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A Geochemical Study of Distribution of Elements in Ores and Limestones from New Jersey Zinc Mines, Hanover, New Mexico

Dasharatham Sayala

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MASTER OF SCIENCE

A GEOCHEMICAL STUDY OF DISTRIBUTION OF ELEMENTS IN ORES AND LIMESTONES

 $\overrightarrow{\mathrm{FROM}}$ NEW JERSEY ZINC MINES, HANOVER, NEW MEXICO

A GEOCHEMICAL STUDY OF DISTRIBUTION OF ELEMENTS IN ORES AND LIMESTONES FROM NEW JERSEY ZINC MINES, HANOVER, NEW MEXICO

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 BY

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THESIS

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in the Graduate School of The University of New Mexico Albuquerque, New Mexico May, 1972

BOOPS

A GEOCHEMICAL STUDY OF DISTRIBUTION OF ELEMENTS IN ORES AND LIMESTONES FROM NEW JERSEY ZINC MINES, HANOVER, NEW MEXICO

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BY Dasharatham Sayala

ABSTRACT OF THESIS

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ABSTRACT

Limestone samples (424) from both surface and subsurface horizons in the New Jersey Zinc mines at Hanover have been analyzed by atomic absorption spectrophotometry for Ag, Cd, Mn, Pb, Zn, Cu and Sn. The leadzinc ore bodies, occurring in Paleozoic limestones are a typical example of hydrothermal deposits; and are related to the Hanover intrusive.

The distribution of trace elements in surface limestones was mainly due to primary dispersion, partly due to secondary dispersion. The depth of ore mineralization, concentration of elements in ore solutions, porosity of limestones, diffusion coefficients of elements, and the chemical nature of elements in the carbonate and secondary leaching environments were responsible for the concentration of trace elements in the present surface limestones. The anomalous concentrations of elements are located on the northern and southern sides of the mines. The surface anomalies of Pb, Mn, Sn, Cu and Zn (to some extent) are most reliable indicators 0£ lead-zinc deposits below.

The lead-zinc ore bodies were concentrated mostly in either the northern or southern half of the mines. The ore solutions were high in Mn and low in Ag, Cd, and Sn. Most of the Cu was deposited as chalcopyrite in early stages, and very little was associated with lead-zinc ores. The ratios between Zn and either Cd, Mn, or Cu suggest three possible types of zinc mineralization. A lateral and vertical zoning of elements (far from a per£ect zoning) exists in the area.

Distribution of Zn/Pb ratios, Zn/Cd ratios, high concentration of

Xl

Cu in the ores of the southern side of the mines, and high zinc ores away from the Hanover intrusive indicate a second source of mineralization on the southern side of the mines (possibly related to the Santa Rita Stock - southeastern part of the mines). The hydrothermal ore solutions from the Hanover intrusive side have deposited ores at shallower depths than the ore solutions from the southern side (away from the Hanover intrusive).

Several factors besides the two sources of mineralization are considered to explain the lack of a perfect zoning and the variations in the concentration and distribution of ores and related elements in subsurface limestones.

The spread of high and low lead-zinc ores in the subsurface limestones indicates seven main channels of ore solutions. Four of these are located near the Hanover intrusive, and two are located away from the intrusive. The last one, deeper than the others, is located in the central part of the mines. The compositional mixing of ore solutions from these channels at different depths is evidenced in the area.

The distribution patterns (isograds) of ores and trace elements (in surface and subsurface limestones) indicate two major fracture systems, one trending northeast and the other northwest.

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INTRODUCTION

Theoretical Background

Hydrothermal deposition of ore and associated elements may result from decrease of temperatures and pressures, direct chemical reaction between elements and wall rock, and neutralization of solution by reaction with wall rock resulting in precipitation of elements. The substitution of elements in the lattices of wall rock minerals should be greater in deep-seated magmatic segregations, pegmatites and hydrothermal deposits where heat and pressure are high, and in altered rocks containing layered minerals with high absorption and base exchange capacity. At high tempera tures and pressures, the lattice disorders in minerals are high and likewise the substitution of elements in them is also expected to be high.

Ore bodies are largely localized along linear or planar structural elements such as faults, unconformities, joint intersections, fractures and margins of intrusives. Similarly the "halo" of associated elements around an ore body may vary with the distribution of structural elements.

Elements which are deposited at high temperatures and under a heavy overburden may be expected to form a uniform aureole of limited extent, while the elements in an epithermal environment are widely distributed along the fractures and fissures. The element content of limestones is therefore related not only to distance from the ore body and intensity of chemical reaction, but also to the nature and amount of

fractures and fissures.

Rose (1967) has divided chalcopyrite from Central district, New Mexico, into four groups, based on geographic location, geology, and trace elements. The chalcopyrite of the New Jersey Zinc mines is included in group IV which is characterised by low contents of both tin and indium as compared to the other groups. All these groups of chalcopyrite mineralization were inferred to be due to a variety of reasons, such as preferential deposition, chemical effects on the ore fluids during transport, differences in temperatures and pressures, wall rock composition, etc. The differences of some of the groups were also expected to arise at the source, and it was thought that the groups might have resulted from separate surges of ore fluids originating either from the same source at different times (perhaps under different conditions) or from different sources with varied composi tions.

Kutina (1963) has used the terms "polyascendant" to describe the origin of minerals arising from more than one dose (surge) of ore solutions ascending at separated periods and "monoascendant" to describe the minerals' origin from one dose of ascending ore solutions. Similarly, Smirnov postulated "Pulsation Theory" (1937, referred to by Kutina, 1963) for different surges of ore solutions arising from one source. The study of trace elements in minerals is believed to disclose empirically the difference between the ore deposits formed by polyascendant and monoascendant ore solutions.

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Such study of the behavior of trace elements in bed rocks to see whether it leads to the same conclusions has not been attempted. The reasons for not attempting such study in bed rocks are perhaps due to nonavailability of drill hole samples, large time consumption in the study, lack of interest, and other unknown factors. However, it is expected that the behavior and dispersion of trace elements in the wall rocks due to monoascendant ore solutions would be different from that of trace elements due to polyascendant solutions. This is considered to be very important in understanding the nature of ore solutions and their behavior during ore deposition. Therefore, such an examination is included in the present work.

Within the sulfide minerals of each group of Central district, Rose (1967 has also indicated certain variation of trace elements. Burnham's study (1959) on metallogenic provinces of the southwestern United States and northern Mexico has indicated that the variations of trace element content within each mining district were generally smaller than the variations between the districts. Schmitt (1939) found two generations of sulfide minerals in the New Jersey Zinc mines, which might suggest two different sources and ages of hydrothermal ore solutions.

However, some of the above features were not studied in great detail within a single mining area such as New Jersey Zinc mines, though they are very important not only in understanding the nature of ore solutions but also in exploration.

The direction of the movement of ore solutions will leave an

imprint, typical of the composition of those solutions in the wall rocks. The imprints (primary dispersions) left by hydrothermal solutions on the channelways through which they pass can be extremely useful guides. It may be feasible to find and identify these channelways by chemical analyses for certain diagnostic trace elements, which were associated with ore and were precipitated from the ore solutions. In this way, it may be possible to restrict the number of directions in which a search is made for the ore.

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Purpose of Study

The main objective of this study was to investigate the nature of dispersion of elements in both surface and subsurface limestones with reference to the location of ore bodies of a single mining area in view of the previously mentioned explanations. Since the elements have a tendency to be dispersed and deposited in the wall rock due to variations in physicochemical conditions during transporation, certain correlations between dispersion of elements and other geological features, such as location and concentration gradients of ore, metamorphic aureoles, skarn zones, igneous intrusives, and depth were expected. From the nature of dispersion patterns of ores and their associated trace elements, flow patterns of hydrothermal ore solutions at different depths were also expected. The patterns of cadmium-zinc and lead-zinc ratios were also studied in order to establish the compositional variation of hydrothermal ore solutions that was expected from the previous studies (Schmitt, 1935; Rose, 1967; Burnham, 1959). Since fractures and fissures are good channels for the migration of ore solutions, the study was therefore designed to draw certain inferences about the fracture system at depth.

The present study included sampling, from both surface and subsurface limestones, preparation and analysis of the samples, plotting of the data, and finally, interpretation of the data.

Choice of Elements

The study of distribution of elements in bed rocks and ores is an empirical approach in determining their behavior in hydrothermal ore solutions during migration and deposition in the host rocks. The kind of elements under study should be related to the ore bodies and should be originally present in the ore-bearing hydrothermal solutions. For the present study, silver, cadmium, manganese, lead, zinc, copper, and tin were chosen for the follow ing reasons:

1) Since lead-zinc ores were under consideration here, it would be ideal and useful to study the distribution of lead-zinc in limestones. This would give direct gradational variation in the spread of lead-zinc from barren areas to the ore zones.

2) From the work of Rose (1967), it is known that silver, cadmium, manganese, lead, and tin are present in variable concentrations in sulfide minerals such as sphalerite and chalcopyrite (Table 4). This indicates that these elements were originally present in hydrothermal ore solutions and would be dispersed in the bed rocks along the channels through which the solutions migrated before ore deposition.

3) Elements under consideration are sensitive to changes of temperature and chemical conditions during the flow of hydrothermal ore solutions in the carbonate environment (Goldschmidt, 1958), and may have had selective dispersions in the limestones.

4) Graf and Kerr's study (1950) of trace elements in limestones

of the Hanover mining district has indicated that manganese, lead, copper, and silver have fluctuated significantly in their distribution in limestones, particularly with reference to the ore bodies, silicate skarns, and intrusive stock. It would thus be interesting to pursue their behavior in limestones of varied depths.

5) Since the above elements are found associated with lead-zinc minerals (Rose, 1967) of the district, it is inferred that these elements were deposited contemporaneously with the ore deposits. Therefore, the dispersion of such elements would be directly related to the ore bodies, and their study in limestones should be of great help in knowing not only the nature of hydrothermal ore solutions, but also in locating the ore bodies in the area.

6) The element compounds and their traces must be resistant to dilute acids, so that ground water will neither dissolve nor enrich them. Sokoloff (1948) stated that compounds of tin and lead are desirable for exploration studies in bed rock because of their low solubility. Hawkes and Webb (1962) likewise indicated low solubility of lead, silver, manganese, and tin, in natural groundwater environments. The original dispersion patterns of these elements will hence be mostly preserved in the limestones. Thus the study of Pb, Mn, Ag, and Sn will be very reliable in disclosing the nature of the primary dispersion patterns in limestones of the New Jersey Zinc mines.

7) Silver, copper, zinc, cadmium, manganese, and lead are

chalcophile elements. Their strong affinity for sulfur would tend to enrich them in the limestones from the sulfide-bearing hydrothermal solutions which have deposited the lead-zinc sulfides. The characteristic dispersive patterns of above mentioned elements which appear in the carbonate rocks during the migration of hydrothermal solutions, would be helpful in delineating the migration channels of the ore solutions and the possible targets for exploration of lead-zinc deposits.

8) Early magmatic sphalerites that are formed at high temperatures show relatively low concentrations of cadmium, and sphalerites that are formed at relatively low temperatures contain large proportions of cadmium (Goldschmidt, 1958). This variation of cadmium in both bed rocks and ores should indicate the different sphalerites and hence different times and temperatures of formation of ore deposits. The ratios of cadmium to zinc in ores and bed rock might also give clues as to the source of ore solutions.

9) The affinity of zinc and cadmium for sulfur is low and cadmium is a more substantial constituent of zinc sulfides (Goldschmidt, 1958). Therefore, the study of cadmium in zinc ores may give valuable information about the composition of ore solutions.

10) Low manganese content in sphalerites is inferred to be due to low and intermediate temperatures of formation of zinc ores (Goldschmidt, 1954). Highest manganese concentration is found incorporated in sphalerites formed at elevated temperatures (Oftedal, 1940, referred to by Goldschmidt, 1958). Accordingly, a different dispersive pattern of manganese is expected in the bed rocks at different depths.

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The manganese sulfides alabandite (α MnS) and laverite (MnS₂) are generally the constituents of metamorphic and sedimentary rocks (usually found in the crystal structures) due to the hydrothermal solutions (Goldschmidt, 1954). Furthermore the manganese sulfides are more readily soluble than the other elements in hydrothermal solutions and therefore, manganese is a highly mobile element. Under these conditions manganese is expected to disperse extensively in metamorphic aureoles and sedimentary rocks which are altered by the hydrothermal ore solutions. The manganese dispersion patterns in these rocks therefore indicate the migration and the volume of ore solutions during the course of deposition and also delineate the targets for exploration. In a sulfur environment (in hydrothermal solutions), manganese will not become separated as sulfide in noteworthy quantities, in spite of its high affinity for sulfur, but instead it is found in the crystal structure of either rock-forming minerals ore ore minerals (Ott, 1936, referred to by Goldschmidt, 1958). In such cases manganese should tend to concentrate not only in the ore horizons, but also in the bed rocks affected by hydrothermal ore solutions.

11) Tin as an oxide is strongly concentrated in the late sulfides during magmatic differentiation, i.e., during the pneumatolytic and hydrothermal processes (Hamaguchi and Kuroda, 1968). Thus its variation of concentrations in sulfide ores would be useful in distinguishing early sulfides from late sulfides. Tin occurs in many sulfides (ores) in the form of tin sulfides or is incorporated with a number of other metals in more complex sulfides (Hamaguchi and Kuroda, 1968). Stannite (Cu₂FeSnS₄) is found

associated principally with chalcopyrite, sphalerite, tetrahedrite, pyrite, and quartz (Hamaguchi and Kuroda, 1968). Therefore, the concentration of tin in sulfide ores and in skarns containing pyrite and chalcopyrite should be high. Away from these areas the concentration should decrease. This type of gradational pattern would be very useful in studying the behavior of hydrothermal ore solutions and hence would be indispensible in the exploration of lead-zinc deposits.

12) The ionic radii of $Mn^{2+}(0.80 \text{ A}^2)$, $Zn^{2+}(0.74 \text{ A})$, and $Cu^{2+}(0.72 \text{ A})$ are close to each other and to the radii of ${Mg}^{2+}$ (0.66 A), Fe²⁺ (0.74 A), and Fe^{3+} (0.64 A). Therefore, they are expected to replace each other and are expected to be found occurring in bed rocks that are affected by the migration of hydrothermal ore solutions.

Location and Regional Setting

The New Jersey Zinc minining area at Hanover, New Mexico is located about 12 miles northeast of Silver City and about 2 1/2 miles northwest of the world famous Santa Rita open pit copper mine. Regional structure of the area places this area at the northern rim of the Sonoran geosyncline near the southeastern margin of the Colorado Plateau (Fig. 1). The geological map of the Santa Rita quadrangle, New Mexico (Hernon, Jones, and Moore, 1965) shows that it lies within the prominent east-northeast-trending belt which is characterized by abrupt changes in the regional strike of the rocks, structural disturbances, and prominent igneous intrusions.

The region is underlain by sediments of Paleozoic and Mesozoic age, which were affected by intrusions of Late Cretaceous and early Tertiary age. The New Jersey Zinc mines are located south and southwest of the Hanover intrusive, and all mines are within zones of various alteration phenomena such as dolomitization, marmarization, bleaching, and sericitization, adjoining the intrusive (Fig. 2A, B).

EXPLANATION

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 $(For Fig. 2A, B)$

History of the Mines

The New Jersey Zinc mines at Hanover have been working since 1902. An estimated 500,000 tons of sphalerite ore, having an average content of 8-15% zinc, was produced from 1902 to 1935. In addition to zinc sulfide, considerable amounts of high-grade zinc carbonate ore and galena ore were also produced, mostly prior to 1918. The recent production statistics are not available and currently the mines are not under production and are under new ownership.

Geological work in the Hanover area and in adjacent mining areas has been carried out by many investigators since 1927. Schmitt (1927, 1935) did one of the pioneering works in geological mapping, structure, metamorphism, and mineralogical studies over the area. Park (1927) and Rove (1930) have also mapped the district in the interest of mining operations. Likewise Spencer and Paige (1935), Horton (1953) and Jones, Hernon and Pratt (1961) have also made detailed geological studies on structure, ore deposits, petrology, mineralogy, etc. None of the above studies has ever concentrated on geochemical work in the mining district.

However, in 1950, Graf and Kerr made a trace-elements study of the rocks of Santa Rita and Hanover mining areas with an interest in studying the variation of trace elements between the two areas. Belt (1960) has made a detailed study of hydrothermal alteration and copper and zinc variation in the Hanover-Fierro intrusive in order to establish a relationship between the origin of ore deposits and the intrusive. He

concluded that ore deposits have originated from great depth and intruded the host rocks after solidification of the Hanover-Fierro intrusive; hence ore deposits are not genetically related to the intrusive.

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The field work was made possible by the New Jersey Zinc Company, and in particular its staff at the mines at Hanover, whose kind cooperation the author acknowledges with thanks.

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FIELD AND LABORATORY METHODS

Field Methods

In the New Jersey Zinc mines, Mississippian and Pennsylvanian limestones, both surface and subsurface horizons were sampled at different intervals depending upon the accessibility of outcrops. In surface horizons, unaltered samples were collected from 16 traverses. The traverses ran in the direction of S 78[°]E, covering the area south and southwest of the Hanover Intrusive. The location of the samples in the traverses are plotted in Figure 2. Subsurface samples from drill cores were collected at different depth intervals, depending upon the location of ore horizons and the availability of samples. The locations of these drill holes are also shown in Figure 2.

Laboratory Methods

The laboratory work was comprised of the following:

1). Megascopic examination of the samples: Samples under consideration were examined under the binocular microscope for discrete grains of leadzinc ores and significant characters such as calcification, grain size, fractures, presence of pyrite and chalcopyrite, marmarization, alterations, skarns, and other features.

2). Sample preparation is considered under two steps: (a) Crushing and sieving and, (b) Dissolution of sample.

> (a) Crushing and Sieving: The samples were prepared for analysis as follows:

i) The sample was broken into small chips by

steel mortar and pestle.

ii) A small portion of the chips was crushed by the Bruan Pulverizer, type U.A. (with clean ceramic discs), and the powder discarded. This set up the background on the discs for that sample and thus the contamination from a different sample was avoided. The remainder of the broken chips were then crushed and powdered. Particular care was taken to brush and air-clean the pulverizing ceramic plates, the pulverizing machine, and the sample collector before using it for the next sample.

iii) The powder thus collected was sieved through 100 mesh nylon and the sieved powder was collected in 10dram vials.

(b) Dissolution of sample: One gram of the sample powder was weighed and transferred into a 250 ml teflon beaker and the weighing paper was rinsed with 1% HNO₃ into the same beaker slowly with the cover-glass in place, so that splashing out of the sample by brisk effervescence was avoided. The solution was then heated (at hot plate temperature of about 300 $^{\circ}$ C) for about half an hour with the cover-glass on the beaker. In some cases, where 50% HNO₃ was not effective in dissolution of the sample, 5 ml of reagent hydrofluoric acid was added in addition to the 25 ml of 50% HNO₃ and the beaker was heated for half an hour. The solution was cooled to room temperature and the cover-glass was cleaned thoroughly and rinsed with 1% HNO₃. The cooled solution was filtered into 100 ml flask. The residue occasionally left on the filter paper was also rinsed 3 to 4 times with 1% HNO₃. This residue was dried and spectrographically analyzed to make sure that none of the elements under consideration remained in the residue. Only a few random residue samples were considered for this purpose and the rest discarded. Table 1 shows that none of the elements under consideration were present in the residue. The filtered solution in the flask was diluted up to the 100 ml mark by adding deionized water, and the flask was stoppered and kept ready for analysis.

3. Sample analysis:

a. Standard solutions of Ag, Cd, Mn, Pb, Zn, Cu, and Sn were prepared, taking the working solution concentration of 10 ppm, 1 ppm, 100 ppm, 10 ppm, 50 ppm, 10 ppm and 100 ppm, respectively. Five different standard solutions of each element, starting from zero concentration, were prepared, by diluting appropriate volumes of the working solution to 100 ml in volumetric flasks (Table 2). To each of the five flasks, 25 ml of 50% HNO₃ was added and shaken thoroughly in order to compensate for any interference of 50% HNO₃ originally added in the dissolution of the samples. An example of such combination of standard solutions is shown in the Table $2.$

b. Both the standard and the unknown sample solutions were analyzed on the Perkin Elmer Model 303 atomic absorption spectrometer under
the specified conditions for each of the seven elements (Perkin-Elmer's Anal. Meth. for AA., 1968).

c. The percent absorption or absorbence readings of each element in an unknown sample were noted from the recorder and the concentration of that element was calculated from the standard working curve for that element by directly reading the concentration (ppm) corresponding to the reading of an element in an unknown sample.

d. The concentration of an element in an unknown thus calculated from the standard working curve was adjusted for its concentration in 1 gm of sample dissolved in 100 ml of the solution. The following example outlines the calculations:

4. Ore and heavy mineral separation: Five representative samples from 5 drill holes, which have shown high concentration of lead-zinc and trace elements, were considered for this work.

Three grams of powdered sample were transferred into the funnel (with release rubber tubing at one end) containing 40 ml of diiodomethane (sp. gr. 3.325) while stirring constantly. Through intermittent stirring for a period of two hours, all the heavy minerals including ore grains sank. Then the heavier fraction was released through the rubber tubing over a funnel with a filter paper. Care was taken not to mix any floating lighter fraction with the heavies. This procedure was repeated with the heavies that were collected on the filter paper in order to eliminate any lighter fraction trapped in the heavy fraction.

The lighter fraction separated by filtration from the diiodomethane was heated for about an hour under the hood until all the traces of diiodomethane was evaporated. One gram of this dried lighter fraction was taken in a beaker and was dissolved with 25 ml of 50% HNO₃ and by heating for about half an hour (at hot-plate temperature of 250° C). The solution was cooled and filtered into a 100 ml volumetric flask. The flask was filled with deionized water to the 100 ml mark and kept ready for analysis of elements mentioned earlier.

Reproducibility of Analyses

Five random samples were selected in the calculation of reproducibility of analyses by atomic absorption spectrometry. For a statistical evaluation, samples were repeated either 3 or 4 times and the

standard deviation as a measure of precision of the analyses was computed. The reproducibilities of the analyses are given in Table 3 . The reproducibility of silver and cadmium is low, when the element concentration is either 1 ppm or less, and is high when the element concentration is above 1 ppm in a sample (Table 3). The reproducibility of Mn, Pb, Zn, Cu, and Sn is relatively high. In general it was found that the higher the concentration of an element in a sample, the greater the standard deviation, thus eliminating the need for scale expansion of the instrument. The 95% confidence limits were also calculated and are given in Table 3.

Table 1. Spectrographic analysis of sample residue

 Bb_8 Traverse B, black color (b) and 8, number of the sample

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Presence of an element

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Table 2 An example of standard solutions

Explanation: (Ag standard - $\underline{1}$)

10 ml -- volume of working standard solution taken in 100 ml flask.

1 ppm -- concentration of above 10 ml of working standard solution diluted to 100 ml.

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Table 3. Reproducibility of Atomic Absorption Spectrometric analysis

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Table 3. (continued)

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GEOLOGICAL SETTING

The stratigraphy of the Hanover and the adjacent Pewabic mining areas consist of sedimentary rocks of middle and upper Paleozoic age and igneous rocks ranging in age from Upper Cretaceous to Lower Tertiary. According to Paige (1935), Lasky (1936), and Schmitt (1935), the following nomenclature follows:

SEDIMENTARY ROCKS:

IGNEOUS ROCKS:

Sedimentary Rocks

The rocks of Paleozoic age are predominantly limestones with some shales and sandstones. These rocks represent 1,093 feet of the total Central mining district's succession of 5,000 feet.

The Fusselman Limestone is Silurian in age and contains the Silurian corals Halysites catenulatus, Favosites niagarensis, and Pentamerus sp. It is a fine-grained, massive-bedded dolomitic limestone. separated from the overlying Percha Shale by a disconformity. The lower part of the Percha Shale is black and fissile, and is Upper Devonian. The upper 100 feet, usually mapped with lower Percha Shale, is marked by thin fossiliferous and nodular limestone beds which increase in abundance and thickness upward until they form the massive Lower Blue Limestone horizon. According to Kindle (in Paige, 1916), the fossils in this zone are Late Devonian.

The Lower Blue Limestone is moderately thick bedded, shaly, dull gray and magnesian in character, (Schmitt, 1939). Thin shale beds occur in the upper three-quarters of the formation and a minor amount of gray chert. is conspicuous near the top. The lower quarter (42 feet) of the formation contains very few impurities and is recrystallized to white marble near the massive intrusives, where it has also been replaced by small lead-zinc ore bodies.

The Hanover or Crinoidal Limestone, where unmetamorphosed, is massive, coarse-grained, white to grayish white and magnesian, and is composed largely of crinoid stems. Chert which occurs most often in

lenses, is a readily seen impurity. The Hanover Limestone is more susceptible to replacement than the other limestones and is a good host rock containing large zinc ore bodies. The lower contact is marked by a change downward from a white calcitoid material to fine, dull-gray chert. No shaly impurities have been observed in this limestone.

The Parting Shale rests disconformably on the Hanover Limestone. and the contact locally is marked by a thin conglomerate, which in places is mainly white chert, derived from the underlying Hanover Limestone (Schmitt, 1935). Some beds within the Parting Shale formation contain fine grained sandstone, which is metamorphosed to quartzite near the main intrusive. The Parting Shale nowhere contains important quantities of zinc ores.

The Middle Blue Limestone is purer than the Lower Blue Limestone, but nevertheless closely resembles it. The lower half of it is fossiliferous and approaches the Hanover Limestone in purity and appearance. The upper half is dull gray because of shaly impurities and contains minor amounts of shaly layers and gray chert. The Middle Blue Limestone also contains a large proportion of the lead-zinc ore in the Pewabic mine (located northeast of the New Jersey Zinc mines) and which includes low grade lead-zinc ore bodies in the New Jersey Zinc mining area.

Overlying the Middle Blue Limestone and separated from it by the Hanover Sill is the Upper Blue Limestone. The Upper Blue Limestone is also dull gray on account of minor shaly impurities, and is massive bedded and non-

magnesian. About 60 feet above the 10-foot black chert, it characteristically contains Chaetetes sp. (Schmitt, 1939).

Most of the sedimentary rocks in the general area have been subjected to contact metamorphism by Cretaceous-Tertiary intrusives. The metamorphism in the Paleozoic limestones has yielded suitable sites for the migration and deposition of lead-zinc ores.

KIND OF BUILDING

CONTRACTOR

Igneous Rocks

The igneous rocks within the Hanover mines and in adjacent Pewabic mines are of different varieties. Schmitt (1939) classified them into three categories:

- 1. Early (pre-ore) diorite porphyry sills, laccoliths, and sheets.
- 2. Later (contemporary to ore) granodiorite quartz monzonite porphyry.
- 3. Late (post-ore) or Tertiary, stocks and dikes (dacite to quartz latite).

1. Quartz diorite porphyry

Quart diorite porphyry occurs mostly as sills. The rock is medium gray and is fine to moderately coarse-grained. It occurs parallel to the strata of Percha Shale. The porphyry contains phenocrysts of plagioclase, hornblende, and quartz, in a fine-grained groundmass which is composed essentially of the same minerals and biotite. Thin sections examined under the microscope show albite and oligoclase only among the plagioclase. The feldspar occurs both as phenocrysts, 3 to 5 mm long, and as small laths that form a trachytic groundmass. Biotite occurs as minute crystals in the form of aggregates with oval cross-sections. Quartz occurs as a minor constituent of the groundmass (Spencer and Paige, 1935). Granodiorite-quartz monzonite porphyry

This intrusive mass in Hanover Basin is called the Hanover Intrusive or Hanover-Fierro Stock. It is the largest intrusive body of the district,

with dimensions of 2 3/4 miles in length from north to south and 1/2 to 1 mile in width. The walls of the intrusive are almost even, and are nearly vertical with respect to the exposed sedimentary formations. The stratigraphic evidence indicates that the intrusion of this pluton occurred at a depth that did not exceed 8, 500 feet (Schmitt, 1939, p. 815). According to Belt (1960), the Hanover-Fierro intrusive has an equigranular to porphyritic texture. The different facies can be distinquished on the basis of textural evidence and field relations. These facies are: 1) an equigranular facies, 2) a porphyry facies, and 3) an aplitic facies. The equigranular facies is a medium-grained tonalite composed predominantly of twinned and zoned hypidiomorphic andesine with idiomorphic hornblende and pseudo-hexagonal books of biotite. Late crystallizing quartz and orthoclase are interstitial to plagioclase and ferromagnesian minerals. Accessory minerals include magnetite, sphene, apatite, and zircon. The equigranular facies occurs almost entirely in the southern lobe of the intrusive and spreads northward along the east and west intrusive contacts.

The porphyry facies ranges in composition from a fine-grained tonalite to a calc-alkalic granite. The minerals of this facies are similar to those of the equigranular facies in shape and optical properties. The porphyry facies encompasses most of the intrusive. The aplitic facies is composed predominantly of orthoclase and quartz and occurs as dikes cutting the other facies.

The copper distribution in the Hanover-Fierro intrusive ranges from 4 to 637 ppm; the southern lobe, near the Hanover mines, contains from 34 to 235 ppm copper (Belt, 1960). From the noncorrelative studies between copper distribution and both weight percentage of groundmass and orthoclase-plagioclase ratios, it is concluded that the copper mineralization in the area is not genetically connected to the intrusive. The zinc content of the intrusive ranges from 12 to 273 ppm. Highest values are found in the southeastern lobe of the intrusive. Zinc, like copper, is related to neither primary nor secondary features of the Hanover intrusive (Belt, 1960)

Tertiary stocks and dikes

The numerous post-lava Tertiary stocks and dikes are located within and near the New Jersey Zinc mines. Within the area, there are two such igneous masses:

1. The Bull Hill intrusive, which lies south of the New Jersey Zinc mines.

2. Irregular intrusive masses (dacite to quartz latite) near the southeast corner of the Hanover intrusive.

The Tertiary intrusives approximate the fine-grained equivalent of granodiorite. Megascopic examination of these shows phenocrysts of plagioclase, quartz, orthoclase, and, sometimes, sanidine in a felsic, hyalophitic groundmass (Spencer and Paige, 1935). Small amounts of pyroxenes, hornblende, or biotite, and sometimes zircon are also present. The groundmass is usually an intimate mixture of quartz or tridymite with

potash feldspar or plagioclase. At most places, the late dikes carry well developed chilled selvages, whereas the earlier dikes show these features at only a few places. These dikes are characteristically found cutting many granodiorite dikes and are, therefore, later than the granodiorite.

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Structure

The New Jersey Zinc mines are located on the south and southwest side of the Hanover intrusive (Fig. 2). The major folding and faulting in the area is mainly due to various intrusives. Deformation due to lateral pressures by the granodiorite stock has resulted in folding of the Carboniferous limestones, creating a tight overturned syncline adjacent to the intrusive and an open upright asymmetrical anticline beyond (Horton, 1953). Thrust faulting in connection with lateral forces is also evident in the district. In the deformed area, the Crinoidal Limestone varies in thickness from 25 to 300 feet, due to folding, thrusting, and plastic flowage of the rock (Horton, 1953). Diamond drilling and development in the New Jersey Zinc mines have suggested an overthrust fault, occurring chiefly in the Hanover Limestone (Schmitt, 1939). This thrust fault was also evidenced at several places in the adjacent Pewabic mines and in the Republic mines (east of the New Jersey Zinc mines) by a low-angle fault plane, which was filled with breccia and silicified gouge.

Subsequent to the thrust faulting, northeast-striking high-angle normal faulting occurred, with small slips. The normal faults are marked by important lead-zinc ore deposits. The normal faulting was probably regional in distribution and attitude as contrasted with the thrust faulting, which is known only locally and is related to the Hanover intrusive (Schmitt, 1939).

Several post-ore northwest-striking faults, with slips up to

15-20 feet, are also found in locality of the post-ore intrusives, which are found offsetting the ore bodies in many places, but have not greatly interfered with development and mining (Schmitt, 1939).

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MINERALOGY

The minerals of the New Jersey Zinc mines, as in adjacent mining areas, are the result of different intrusions. The minerals of one area closely resemble the minerals of the other adjacent mining areas, since the two areas have the same kind of sedimentary rocks and intrusives and have been subject to the same geological events. The minerals of the district may be broadly classified as: 1) sulfides, 2) oxides, 3) silicates, and 4) car bonates.

Sulfide Minerals 1.

2. Oxide Minerals

Hematite

Magnetite

Limonite

 $FeO(OH)$, nH₂O

Silicate Minerals 3.

Among the silicate minerals only the most common minerals are

listed.

Quartz

 $SiO₂$

ZnS

PbS

 $CuFeS₂$

 Fe _(1-x)S

 $FeS₂$

 $Fe₂O₃$

 $Fe₃O₄$

Sericite

 $KAI₃Si₃O₁₀(OH)₂$

Chlorite

Biotite

Actinolite

Serpentine

Augite

Hedenbergite

Salite

Zoisite

Piedmontite

Epidote

Ilvaite

Orthoclase

Labradorite

Andradite

Carbonate Minerals $4.$

> $CaCO₃$ Calcite Dolomite $CaMg(CO₃)₂$ Malachite $CuCO₃$, $Cu(OH)₂$ Smithsonite $ZnCO₃$ $MnCO₃$ Rhodochrosite

The sulfide minerals invariably occur in either limestone or its

 $K(Mg, Fe)$ ₃A1Si₃O₁₀(OH)₂ $Ca₂(Mg, Fe)₅Si₈O₂₂(OH)₂$ $Mg_3Si_2O_5(OH)_4$ $Ca(Mg, Fe, A1)(A1, Si)$ ₂O₆ $CaFe(SiO₃)$ $Ca(Mg, Fe)(SiO₃)₂$

 $(Mg, Fe)₅(A1, Fe¹¹¹)₂$
Si₃O₁₀(OH)₈

 $Ca₂A1₃(SiO₄)₃(OH)$ $Ca_2(A1, Mn)$ ₃(SiO₄)(OH)

 $Ca_2(A1, Fe)_3(SiO_4)_3(OH)$ $\text{CaFe}_2(\text{FeOH})(\text{SiO}_4)_2$

 $KAISi₃O₈$

 Ab_{30-50} An₅₀₋₇₀

 $Ca_3Fe_2(SiO_4)_3$

metamorphosed skarns. Among the sulfides, sphalerite is the most important ore mineral in terms of economic value, followed by galena and chalcopyrite.

Iron-oxide minerals, (magnetite, hematite, etc.) do not occur very widely in the area, and are secondary in economic importance. Usually, the magnetite and hematite are massive and fine-grained, except in a few cases where medium-grained and subhedral masses of grains are found. Much of the magnetite is pure enough to be iron ore, and, in fact, some iron ore was shipped in 1936 by the Empire Zinc Company from ore bodies in the andradite zones of this district (Schmitt, 1939). Hydrated oxides and carbonates of iron such as limonite, geothite, and siderite are widely seen in gossans and are exposed in many places of the district.

The silicate minerals found in the district are confined to igneous rocks and metamorphic aureoles in the contact zones of the limestones. In some places they are localized by faults and xenoliths of sedimentary rocks in igneous intrusives. The mineralogical constituents of skarn zones are andradite, pyrite, chalcopyrite, hedenbergite, ilvaite, salite, etc. Hedenbergite and ilvaite are most often associated with sphalerite and chalcopyrite in the metamorphic aureoles near the Hanover intrusive. Minerals, such as sericite, zoisite, and chlorite, are formed due to metamorphism by the igneous activity in the district.

ORE BODIES AND THEIR LOCALIZATION

The distribution and relationship of ore bodies at New Jersey Zinc and 4). As a result mines are shown on the composite plan in Figures 3 A, B, of sequential geological events (as mentioned earlier), a zonal distribution and deposition of minerals had taken place in the mining district. The area next to the intrusive is occupied by a skarn or tactite zone, and is followed by magnetite, hematite, and sulfide mineralization. The sulfides and the oxides have penetrated the silicates along the fractures and fissures to form an outer ore zone at the silicate-limestone contact (Schmitt, 1935).

The principal ore mineral in the New Jersey Zinc mines is sphalerite and it is associated with minor amounts of galena, chalcopyrite, pyrite, and in places with rhodochrosite. Zoning of these minerals is quite apparent in several stopes, for example, a narrow band of galena envelopes the outer perimeter of the zinc sulfide, and frequently a narrow band of rhodochrosite occurs between the galena and the limestone, giving a zonal sequence of sphalerite, galena, rhodochrosite and limestone (Horton, 1953).

The zinc ores in the mines are typical pyrometasomatic replacement deposits in limestones, which occur either as veins or as upright tabular masses, and which were controlled by steeply inclined fractures. The typical ore bodies of the mines may be described as pod-like and cigarshaped masses, about 20 to 40 feet in diameter and 200 to 400 feet long (Schmitt, 1939). The largest of the ore bodies enclosed by the Middle Blue or the Hanover Limestone was reported by the mines supervisor (Parker,

1968 personal communications) to be 1,000 feet long, 32 feet wide, and 110 feet high.

The sphalerite in general is found in the outer part of the metamorphic aureole associated with hedenbergite, ilvaite, and manganoan calcite. Magnetite, on the other hand, is found next to the contact of the granodiorite stock, and between the magnetite and zinc ores are masses of garnet and epidote carrying disseminated sphalerite. The zinc ores contain greater proportions of lead as distance increases from the intrusive (Spencer and Paige, 1935). The position of zinc ore bodies in the southern and southwestern part of the granodiorite stock (Hanover intrusive) appear to have been controlled by the pre-existing faults and dikes. The accumulation of ore bodies appears to have been directed along the west side of some of the dikes (Spencer and Paige, 1935) and such a structural relation is evidence that some of the granodiorite dikes were earlier than the ore. However, this is not offered as conclusive evidence. The blanket ores that lie west of the granodiorite contact are continuous along the strike of the Crinoidal Limestone and are aligned along the faults and dikes.

Some field and underground evidence show that ore mineralization in the Crinoidal Limestone was controlled by the Parting Shale as a barrier to the upward movement of the ore solutions, for the ore terminates abruptly against it and fades away laterally beneath it. Post-ore events, such as intrusions and groundwater leaching, must have remobilized and localized some ore mineralization.

to the intrusions.

ORIGIN OF MINERALIZATION

Different concepts regarding the origin of mineralization at the New Jersey Zinc mines have been put forward by Schmitt (1935 and 1939). Spencer and Paige (1935), Belt (1960), and Hernon, Jones, and Moore (1965). These concepts are briefly mentioned in the latter part of this chapter. The lead-zinc deposits of New Jersey Zinc mines are genetically related to the Hanover-Fierro intrusive and are classified as contact ore deposits. Schmitt (1939), Spencer and Paige (1935), Hernon, Jones, and Moore (1965) believed that the hydrothermal ore solutions were the end product of magmatic crystallization and hence were related genetically to the Hanover-Fierro intrusive. However, on the basis of petrology, hydrothermal alterations and the distribution of copper and zinc in the Hanover-Fierro intrusive, Belt (1960) discards this relationship.

According to Belt (1960) the ore deposits of the Hanover mines came from depth instead of the adjacent exposed pluton, because the ore deposition occurred after the solidification and complete cooling of the exposed part of the Hanover-Fierro intrusive. It is also improbable that the ore deposits have originated as a result of the contact metamorphism of the presently exposed country rock. Belt believes that the ore-carrying volatiles in the magma which became the Hanover-Fierro intrusive were expelled at a greater depth than the exposed portion of the intrusive. The time sequence of intrusion, structural events, alterations and mineralization within the Santa Rita quadrangle (New Jersey Zinc Mines fall in sections

21 and partly in 22 of T 17 S. and R 12 W) as proposed by Hernon, Jones, and Moore (1965) is shown in Figure 5.

Pre-mineralization processes (Park and Macdiarmid, 1964) in the rocks, such as chemical changes, metamorphism, silicification, garnetiza tion, epidotization, marmarization, dolomitization, fracturing and faulting, which were due to effects of the intrusion, have left well developed channelways and sites for the transportation and deposition of ore solutions in the area. However, faulting, fracturing, and reopening of the channels, garnetization and epidotization may have recurred by post-ore intrusives, as indicated in Figure 5.

The zinc mineralization shown in the diagram (Fig. 5) is that of New Jersey Zinc mines, Pewabic and Philadelphia mines. The copper mineralization is seen in the copper deposits of Santa Rita. Most geological events which have taken place in New Jersey Zinc mines are in good agreement with the events shown in the diagram. The exception being that, instead of biotitization, extensive dolomitization and marmarization have taken place (Fig. 6 A-D).

The paragenetic relationship (Fig. 7) established by Schmitt (1939) for ore deposition in the Pewabic mines also closely agrees with the relationship in the New Jersey Zinc mines. The origin of the mineralization in the New Jersey Zinc and other adjacent mines according to Schmitt (1939), Paige and Spencer (1935), and Jones et al (1965) are summarized briefly as follows:

1) The major granodiorite stock is of primary importance in the origin of the mineralization. The intrusive stock has provided favorable structures for the deposition of ore. This was followed by the formation

of skarn at the contacts.

2) The fact that minerals that have formed at higher temperatures are most abundant on the intrusive side of the metamorphic zones therefore suggests that a large proportion of the mineralizing solutions have moved from the intrusive toward the Paleozoic limestones, in the block of broken, fractured, faulted, and folded ground.

3) The first phase of mineralization was the silicate mineralization producing such minerals as andradite, hedenbergite, and epidote. followed by salite, ilvaite, and magnetite, as evidenced by veinlets of ilvaite and magnetite found cutting the early silicates. This was immediately followed by recrystallization of limestones, with or without bleaching.

4) The second phase consisted of sulfide mineralization. During this phase, ferrous iron seems to have derived from silicates, which indicates the reducing character of the fluids, and was deposited along with the sulfides. Using Kullerud's data (1953, referred to by Rose, 1967) Rose, from the estimation of the iron content of sphalerite, suggested that the temperature of ore deposition reached at least 550°C adjacent to the Hanover intrusive and at least 350° C in the lead-zinc deposits in the southwestern part of the Central district.

5) Because hematite, magnetite, and silicates are formed earlier with ferric iron, and sulfides later with ferrous iron, it may be inferred that the fluids responsible for mineralization was oxidizing in the be-

ginning, but became reducing in character towards the later sulfide stage of mineralization. Further, it is also inferred that the ore fluids were acidic at first and attacked the limestones intensely. Later the fluids became less acidic and were less reactive with the limestones. In the final stage, the fluids gradually became alkaline and the carbonates were thus stabilized.

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Fig. 6 C Outcrops showing alteration of limestones by hot migrating solutions rich in iron and manganese, which caused reddish brown(varnish color) and grayish brown colors on the lime-United to an of the stones. を提示 消えられ

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D Marmarized limestones with bluish gray altered latite intrusive(post-ore), shows no signs of mineralization.

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Fig. 7 Paragenesis of the Pewabic ores (After Schmitt, 1939)

DISTRIBUTION OF **ELEMENTS**

The elements of interest, namely, Ag, Cd, Mn, Pb, Zn, Cu, and Sn are found in three separate types of occurrences:

- 1. As grains of minerals such as sulfides, carbonates, etc. deposited in fractures and fissures of the limestones.
- 2. As trace-mineral inclusions in the sulfide minerals.
- 3. As trace elements in the crystal structures of the sulfide and rock-forming minerals.

The first type of occurrence of lead, zinc, copper, and manganese is revealed by the megascopic and microscopic studies of the limestones. Field studies have also indicated massive and sparingly scattered occurrences of sphalerite, chalcopyrite and pyrite. The mineralogy of the New Jersey Zinc mines, described earlier, exemplifies the first type of occurrence of these elements.

The second mode of occurrence of these elements as mineral inclusions is described in the mineralogical studies by Schmitt (1927 - 1939) and Horton (1953). Rose (1967) found numerous chalcopyrite blebs in polished sections of sphalerite from the New Jersey Zinc mines. The chalcopyrite blebs are probably of ex-solution origin, but may also be of replacement origin. Evidence of mineral inclusions of other elements is not known, but is expected to have formed during the evolution and deposition of ores.

The third type of occurrence of these elements is documented by the study of trace-element concentration in sulfides (sphalerite and chalco-
pyrite) by Rose (1967). The range of concentrations found by him is given in Table 4. The light fraction of carbonate rocks (see heavy mineral separation procedure on page 23) was analyzed for trace elements. From the analyses, it is found that traces of these elements are also present in the carbonate rocks devoid of ore grains (Table 5). These trace elements most probably are incorporated in the crystal structures of rock forming minerals.

Distribution of Trace Elements in Surface Limestones

The surface samples were collected primarily from Pennsylvanian and Mississippian limestones (see Fig. 2, for sample location). A total of 211 samples were collected and analyzed for seven elements: Ag, Cd, Mn, Pb, Zn, Cu, and Sn (see App. 1 for analytical results). The results of the analyses of elements were plotted as isograd (contour) maps and graphs. It is reasonable to assume that the trace-element distribution in the surface limestones is due to primary dispersion of the elements during the events of ore deposition. It is also reasonable to expect secondary dispersion of elements, on account of post-ore events such as weathering, leaching, transportation and deposition of elements by surface runoff. Post-ore modification of primary dispersion patterns of elements is difficult to demarcate.

Silver

The concentration of silver in surface limestones is very low. (Fig. 8, A, B). The upper limit being only 11 ppm, silver in the surface limestones does not furnish any indications about the locales of lead-zinc ore deposits. Of the several reasons advanced for the low concentration of silver in the

Table 4. A range of trace elements in sphalerite and chalcopyrite samples of the New Jersey Zinc mines (after Rose, 1967)

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surface limestones, the following are the most important:

The silver content of the sulfide ores is low (Rose, 1967) and, there-1. fore, it is concluded that ore solutions were poor in silver.

2. Depositional conditions for silver were not favourable; therefore, it could not be dispersed in the present surface horizons of limestones.

3. Post-depositional events may have altered the concentration of silver in surface limestones.

From the series of graphs drawn, it is further inferred that silver closely follows the trends of cadmium and in many instances the higher values fall along the same anomalous peaks of the other elements (App. 2). Cadmium

Cadmium, like silver has very low concentration (Fig. 9 A, B). The highest reading found in the surface samples is 6 ppm. From such low values, it is impossible to form any inferences about the localization of ore bodies in subsurface zones. The reasons attributed to low concentration of silver would also be valid in the case of cadmium.

Manganese

The dispersion pattern of manganese in the surface limestones is wide and concentrations show a marked variation (Fig. 10 A, B). High values of manganese are found in the northern side of the mines, whereas in the southern side the concentration of manganese is lower and sparingly scattered. During the transportation and deposition of hot, emanating hydrothermal ore solutions, manganese, along with iron seems to have dispersed in large quantities into the limestones. As a result of this, the limestones show

characteristic reddish brown to dark gray color (varnish color) on the surface of fractures and joint planes (Figs. 6 A-D). The background values of manganese vary from 100 to 200 ppm in different limestone formations. According to Rose (1967) the manganese content of sphalerite and chalcopyrite samples from the New Jersey Zinc mines is high (Table 4) unlike the content (relative) in surface limestones. Therefore, it may be inferred that most of the manganese was deposited along with the sulfides in subsurface limestones and comparatively less manganese had migrated and dispersed in the present surface horizons of limestones. The trends in the distribution of manganese in outcrops may be due to both primary and secondary dispersions. Manganese concentration is susceptible to changes of temperature, pressure, Eh and pH conditions in the carbonate environment, and these conditions might have altered the primary dispersion patterns to a certain extent in the surface limestones.

The magnitude of the surface anomalies of manganese is inversely proportional to the depth of the lead-zinc deposits. The shallower ore deposits located at 10-30 feet below the surface are reflected by the manganese anomalies directly above them, whereas the ore deposits located below 80 feet do not show any surface anomalies. The reason may be that manganese could not migrate over longer vertical distances. The manganese anomalies are thus found to be concordant with the location and depth of ore bodies below the surface. From the manganese dispersion patterns in surface limestones, it is found (with an exception in northwestern part of the mines) that the manganese concentration increases away from the igneous

contacts. Likewise it is found that manganese increases from Lower Blue Limestone to Upper Blue Limestone. This pattern of manganese distribution in the New Jersey Zinc mines limestones was also observed by Graf, et al, (1950). There are two plausible factors which govern the increase of manganese in the Upper Blue Limestone: 1) The presence of ore bodies below. 2) The intrusion of the Hanover sill might have remobilized the high manganese from the depths to the present surface levels. Similarly the anomalous manganese in the Upper Blue Limestone of the southern side also indicates an ore body below. This anomaly is as high as the anomaly found near the Hanover intrusive, therefore it suggests a different source of ore solutions (far away from the Hanover intrusive) on the southern side. The metamorphic aureoles of limestones invariably show high contents of manganese. From the graphs, it is inferred that the anomalies of manganese coincide with those of lead, zinc, and copper, and manganese is considered to be a good indictatory element in the exploration of lead-zinc deposits (App. 2).

Lead

The concentration of lead in surface limestones is moderately variable as compared to manganese (Fig. 11 A, B). Out of seven anomalies that are found in the area, only two exhibit a wide extent of area, with highest values of lead being 300 ppm. The most anomalous zones are found towards the northern part of the mines, between the Buckhorn and U.S. adit, whereas the dispersion of lead in the southern part of the mines is low in concentration, High values of lead are found sometimes in or near the skarns and metamorphic

aureoles of limestones. The concentration of lead increases from Lower Blue Limestone to Middle Blue Limestone, but from there downwards, it decreases again. All the anomalous zones of lead in the surface limestones are concordant with the ore bodies located below them, and lead is considered to be a valuable indicatory element in the surface limestones for the exploration of lead-zinc deposits located at depths. The low-value dispersions of lead are located either above the barren zones or above the ore bodies located at depths below 80 ft. Perhaps in the latter case the ore solutions did not have enough volume to reach the surface. Low distribution values of lead in surface limestones may also be due to the unsuitable physicochemical conditions of deposition, and removal of lead by post-depositional effects such as weather ing, leaching, and transportation.

Zinc.

Sphalerite is the primary ore mineral of the New Jersey Zinc mines, and therefore, the dispersion of zinc traces in surface limestones is signficantly related to the zinc ore bodies at depth. The distribution of zinc is wide, and changes gradationally with reference to the Hanover intrusive, skarns, and the ore deposits at different depths (Fig. 12 A, B). The anomalies of zinc in surface limestones indicate directly the lead-zinc deposits located below. The concentration of anomalies is governed by the depth of the ore bodies, i.e., high anomalies are located above shallow ore deposits (10-30 ft.) and low anomalies are found above ore deposits situated below 80 feet. The spread of anomalies is wide, which indicates a wide area of influence by the hydrothermal ore solutions at depths. Higher values of zinc are found either

close to the skarns or to the igneous contacts (except for one in southeastern part of the mines). Similar to the location of the anomalies of manganese and lead, wide anomaly spread of zinc is also found in the northern part of the mines. The high value spread of zinc traces is mostly found in the Hanover and Middle Blue Limestones, located next to the Hanover intrusive. This might imply that ore solutions had evolved from the Hanover intrusive side. The dispersion gradients decrease away from the contacts. In some zones high zinc values are found exceptionally above the non-ore bearing horizons. This is attributed to the deposition of leached out primary zinc (dispersed above the ore deposits), on account of its high mobility in the surface environmental conditions.

Copper

The copper distribution, expressed in isograds, is low in concentration and is uniform throughout the mines area, except for two anomalies located in the northern side of the mines (Fig. 13 A, B). The highest anomaly of copper registered in surface limestones is 130 ppm of copper. The anomalies are concordant with the ore bodies. The low concentration of copper sometimes observed directly above the shallow ore deposits does not preclude the use of copper as an indicator. In such case, care should be taken to evaluate the reasons for low concentrations of an element. The reasons explained earlier for such low concentration may also be valid here. Besides the previously offered reasons, the following are also possible: The mobility of copper in carbonate environment (underground) is limited 1.

at neutral to alkaline pH (Hawkes and Webb, 1962), since it is plausible for the copper to be deposited as copper carbonates and thus hamper further migration or dispersion of copper to the shallow horizons (present surface levels). The presence of copper carbonates in the mines is a good example of such phenomena. 2. Most of the copper from the ore solutions was deposited as chalcopyrite in or near the contacts and whatever had migrated away from the contacts, was deposited along with the lead-zinc ores. In the process, a very little copper was diffused to the present surface levels of the limestones.

Tin

The distribution patterns of tin in surface limestones show a marked variation (Fig. 14 A, B). Anomalies are found in the northern side of the mines, whereas in other parts of the mines, the concentration of tin is low. Since a major area of the mines shows low concentration of tin, it may be inferred that the tin that accumulated in subsurface limestones during the deposition of ores was not enough to reach the present surface levels of limestones. The concentration of tin increases from Lower Blue to Upper Blue Limestones, and this increase is due to: 1. the presence of ore bodies nearby (underground), from which the high tin was dispersed in the surface levels above during ore deposition. 2. the intrusion of the Hanover sill next to the Upper Blue Limestone might have remobilized the subsurface tin to the present surface levels.

The anomalies of tin are concordant with the ore bodies either

directly below or near by them. Like other elements, the surface distribution values of tin are reflected by the depth of ore bodies and the concentration of tin in them. According to the study of Rose (1967), it is found that the tin content of sulfides is low (Table 4). Therefore, it may be inferred that most of tin from hydrothermal ore solutions is precipitated either in the surface or subsurface limestones. The high concentration of tin in the surface limestones is also due to the resistance of tin compounds to weathering and any amount of tin that was removed from the surface limestones (under possible chemical conditions) was promptly precipitated. The high volatility of tin must have also enabled it to escape from hydrothermal ore solutions to the present surface levels of the limestones (by diffusion) and to be deposited in higher concentrations than most of the other elements.

Surface anomaly trends of the trace elements

The anomalies of elements in surface limestones overlap each other in the northern part of the mines. Whereas in the southern part, the anomalies are quite independent of each other, except for two (Cu and Sn anomalies). Under simple conditions of deposition, i.e., one event of ore mineralization, without the interaction of different surges of ore solutions and under gradational changes in chemical conditions of transportation and deposition, the dispersion of elements is expected to occur in a zonal configuration, as for example, zinc is deposited in the host rock near the skarn and lead is deposited away from the skarns (Lovering, et al, 1952). But in the New Jersey Zinc mines area such zonal distribution of trace elements in the surface lime stones did not occur. Therefore, the lead-zinc ores were not deposited under simple conditions. The overlapping of the surface anomalies and lack of zonal distribution of elements in the mines area may be attributed to the following:

> 1) Variations in the physicochemical conditions during the transportation and deposition of ore fluids. Difference in the diffusion coefficients of the elements.

2) The fracture system is interconnected in such a way that the ore solutions migrating from different directions must have mixed at one stage or other, resulting in the precipitation of ore. Likewise their associated trace elements were also dispersed in the surface limestones, resulting in over-

lapping of the anomalies.

3) Post-ore depositional effects such as weathering, dissolution, transportation and redeposition of elements, may have modified the primary dispersion trends and given rise to the present trends in the distribution of elements. Perhaps the surface runoff might have contributed a part of the concentration of trace elements from time to time during the post-depositional period.

The concentration of manganese and tin increase away from the Hanover intrusive, whereas zinc is found increasing towards the Hanover intrusive. However, high zinc anomalies also occur away from the Hanover intrusive at the southern side; likewise, manganese and tin also show exceptional anomalies near the intrusive at the southern side of the mines. These independent anomalies of southern part of the mines indicate the ore bodies below and these ore bodies with high zinc (similar to the high zinc ores at the Hanover intrusive) suggest a source for the ore mineralization on the southern side of the mines, different from the one on the Hanover intrusive side. This second source perhaps is related to the Santa Rita Stock, southeast of the New Jersey Zinc mines.

Since the ore bodies were localized along linear or planar structural elements such as fractures, joint intersections, fissures, etc., the "halo" of anomalies of trace elements around an ore body at depth and above an ore body in the present surface limestones was expected. It follows the directional trends of the planar structural elements, through which the

elements migrated and dispersed in the present surface levels. The direction of longer axis of the anomaly trend (isograds of trace elements) were measured, and certain inferences were drawn about the directional patterns of shallow fracture system in the limestones. Out of 55 surface anomaly zones of elements, 35 amomalies (63.6%) showed northwest trend, 13 (23.6%) have a northeast trend, 6 (10.9%) showed north trend and the remaining 1 (1.9%) showed east trend. From this it is clear that the majority of the fractures in shallow depths have a northwest trend.

Distribution of Elements in Subsurface Limestones

For the study of the distribution of elements in subsurface limestones of the New Jersey Zinc mines, 213 samples were collected from 29 drill holes in the mines area (see Fig. 2 A, B and 15 for drill hole locations). The results of the analyses of these samples are given in Appendix 3. The subsurface horizons of limestones were divided into 5 intervals depending upon the depth and the availability of samples. These intervals are described as follows:

The subsurface isograds of lead and zinc distribution were drawn in each of the above-mentioned depth intervals. The behavior and the distribution of each element in each depth interval was studied with reference to the Hanover intrusive, skarns, ore bodies and metamorphic aureoles. Interval A differs from the surface by the presence of ore bodies (sometimes), unweathered nature of the limestones, and the absence of leaching by surface runoff. Silver

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The concentration of silver is low throughout all the intervals (Fig. 16). Relatively high values are found either in ore or in metamorphic aureoles. There is no correlation between silver and either manganese, copper, tin, lead or zinc (App. 4).

The distribution of silver in depth intervals A to E (0-330 ft.) does not show an gradational variation with reference to the igneous contacts, depth, skarns, and ore deposits. Exceptionally, interval D (130-330 ft.) shows a maximum value (77 ppm) higher than the other zones. Rose (1967) has also found very low concentrations of silver in sphalerite and chalcopyrite of the New Jersey Zinc mines (Table 4). This indicates that ore solutions originally were very low in silver. The low concentration distribution patterns of silver do not indicate the location of ore bodies.

Cadmium

The distribution of cadmium in subsurface limestones is somewha higher than silver. The anomalies are characteristic of lead-zinc ores. is a gradational increase in the values of cadmium from non-ore zone to orezone and cadmium is a better indicator of zinc ores than the other elements. The highest anomalies are found either at U.S. adit (northwestern part of the mines) or around the Theta incline (southern part of the mines) (Fig. 17). Cadmium invariably increases away from the Hanover intrusive contacts (Fig. $17).$

A wide range of distribution with high anomalies are found in interval A, whereas in other intervals, the intensity of anomalies decreases drastically. Gradational increase of values are found only in the southern mines area. According to the analyses of sulfide minerals by Rose (1967), relatively high concentrations of cadmium are found in sphalerite and chalcopyrite samples of the New Jersey Zinc mines (Table 4). From this it is inferred that most

of the cadmium was precipitated along with the sulfides leaving behind its traces in the pathways of ore solutions.

Cadmium, being a chalcophile element, is abundant in the zinc sulfides (and rarely in lead sulfide). However cadmium shows variable concentrations within the zinc sulfides (App. 3). This variation of cadmium is not confined to any one depth interval, but prevails throughout all the subsurface limestones. The variation of cadmium in the subsurface limestones is studied by calculating the ratios of Zn and Cd in both the ore and in the anomalous horizons. Comparatively, three types of Zn/Cd ratios are found and henceforth three different types of zinc ores in the New Jersey Zinc mines:

> Type A 20 - 250 ppm. Type C 800 -1000 ppm.

These three types of ratios demark different areas (influenced by them) within the New Jersey Zinc mines (Fig. 18). The type "B" ratio zinc mineralization is found close to the Hanover intrusive, followed by "A" type zinc mineralization. Located next to "A" type on the southwestern side is the type "C" zinc mineralization. Type "B" zinc mineralization is also found away from the Hanover intrusive on the western side, but only one ratio value influences this, and is therefore, inadequate for any conclusions about such mineralization there. However, the boundaries of these areas (influenced by the ratios of Zn and Cd) overlap with each other. The variation in the Zn/Cd ratios suggests three possible compositions of ore solutions, which may be due to either different physicochemical conditions and the time of

deposition of one surge of ore solutions, or different surges of ore solutions from different sources.

Early magmatic sulfides with high temperature conditions of formation show the amount of Zn/Cd ratios relatively high compared to the strongly enriched Zn/Cd ratios of the ores formed at relatively low temperatures (Goldschmidt, 1958). Therefore, the temperature of formation of zinc ores in hydrothermal ore solutions may be one of the strong reasons for the compositional variation of zinc ore bodies in the New Jersey Zinc mines. The distribution of type ratios of zinc and cadmium suggest in general that the zinc ores near the Hanover intrusive are formed at higher temperatures than the zinc ores on the southwestern side of the mines (far away from the Hanover intrusive). The presence of type "A" ratio zinc mineralization next to the type "B" makes one disbelieve the influence of temperature on the origin of Zn/Cd ratios, unless there is a channel, which fed the high temperature ore solutions at different depths. However, the low ratios of zinc and cadmium could be due to either the low concentration spread of these elements away from the Hanover intrusive, or the presence of a different source on the southern side of the mines, which deposited ores under high temperature conditions.

Manganese

Manganese is a good indicator of lead-zinc ore deposits in the area, since high manganese is invariably found occurring in the pathways leading to the ore bodies. The distribution of manganese in the subsurface limestones

has a marked variation with the background, and the highest values are 38, 111, 250 ppm (11.12%) respectively. The concentration of manganese in subsurface limestones is high and it is extensively distributed. A gradational increase of manganese is found from interval A to interval E, and the highest values occur in interval D and E (Fig. 19). This suggests that the manganese rich ore solutions that migrated from depths have deposited the high manganese in deep zones. The skarns in the subsurface limestones are characterized consistently by high manganese also, and away from them, manganese decreases. Exceptions are found at depths 60-130 ft. and 230-330 ft., where Mn increases away from the skarns. Extensive high manganese distribution is found in the southern sections of the mines, whereas in the northern sections, the values are relatively low.

The manganese content of the zinc ores varies at different places at depth. In general, three patterns of manganese concentration in the zinc ores are found, from which it is inferred that there are three different types of zinc ores in the New Jersey Zinc mines: 1. High grade zinc ore with high manganese. 2. High grade zinc ore with low manganese. 3. Low grade zinc ore with high manganese.

These three types of ores may be due to one or two of the following: 1. Variation of temperature during the transportation and deposition of ore, since according to Goldschmidt (1954), high manganese is found in sphalerites formed at elevated temperatures and low manganese in sphalerites formed at low to intermediate temperatures. 2. Evolution of

ore solutions at different times from the same source. 3. Different sources of ore solutions. The presence of highest manganese in intervals D and E indicates high temperature of formation of ores in those depths. In general, high manganese distribution is often found near the Hanover intrusive. Exceptions are found at depths 60-130 ft. and 230-330 ft. Copper

The intensity of distribution of copper in subsurface limestones is a function of the localization of ore deposits, i.e., the anomalies of copper are found directly within the ore zones, and the concentration of copper decreases drastically away from them (App. 3). The distribution values of copper in subsurface limestones are variable (Fig. 20). The background value of copper range from 1 ppm to 5 ppm, depending upon the limestone formation. The highest anomaly registered is 3850 ppm of copper. The high anomalies are found in the southern sections (away from the Hanover intrusive) of the New Jersey Zinc mines. Unlike manganese, copper invariably increases away from the Hanover intrusive contacts, except at depths 0-20 ft. and 130-230 ft. (on the northern side) next to the Hanover intrusive. However, similar to manganese, highest copper distribution is restricted to depth intervals D and E, and this property may be due to the upward migrating copper rich (relatively) ore solutions, which deposited copper along with the lead-zinc ores at high temperatures.

From the analyses of the limestones, it is also found that the copper concentration in zinc ores varies from place to place, but there is

no regularity in these variations. An example of such variation of copper concentration in zinc ores is shown in Appendix 3, and in the following:

The possible reasons explained earlier for such variations could also be valid here for copper.

Tin

The concentration of tin in subsurface limestones is high and shows a moderate variation (App. 3 and Fig. 21). Most of the anomalies occur close to the ore zones and, therefore, tin qualifies as a good indicatory element in the exploration of zinc deposits. The background value varies from 0 to 75 ppm depending upon the limestone formation, and the highest anomaly of 1325 ppm of tin is found in interval "C" (60-130 ft.). Rose (1967) found a highest value of 100 ppm of tin in sulfide minerals of the New Jersey Zinc mines, but tin in the subsurface limestones is much higher than 100 ppm. From this it is inferred that the ore solutions were moderately rich in tin, but most of the tin had escaped from the hot emanating fluids into the limestones before the deposition of sulfides, owing to its high volatility.

Invariably, tin increases away from the Hanover intrusive, and higher anomalies are most often found in the southern part than in the

northern part of the mines.

The spread of high values of tin is found mostly either in ore horizons (in limestones near the ores) or in metamorphic aureoles of the limestones and therefore, tin indicates the probable targets of exploration of the lead-zinc deposits.

Lead

The distribution of lead in subsurface limestones shows moderately high concentration adjacent to the ore zones, and it has a background value range of 8-10 ppm (Fig. 22-26). The values of lead consistently increase toward the ore horizons and decrease away from it (App. 4). There is no consistent gradational change in values of lead in subsurface levels, with reference to either the Hanover intrusive or to the exposed skarn zone next to the intrusive (Fig. 22-26). The ore and the anomalies of lead are found localized near the granodiorite dikes (contemporary to ore), in the silicate skarn and in the intensively altered and fractured metamorphic aureoles of the limestones (App. 3, 4). High concentration gradients of lead do not always extend throughout the whole length of the skarn, and perhaps some lead that was introduced during silication might have been dissolved, transported and redeposited at points of low temperatures. Exceptionally high values (anomalies) of lead ore are also found near the post-ore intrusives (App. 3), where the primary lead minerals had been remobilized and deposited by the post-ore intrusives. The ore zones of lead most often coincide with the anomalies of Cd, Mn, Cu and sometimes with the Sn, and

invariably the lead ores are associated with zinc ores. However, in some depth intervals lead shows low values where zinc and manganese are high and vice versa. The distribution of lead in different depth intervals is described as follows: The lead in interval A is moderately high, with a maximum concentration of 3000 ppm (Fig. 22). The concentration of lead in the northern sections of the mines is lower than in other sections. In general, the anomalies are broad, and coincide with the surface anomalies of lead. Only two ore horizons are encountered in this depth interval, one is immediately next to the skarn (northern side of the mines) and the other is away from the skarn on the southern side, located north of the Theta incline section; both show 0.3% concentration of lead (Fig. 22). Lead increases away from the Hanover intrusive only in the southern side of the mines, but in the northern side, high values are found near the intrusive.

The distribution of lead in interval B is significantly variable (Fig. 23). Low concentration of lead is found in the northern part of the mines, but the high concentration is found in the southern part of the mines, near the Theta incline. Here also, only two ore horizons are encountered, but they are located in the southern part of the mines. The lead ore located on the southern end of the Theta incline shows the highest value of 10,000 ppm (1%) of lead. The distribution patterns in interval B indicate that lead increases away from the Hanover intrusive contacts.

The trends of the distribution of lead in interval C shows a marked change compared to the trends in A and B depth intervals. The ore

zones are widely spread not only on the southern sections, but also on the northern sections of the mines within the U.S. tunnel area (Fig. 24). However, the concentration of lead ore on the southern sections of the mines is much higher than on the northern sections. The concentration of lead in interval C is significantly higher than in intervals A and B. The lead in interval C also increases away from the Hanover intrusive, and the lead in the southern side is much higher than in the northern side of the mines.

The distribution of lead in interval D is not as extensive and high as in interval C. However, a gradational change of values is found from ore to non-ore horizons (Fig. 25). The highest value of lead (16, 500 ppm or 1.65%) is found (near the Hanover intrusive) on the southeastern section of the mines. On the northern side of the mines a low grade ore (0.15%) horizon is located near the Hanover intrusive. The concentration of lead decreases away from the Hanover intrusive in this depth interval.

The variation in the distribution of lead in interval E is high, with the highest and lowest values of 13,000 ppm and 40 ppm of lead respectively (Fig. 26). As in other depth intervals, the lead ore of this interval occurs in the southern sections of the mines (away from the intrusive), near the Theta incline. The lead from ore to non-ore horizon shows a sudden decrease in the concentration gradients. The depth of the drill holes on the northern side of the mines is not deeper than 230 ft., therefore, no inference is drawn about the behavior of lead in that area. However, the anomalies of lead, Cd, Mn, Cu and Sn and the presence of zinc ores at depths of 130-230 ft.

strongly suggest a possible ore body below, and it would be worth considering for exploration (App. 3, 4).

Zinc

Zinc in subsurface limestones is higher and more abundant than lead (Fig. 27-31). The background values range from 6 to 16 ppm of zinc, depending upon the limestone formation. There is a gradational increase in the distribution of zinc from non-ore to ore horizons (App. 4). The distribution patterns of zinc in the subsurface limestones is not consistent with reference to the Hanover intrusive and skarn. In some sections of the mines, high concentration of zinc ores are found near the Hanover intrusive and skarn and in others the concentration is low. However, most of the anomalies and ore bodies are localized near the intrusives (contemporary with ore), in the skarn, and in the intensively altered and fractured limestones (App. 3, 4). Sometimes high zinc (including low grade ore) is also found near the post-ore intrusives, and perhaps is a remobilized zinc by those intrusives. The ore zones and the anomalies of zinc coincide with the anomalies of cadmium, manganese, copper, and, sometimes with tin (App. 4). Variations of cadmium, manganese, copper, and lead are found within the zinc ore hori-There is a definite correlation between Cd and Zn and between Mn and zons. Zn, which is illustrated earlier, but there is no definite correlation between Cu and Zn. However, there is a possible variation of lead in zinc ore and in anomalies in every depth interval, which is described later.

The distribution of zinc in different depth intervals is described

as follows: unlike lead, zinc in interval A is highly concentrated and extensive (Fig. 27). The background and the highest values of zinc are 13 ppm and 207, 500 ppm (20.75%) respectively. The high grade zinc ore occurs on the southern part of the mines. In interval A, zinc decreases away from the Hanover intrusive in the southern part, while it increases in northern part of the mines. The concentration of zinc in interval A is higher than in all the other intervals, and reflects significantly on the anomalous distribution of zinc in the present surface limestones.

In interval B, the concentration of zinc is moderately high (Fig. 28). The zinc mineralization is restricted to two extreme corners, one southwest of the Theta incline and the other at U.S. tunnel (on the northwestern side), both are away from the Hanover intrusive. Two small low-grade ore bodies (0.12% of zinc) are also found next to the Hanover intrusives. There is no gradational change in the distribution of zinc between these two ore bodies; therefore, the volume of ore solutions responsible for the ore bodies has faded out within the premises of the ore deposition. Unlike the distribution in interval A, zinc in interval B increases away from the Hanover intrusive. There is a significant decrease in the concentration and abundance of zinc ore from interval A to interval B.

The abundance and the concentration of zinc in interval C is much more than in interval B (Fig. 29). The background and the highest ore values registered in this interval are 30 ppm and 142, 500 ppm (14. 25%) of zinc respectively. Similar to the location of the zinc ore in intervals A and B,

the concentration and the extent of zinc ores in the southern side of the mines are greater than in the northern side. The concentration of zinc ores increases away from the intrusive in this interval also.

As in intervals A and C, zinc in interval D is widely distributed (Fig. 30). The background and the highest ore values of this interval are 10 ppm and 53, 750 ppm (5.375%) of zinc respectively. High zinc concentration is found near the Hanover intrusive and the skarn on the northern side, whereas on southern side the high concentration is found away from the Hanover intrusive. This character is very typical of interval D only. There is a gradational decrease in the distribution of zinc between the two ore bodies, which is perhaps due to the lateral migration of ore solutions with decreasing volume of zinc.

The distribution of zinc in interval E is less extensive, and the background and highest ore values of zinc are 19 and 55,000 ppm (5.5%) respectively (Fig. 31). The zinc ore in interval E continues to occur on the southern side of the mines. Lacking data, little can be said about the distribution of zinc in the northern side of the mines. However, the leadzinc ores are expected to occur at depths below 230 ft., since the indications (explained earlier under lead) are good for such occurrence. From the available data, it is found that zinc increases away from the Hanover intrusive similar to the above interval.

Zinc - Lead ratios in subsurface limestones

According to the work of Rose (1967), the Zn/Pb ratio of ores in the Central district, New Mexico, shows a consistent decrease in value

as the distance increases from the nearest intrusive stock. This decrease in Zn/Pb ratio according to the increase in distance indicates, 1) relatively more zinc was deposited nearer the source intrusive than lead; 2) presence of lateral zoning in lead-zinc mineralization. However, it is not known whether such correlation exists in subsurface limestones within New Jersey Zinc mines at Hanover, where the ores of lead-zinc occur in high concentrations in the limestones.

To pursue such studies, data from 29 drill holes spanning the different depth intervals (A-E, mentioned earlier) were considered. From each interval, either ores or lead-zinc anomalies were considered in calculating the Zn/Pb ratio. The shortest distance from the known boundary of the Hanover intrusive to each drill hole location was measured. Zn/Pb ratios in each depth interval of a drill hole corresponding to the shortest distance from the Hanover intrusive are given in Table 6. The same data are shown graphically (semi logarithmic plotts) in Figure 32.

The ratios of Zn/Pb in subsurface limestones change markedly, depending upon the depth. It is obvious from the graphs (Fig. 32) that there is a possible decreasing trend of the ratios with increasing distance from the Hanover intrusive, and a vertical and horizontal zonal relationship ob lead-zinc is found. This zonal relationship of Zn-Pb is far from perfect.

In intervals $A - C$, there is a decreasing trend of Zn/Pb ratios with increase of distance from the Hanover intrusive. However, in these

depth intervals the ratio points are scattered (deviation from normal distribution, Fig. 32). The scattering of these ratios is expected to result from the effect of mixing of depositing ore solutions from different feeders, either related to one source or different sources. Mixing of ore solutions at depths of 60-130 ft. appears to be greater than 0-60 ft. depth, since the scattering of the ratios is greater (fig. 32).

In interval A, a greater number of anomalous ratios are present (between distances 1600-1800 away from the intrusive) than in intervals B and C. This is perhaps also the result of mixing of depositing ore solutions. However, these anomalies show that the concentration of lead increases (between above mentioned distances) from intervals A to C.

In interval D, a greater degree of scattering of the ratios is found, and there is no definite decreasing trend of the ratios, hence no lateral zoning of Pb-Zn mineralization (Fig. 32). The strong scattering of ratios suggest a heavy mixing of depositing ore solutions migrated from different directions. The high ratios, found farther away from the Hanover intrusive are from the southern side of the mines. These ratios show zinc concentration almost as high as its concentration near the Hanover intrusive. The fact that some of the high Zn/Pb ratios are found away from the Hanover intrusive on the southern side suggests that there is another source of ore solutions on the southern side which is responsible for high zinc in that area. This source is different from the source on the Hanover

intrusive side.

A prominent reverse trend of the ratios in interval E strongly supports the above inference about the southern source of ore solutions. The Zn/Pb ratios decrease as a function of decreasing distance towards the Hanover intrusive. The reverse of lateral zoning of Pb-Zn mineralization cannot be due to the deposition of ore solutions migrated from the Hanover intrusive side under any condition, since the presence of high zinc ores away from the Hanover intrusive cannot be explained by one source. The absence of ore near the intrusive in interval E (on the northern and southern sides) indicates that the ore solutions from the southern source have migrated upward and could not migrate laterally towards the Hanover intrusive side. However, not much can be interpreted about the northern side of the mines, since there is no drill-hole record below 230 ft. (Fig. 32),

Similar to the present findings, Schmitt (1939), Hernon, Jones, and Moore (1953) and Spencer and Paige (1935) have suspected a metal zoning around the south lobe of the Hanover stock. Zinc ores with low lead are found near the contacts and farther away from the contact, the zinc ores contain high lead (including lead ores). However, the presence of high zinc ores near and away from the Hanover intrusive (or reverse lateral zoning) is not noted. Likewise, the depth of metal zoning has not been studied by any of the previous workers.

However, this reverse of metal zoning found beyond 2250 ft. of the Hanover intrusive strongly suggest a possible second source from the south, perhaps related to the Santa Rita stock located southeast of the New Jersey Zinc mines.

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Table 6 (continued)

Fig. 32 Graphs representing the relationship between Zn/Pb ratios and the distance from the Hanover intrusive in different depth intervals.

MIGRATION OF ORE SOLUTIONS

From the study of distribution of lead-zinc ores certain inferences may be drawn about the migration of ore solutions in the New Jersey Zinc mines. Only lead and zinc ores are considered for this purpose because the gradational changes of ores from horizon to horizon are the better measure of the migration of ore solutions. For this type of study, five reference lines were drawn parallel to each other and trending in an approximately northerly direction, (Fig. 15). The distance between the two lines is 400 ft. The first two lines were chosen to cover the skarn and the area close to the Hanover intrusive. The remaining three lines covered the rest of the area adjoining to the skarn, and these lines were superposed on the isograd maps of lead and zinc and the spread of the anomalies and ores pertaining to each depth interval are marked. The anomalies and ores of lead and zinc along the reference lines are represented in block diagrams (Fig. 33, 34).

These block diagrams show a systematic accumulation of ores in two horizons, one towards the northern side and the other towards southern side of the New Jersey Zinc mines (Fig. 33, 34). A few exceptions are found along reference line 3, where the zinc ores are found throughout all the directions at depth intervals A and C.

Along reference line 1, near the Hanover intrusive, high grade ores of lead-zinc are found either at depths of 0-20 ft. or 60-230 ft., while at other depths, only traces of the ores are found (Fig. 33, 34). This obviously indicates that there are two sets of feed ways (feeders or channels) near

the Hanover intrusive, one set on the northern side and the other on the southern side of the mines. Each of these sets consists of two feeders, one at a depth of 0-20 ft. and the other at depths of 60-230 ft. (Fig. 35-38). These feeders were responsible for the migration of ore solutions from the Hanover intrusive side into the limestones. In the above mentioned depths, the spread of ores is continuous throughout the area represented by the reference lines, thereby indicating a continuous migration of ore solutions in those depths. Absence of either anomalies or ores at depths of 230-330 ft. on the northern side indicates that the ore solutions did not evolve from the depth below 230 ft. from the intrusive side. On the southern side of the mines, this is not true. The presence of high grade ores below 230 ft. suggests a different feeder of ore solutions below 330 ft. and is confined to the area represented by the lines 2, 3 and 4 (Fig. 35-38).

Likewise away from the Hanover intrusive, high-grade ores are also found at depths of 20–130 ft. on the southern and at depths of 0–60 ft. on the northern sides of the mines, along the reference line 5 area (Fig. 33, 34). Such high grade ores and their dispersive traces vertically on either side along the line 5 area indicates two other feeders, one on the northwestern and the other on the southern sides of the mines (Fig. 35-38). The feeder on the southern side is thought to be from a source different from that of the Hanover intrusive side.

Overall, seven main feeders of ore solutions are inferred in the New Jersey Zinc mines at Hanover (Fig. 35-38). Four of these are located near

the Hanover intrusive (two on the northern side and two on the southern side of the mines). Two are located away from the Hanover intrusive (one on the northwestern side and the other on soutthern side) and the remaining one is a deep-seated feeder located betwreen the reference lines 2 and 4 areas.

Certain compositional variations are found in the ores of different channels and these variations obviously reflect the composition of ore solutions that migrated through the above-mentioned different channels. On the northern side of the mines (near the intrusives) the ore solutions, which migrated from 0-20 ft. depth were comparatively low in zinc but were high in lead, while the ore solutions from the depths 60-230 ft. were high in zinc and relatively moderate in lead. Likewise, on the northwestern side, farther away from the Hanover intrusive, the ore solutions from the depth 0-60 ft. were high in zinc and low in lead.

Similar variations are found in the channels present on the southern side. Ore solutions that migrated from 0-20 ft. depth (near the Hanover intrusive) were relatively high in zinc but low in lead, while the ore solutions from the deeper horizons had relatively low zinc and high lead. However, the ore solutions characteristic of the channel at depths 20-130 ft. (away from the Hanover intrusive) were high in both zinc and lead. There is also a general difference between the lead-zinc ores of the northern and the southern sides of the New Jersey Zinc mines. The ores present om the northern side show lower copper than the ores present on the southerm side of the mines. This

broad variation of copper in ores of two sides suggests that the ores on the southern side are from a different source, and this is perhaps related to the Santa Rita Stock located at southeast of the New Jersey Zinc mines.

The compositional variation of ore solutions in different channels is expected to occur due to separate surges of ore solutions from a single source during different stages of magmatic differentiation. Each surge of ore solution with different composition has followed separate channel at different depth. This process of different surges is explained in the "Pulsation Theory" by Smirnov (1937, referred to by Kutina, 1963). However, the ore solutions derived from separate sources may also show a compositional variation. Since the ores in channels near the Hanover intru sive show different composition (likewise the ores in channels away from the intrusive), therefore, it is suspected that different surges of ore solutions pertaining to two sources (one on the Hanover intrusive side and the other on the southern side) may be the cause for the compositional variation of ores in different channels on either side. However, a study of most important chalcophile trace elements in the lead-zinc ores from these channels will further prove the above inference.

The temperature is also expected to influence the compositional variation of ores, if the ore solutions have evolved from one source and migrated through one main channel (feeder) to different depths. The presence of more than one channel in the area do not favor the effect of temperature on the currently found lead-zinc variations in different channels. However, certain compositional variation of ore solutions due
to temperature within each channel is expected and is evidenced in the area (Fig. 33-38).

The spread of the ores show that the ore solutions at depths 0-20 ft, and 60-230 ft, have migrated horizontally to a distance of about 1000 ft. from the Hanover intrusive contact. From that point, they appeared to have migrated down (Fig. 33-38). Likewise, the ore solutions at depths of 0-60 ft. farther away from the intrusive appear to have migrated horizontally towards the Hanover intrusive (Fig. 33-38). However, the direction of migration has changed downward in the area referred by line 3. In contrast to the other channels, the ore solutions which came from the depth below 330 ft. on the southern side of the mines have migrated almost vertically upwards, joining with the downward migrating ore solutions from other channels (Fig. 35-38). Thus, the mixing of the ore solutions of different compositions seems to have taken place at depths of 60-130 ft. in the area represented by line 3. As a result of this mixing of ore solutions, certain anomalous lead-zinc ores are found in those depths $(Fig. 33-38)$.

The location and the distribution of ores at different depths are governed by fractures and fissures present in the rocks. So certain inferences are drawn about the fracture patterns and also about the direction of movement of ore solutions in the subsurface limestones from the study of the trends of contour distributions represented by the anomalies and ores of lead and zinc. The direction of longer axis of these contour trends

at different depths was measured. From 33 such measurements, it is found that each depth zone has different fracture system with varied trends and some zones are interconnected by the same fracture system. However, in overall measurements, 13 (39.4%) of them strongly indicated a fracture system with a northwest trend. Likewise, 12 (36.4%) of the contour patterns suggest a northeast-trending fracture system on the north and northwest sides of the mine. Among the rest, 9.1% contour trends suggest a north-trending fracture system and 15.2% of them indicate an easttrending fracture system at different depths in the area.

Fig. 33 Block diagrams of anomalous and ore zones of lead in depth intervals along each reference line. \mathbf{r}_1 r - \mathbf{u}

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 $\frac{\partial}{\partial x}\frac{\partial}{\partial y}\frac{\partial}{\partial z}=\frac{\partial}{\partial x}\frac{\partial}{\partial x}$ u. 机相 医麻 $\alpha = \alpha$ Fig. 34 Block diagrams of anomalous and ore zones of zinc in depth
intervals along each reference line. provided to the Section 反流角的动物的物 ÷ H) 136

line 1: Expressed in ppm.

line 3: Expressed in ppm.

Depth Intervals

the mines, showing the channels and the direction of migration of ore solutions.

SUMMARY AND CONCLUSIONS

Trace elements in surface limestones

The distribution of trace elements in surface limestones is mainly due to primary dispersion during mineralization in the area. However, a part of the elemental concentration has been contributed by secondary dispersion due to post-ore events, i.e., weathering, leaching and redeposition by surface runoff and by post-ore intrusives. It is obvious from the post-ore events that the primary dispersion patterns of elements in the surface limestones have been altered to a certain degree, depending upon the behavior of the element in the surface environments. It is very hard to demarcate the secondary dispersion patterns from the primary dispersion patterns in the surface limestones.

The primary dispersion is the result of the emplacement of elemental traces during ore deposition into the wall rocks by:

1. Circulation of ore-depositing solutions through the open spaces of the limestones, which is dependent on the pressure gradient of the system.

2. Diffusion of metal ions through the solutions that filled the available pore spaces of the limestones. The rate of diffusion is proportional to the coefficients of diffusion of the different ions. Of the above two processes, diffusion is probably dominant in the dispersion of elements to the present surface levels from the shallow ore deposits during ore deposition. The reasons for such preference are:

1. The initial pressure gradient of the flowing media (ore solutions) would be considerably reduced when all the connected pore spaces

in the wall rocks are filled by the earliest solutions (closed system) and probably the circulation of ore solutions will cease in the wall rocks. This perhaps hampers the dispersion of elements to greater distances, unless brecciation has occurred, providing ideal conditions for migration.

2. The migration of elements, which is as great as 80 feet vertically, to the surface from the ore bodies, can be possible by diffusion.

3. Absence of brecciation. In general, the concentration and the dispersion patterns of elements in the surface limestones are controlled by the depth of diffusion (depth of ore mineralization), degree of supergene leaching, and the addition of elements by secondary dispersion.

The dispersion patterns of silver and cadmium show relatively low concentrations. The silver and cadmium content of sulfide ores in the New Jersey Zinc mines is also low (Rose, 1967), and this is reflected in the dispersion of these elements in the present surface limestones. Manganese, lead, zinc, copper, and tin have high dispersion values. The concentration of these elements in the outcrop is related to the depth of occurrence of ore bodies, i.e., the shallower the ore body the higher the concentration of trace elements and the deeper the ore body the lower the concentration of trace elements at the present surface. This is due to the nature of diffusion fronts and circulation fronts governed by several factors, perhaps the most important of which are:

1. The highly neutralizing effect and reactive nature of the carbonate rocks;

2. the low porosity of the wall rocks (limestones);

3. concentration of elements in ore solutions:

4. depth of migration of depositing ore solutions; and

5. temperature conditions.

Manganese and tin are high and are widely dispersed in the surface limestones, while the moderately high zinc, lead, and copper show limited extent of dispersion, perhaps owing to the different chemical conditions of the transporting media and dispersion coefficients of ions during and after the primary dispersion. The great number of anomalies of Mn, Pb, Zn, Cu, and Sn in general are found either on the northern or on the southern sides of the New Jersey Zinc mines. The anomalies of Mn, Zn, and Sn on the southern side of the mines (away from the Hanover intrusive) have approximately the same concentration as the anomalies near the intrusive on the northern side of the mines. These anomalies reflect the zinc-lead deposits present below them. On both sides of the mines, the anomalies show an imperfect lateral zoning. Mn, Zn, Cu and Pb on the northern side, decrease away from the Hanover intrusive, while Sn increases away from the intrusive. However, on the southern side of the mines, Mn, and Zn also increase away from the Hanover intrusive. The overlapping of anomalies noted in certain places may be due to several reasons such as:

1. different chemical conditions of dispersion;

2. ore solutions belonging to different surges;

3. post-ore events such as weathering, leaching and redeposition; and

4. nature of the depth and lateral zoning of lead-zinc ores and related diffusion rates of elements from them.

Since Ag, Mn, Pb, Sn, and, to some extent, Cu have low mobility in surface environment, these elements are considered to be reliable indicators of primary dispersion patterns related to the ore deposits in the carbonate rocks.

Elements in ores and subsurface limestones

The subsurface distribution of major and trace elements in lime stones is more significant to ores than their distribution in surface limestones, The low concentration of silver in subsurface limestones indicates that the ore solutions were poor in silver. This is further documented by the low silver content of sulfide minerals of the New Jersey Zinc mines (Rose, 1967).

As in the surface limestones, manganese is abundant and widely distributed in the subsurface limestones. Rose (1967) has also found high manganese in sulfide minerals of the New Jersey Zinc mines (Table 4), from which it is concluded that the hydrothermal ore solutions were rich in manganese, and the carbonate environment favoured manganese deposition. Similar to manganese, the distribution of tin in subsurface limestones is extensive with high concentrations, but tin in sulfide minerals is relatively low (Rose, 1967). This indicates that the ore solutions were moderately rich in tin (but not enough to make ore) and most of the tin was removed in vapor phase from the sulfide system and deposited in the limestones before the deposition of sulfide minerals. The separation of tin from the sulfide ore solution is due to its higher volatility than lead, zinc, copper and manganese under a given condition of temperature and oxygen partial

pressure of a system. Anomalous dispersion concentration of Mn, and Sn (to some extent) present in the pathways leading to ore horizons are good indicators of nearby ores.

The highest anomaly of copper is located in the southern side of the mines, and is found within the ore bodies. Most of the copper anomalies are located below 130 ft. The concentration of copper in limestones and in ore horizons is moderate and this was true in the ore solutions. The dispersion fronts of these elements extend to at least ten feet, and sometimes as much as thirty feet, beyond the ore, as indicated by the abrupt decrease in their concentration at these distances (App. 3, 4). These short range dispersion fronts as shown in Appendix 4, strongly suggest diffusion of elements from a short lived source, which probably underwent rapid precipita tion and concomitant decrease in the concentration of these ions in the mineralizing solutions.

Varied concentration of Cd, Mn, and, Cu is found in lead-zinc ores. Manganese in general is found increasing in ores with depth, and the increase is perhaps governed by the temperatures of formation of zinc ores, i.e., the high manganese is found incorporated in sphalerite formed at elevated temperatures (Goldschmidt, 1954), and elevated temperatures are expected in deeper horizons. Cadmium concentrations also have a direct correlation with zinc. However, copper does not show any direct relationship either with the increasing gradient of zinc concentration or increasing depth.

There are three different types of Zn/Cd ratios, which characterize three kinds of zinc ores in the New Jersey Zinc mines. These Zn/Cd ratios are:

Type A (Zn/Cd-20-250), type B (Zn/Cd-300-600) and type C (Zn/Cd-800-1000). There appears to be a zonal distribution of the three Zn/Cd ratio. types. In general they show a lateral zoning of zinc mineralization (of different composition) at different depths. Type B zinc mineralization is located close to the Hanover intrusive. Next to type B mineralization is type A. Type C zinc mineralization is located away from the Hanover intrusive (next to type A), on the southern side of the mines. These three types of zinc mineralization are not confined to any particular depth interval. The varied concentrations of Mn and Cu also suggest three kinds of zinc ores. These compositional variation of zinc ores indicate at least three different ore solutions responsible for the lead-zinc mineralization in the New Jersey Zinc mines. Such variation in the composition of depositing ore solutions is due to a number of different physicochemical variables, the most important of which are:

1. different ore solutions from different sources;

2. temperatures of formation of ores, pressures and pH conditions during transportation of ore solutions;

3. different times of deposition of ores; and

4. the differences between the behavior of the host element and the trace element during the processes of ore formation.

Smirnov (1937, referred to by Kutina, 1963) has postulated a "Pulsation Theory" for the solutions arising from the same source at

different times, which will cause the above mentioned compositional variation of hydrothermal ore solutions. Likewise Kutina (1963) explained such changes by the "polyascendant" ore solution hypothesis. Rose (1967) has found low cobalt content in the late sphalerite of New Jersey Zinc mines. and he thus favoured two stages of mineralization in the New Jersey Zinc mines (analogous to the polyascendant ores of Kutina). This is also authenticated by the identification of two sulfide generations by Schmitt (1939). So there is every possibility that the origin of different kinds of zinc mineralization in the area is due to the polyascendant ore solutions, probably related to different sources.

Depositional conditions governed by differences in temperature pressure, rate of deposition, etc. may equally well account for the previously mentioned Zn/Cd ratios and the variations of Mn and Cu in zinc ores. Goldschmidt (1933, referred to by Rankama, 1958) indicated that low temperature hydrothermal ore solutions deposit higher cadmium in zinc than the high temperature hydrothermal ore solutions. Such differences due to temperature are also found to be true for Mn in Pb ores (Goldschmidt, 1933, referred by Rankama, 1958). Goldschmidt (1954) found higher manganese in sphalerite formed at elevated temperatures than in sphalerite formed at low temperatures, therefore the temperature may be one of the major causes of varied concentrations of manganese associated with lead-zinc ores of the New Jersey Zinc mines.

With lack of any drastic differences in the composition and porosity

of different limestone formations, it is suggestedl that the pressure, rate of deposition, and the other variables at the site of deposition were not the speculative causes of the Zn/Cd ratios and Mn and Cu variations in ores. The depth and environment of wall rocks, off which we have very little knowledge, might or might not have had an effect on the cadmium, manganese and copper variations in lead-zinc ores. However, lithology, texture, and chemical nature of the limestones suggest that the wall rock of limestones along the path followed by the ore solutions at depth cannot be different in any manner that would cause such differences in the zinc ores. However, the preferential deposition of trace elements might also have caused such variations in zinc ores.

The distribution of lead and zinc ores and their traces indicate that an extensive migration of ore solutions in the substurface limestones occurred on the northern, and southern sides of the New Jersey Zinc mines. The leadzinc distribution patterns vary according to the depth and the side on which they occur. On the northern side at a depth of $0-20$ ft., lead is found to increase towards the Hanover intrusive, while zinc is found to increase away from the intrusive. However, on the southern side this lead-zinc pattern (lateral zoning) has reversed. At depths of 20-130 ft. (on both sides) both lead and zinc increase away from the Hanover intrusive. At depths of 130-230 ft. again a good lateral zoning is observed on the southern side of the mines; high lead is found near the Hanover intrusive, while high zinc is found away from the intrusive. However, on the northern side (at the

same depth), both lead and zinc increase towards the Hanover intrusive. Lead and zinc at depths of 230-330 ft. behave the same way as of 20-130 ft. depth. Under ideal conditions of deposition and under conditions of equal concentrations, lead should be deposited farther outward than zinc (Morris and Lovering, 1952), thus showing a lateral zoning of lead-zinc mineralization. In New Jersey Zinc mines, such lateral zoning exists only in the depth intervals A (0-20 ft.) and D (130-230 ft.), but in other intervals (B, C and E) no such zoning is observed. This is perhaps due to the mixing of ore solutions that migrated from different directions and depths, obliterating the lateral zoning in those depths. Similar to the lead-zinc distribution patterns, Cd, Mn. Cu, and Sn patterns also show lateral variations at depth. Sn, Mn, Cu and Cd usually increase away from the Hanover intrusive. However, a few exceptions are found for Sn and Cd at depths of 130-230 ft. and for Cu and Mn at depths of 0-20 ft. and 20-60 ft.

A significant compositional variation of hydrothermal solutions responsible for the deposition of the Pb-Zn ores furthest south of the Hanover intrusive is indicated by the following observations:

1. the presence of high zinc ores away from the Hanover intrusive, especially on the southern side;

2. higher copper concentration in the lead-zinc ores of the southern side than the northern side ores;

3. the presence of 'C' type (Zn/Cd-800-1000) zinc ores exclusively on the southern side (away from the Hanover intrusive); and

4. clustering of anomalies of elements in the surface limestones on the southern side of the mines, (away from the Hanover intrusive). This suggests a different source of ore solutions on the southern side, which can cause the above mentioned variations. So many changes can not be expected (under any chemical variables) from the ore solutions migrating from the source on the Hanover intrusive side. It is suspected that the source on the southern side is related to the Santa Rita intrusive, southeast of the New Jersey Zinc mines,

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Zn/Pb Ratios

Such a second source of ore solutions at the southern side of the mines is also suggested from the study of zinc/lead ratios as a function of distance from the Hanover Stock. From the plots of Zn/Pb ratios of ores against the distance from the nearest stock in the Central district, Rose (1967) showed a lateral zoning, i.e., a logarithmic decrease in the ratios with the increase of distance. This indicates a source and a direction of migration of ore solutions. If there is more than one source of ore solutions, which affected the area at two different corners (about 2500 ft. apart). then the ratios would show altogether a different pattern. From the low cobalt content of the sphalerite from the southern and southwestern part of the New Jersey Zinc mines, Rose (1967) has suggested a different source for such mineralization. In summary of all the evidences given above, it is concluded that there were at least two different sources of hydrothermal ore solutions which were responsible for the sulfide ores in the New Jersey

Zinc mines.

Migration of ore solutions

The spread of high and low lead-zinc ores in the subsurface lime stones has indicated seven main channels (feeders) through which the ore solutions migrated and deposited the ores. Four of these channels are located near the Hanover intrusive, two on the northern and two on the southern sides of the mines. Away from the Hanover intrusive, two other channels are found, one on the northern side, and one on the southern side. The remaining one is located on the central part of the mines area, about 500 ft. away from the intrusive. The feeders which are close to the Hanover intrusive are at depths of 0-20 ft. and 60-230 ft. The feeders, located away from the Hanover intrusive are at depths of 0-130 ft. However, the feeder, present on the central part of the mines area is relatively a deep seated one, located below 330 ft. The ore solutions which migrated from these channels have mixed at depths between 60 and 130 ft. and at distances about 800-1400 ft. from the Hanover intrusive. This mixing of ore solutions has obliterated the normal distribution patterns of elements, and given rise to the elements variation explained earlier.

The distribution pattern of ores in rocks is a function of the directional trends of fractures and fissures present in the rocks, so certain inferences are drawn about the fracture system (through which the ore solutions have migrated and deposited the ores) from the distribution trends (isograd trends) of lead-zinc ores and their related trace elements. Out

of 55 anomaly trends measured in surface limestones 64% of them have a northwestern trend; 24% have a northeastern trend and the rest showed either eastern or northern trends. Likewise from 33 measurements of ores and anomaly trends of lead-zinc in the subsurface limestones, 39% of them have strongly indicated a northwest-trending fracture system; 36% indicated northeast-trending fracture system, and the rest showed either north - or east-trending fracture system. There is no definite trend of the fracture system characteristic of each depth intervals and each interval shows different fracture patterns. All these fracture patterns might have developed and might have been renewed by the series of pre-ore, contemporary, and post-ore intrusives present in the district, and perhaps the forces involved in the tectonic development of the region might have also contributed 医自发育病 to some degree in the development of the fractures in the New Jersey Zinc mines area.

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Analytical results of surface limestone samples along the traverses $A'-O$ (sample traverses are shown in Figure 2 A , B).

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APPENDIX 1

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TRAVERSE $\texttt{A}^\texttt{1}$

Concentration of Elements in Parts Per Million

Sample							
Location	<u>Ag</u>	Cd	Mn	$_{\rm Pb}$	$_{\rm Zn}$	Cu	Sn
1	$\mathbf 0$	$\boldsymbol{2}$	248	35 ₅ and a	28	5	480
$\mathbf{2}$	$\overline{\mathbf{2}}$	$\boldsymbol{4}$	390	26	24	5	490
3	5	$\bf 4$	428	22	24	6	614
$\overline{4}$	5	\overline{c}	210	30	22	б	218
5	6	3	250	40	33	5	388
$\overline{6}$	\overline{c}	$\overline{2}$	260	42	20	4	340
$\overline{\mathcal{I}}$	$\mathbf 0$	3	162	35 ₁	20	$\overline{7}$	420
8	4	$\overline{4}$	150	35	20	11	419
9	3	3	210	43	24	12	420
10	$\overline{2}$	3	182	$42-$	22	13	358
11	4	4	180	42	22	10	358
12	4	4	168	41	22	9	620
13	3	3	110	40	$14\,$	14	500
14	3	$\boldsymbol{4}$	208	88	60	28	510
15	3	$\boldsymbol{4}$	232	68	78	20	600
16	3	$\bf 4$	488	100	120	34	720
17	6	4	420	120	230	129	801
$18\,$	7	3	468	300	150	41	1001
19	6	$\mathbf 2$	928	310	249	38	400
20 \bar{r}	ϵ	3	480	240	214	20	698
21	$\overline{7}$	3	192	112	96	28	480
22	$\overline{}$	$\mathsf 3$	380	110	20	13	585
23	6	4	210	110	43	5	550

TRAVERSE A

Concentration of Element in Parts Per Million

TRAVERSE B

Concentration of Elements in Parts Per Million

TRAVERSE C

Concentration of Elements in Parts Per Million

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APPENDIX 2

Graphs showing the dispersion patterns of trace elements along the traverses $A'-O$ (traverses are shown in Figure 2 A, B).

APPENDIX 3

Analytical results of subsurface limestone samples from drill holes
(the location of drill holes is shown in Figure 15).

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APPENDIX 4

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Charles Fir

 \mathbb{R}^{n} . \mathbb{R}

Graphs showing the dispersion patterns of elements at depth in each drill hole.

Explanation for stratigraphic columns in graphs.

ELEMENT

IN FEET - D.H. 509-Conta. HIGE DEPTH

SYMDTE **DEPTH** N_I \cdot H \cdot u -**LEEL** 80Z

 \texttt{DEbL} **SAMPLE** EEEL- D'H' III contq: $N1$

SAMPLE DEPTH IN

FEET $-D.H. 82I.$

- D'H' 851 **TEET** DEPTH $\mathbb{N}\mathop{!}$ SAMPLE 283

