with the result that the metal content of the wallrock would be increased and the anomaly would be extended to greater distances from the vein.

The greater mobility of zinc, plus the larger quantities present, resulted in zinc penetrating twice as far into the wallrock as lead. The host formation also affected the metal contents found as the more porous Lower Fredonia limestone contained, on the average, twice as much zinc and three times as much lead as did the St. Louis limestone.

Neither lead nor zinc appear in the composition of the unaltered formations but small quantities of manganese are present. The concentrations of manganese are relatively uniform throughout all the samples tested and no introduction of this element from the ore solutions can be detected.

It was mentioned earlier that irregularities in the dispersion curves are the rule rather than the exception. The irregularities are particularly obvious when dealing with metal concentrations as minute as are found here because the slightest increase or decrease shows up quite prominently.

The causes of such deviations are many. It was stated in the preceeding chapter that errors in sampling (especially as to the samples' proximity to tiny veinlets within the wallrock) and in the chemical analysis alone are sufficient to explain the irregularities. Other causes result from variations of the rock in porosity and permeability and include such factors as the size of pore spaces, interconnecting channels, adsorption, and chemical reactibility. Additional factors are the intensity of minor fracturing, the susceptibility to recrystallization, and the quantity of clay present which is affected by clay swelling.

In all probability, lead and zinc mineralization occurred over a period of time long enough to allow changes in the ore solutions. Thus, deposition within the wallrock may have varied along with variations in concentration, pH, and temperature of the solutions.

Applications

The use of geochemical trace element analysis as a prospecting tool is becoming increasingly more common and the results of this study support its value. In chosing a prospecting program, several things must be kept in mind. The indicator elements should be ones that can be easily analysed and the chemical methods used must be rapid and sensitive; high accuracy is generally not as important. Often it is more convenient to do the work in the field and so it is desirable that the equipment be portable.

The full value of this method of prospecting cannot be realized at Rosiclare because the faults are so well defined and so easily followed by the miners who drive the drifts. In other mineralized areas, however, ore bodies may be much more difficult to detect. Such a case is the Tintic District, Utah where "mine workings may pass within a few feet of an ore body without disclosing mineralized ground" (Morris and Lovering, 1952). In situations as this, regular sampling of drift walls at close intervals would serve to detect nearby ore. Another use might be to distinguish unmineralized fractures from feeding channels through which ore has passed to supply otherwise isolated ore shoots.

The presence of oxidized ore bodies are similarly detectible because of the anomaly set up in the surrounding rock by outward movement of the chemical products of oxidation. The use of ions of high mobility for indicators would achieve the best results.

The above refers only to possibilities of the application of geochemical techniques to underground prospecting and makes no mention of the opportunities of soil, water, and plant analysis. Discussions of the latter are to be found in many of the articles referred to in the bibliography.

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