THE GEOCHEMISTRY OF QUICKSILVER MINERALIZATION

Thesis by

Robert M. Dreyer

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ILLUSTRATIONS

ABSTRACT

This investigation has involved a geochemical, petrographic, and spectrographic study of quicksilver mineralization. It has been found that cinnabar can be deposited only from alkaline sulphide solutions. The solubility of cinnabar is dependent solely on the sulphide ion concentration which is, in turn, partially dependent on the alkalinity of the solution. Such alkaline solutions are capable of dissolving silica, but carbonate and alkaline earth ions cannot exist together in such alkaline solutions. Any carbonatization of quicksilver deposits must thus represent a stage in the period of mineralization distinct from the period of cinnabar deposition. However, silica is often deposited syngenetically with cinnabar and the relationship of cinnabar and silica (unlike that of cinnabar and carbonate) is so intimate that the cinnabar occurs, in some places,as an extremely fine dispersion throughout associated silica. Associated with quicksilver mineralizing solutions are small amounts of a number of heavy metals as iron, chromium, manganese, arsenic, antimony, gold, silver, copper, zinc, nickel, germanium, lead, and cobalt. Of these elements, copper, silver, cobalt, lead, and germanium are always differentially concentrated in the cinnabar and such differential concentrations as have been observed are independent of the geographical and geological location of the deposit and are likewise independent of the type of wall rock in which the deposit occurs. The varying shades of cinnabar coloration cannot be attributed to any spectrographically determinable concentrations of any elements nor to the total amount of impurity which is differentially concentrated in the cinnabar.

The cinnabar-bearing solutions gain access into the wall rocks through fractures and intergranular voids and the greater part of all cinnabar ores is the result of such open-space filling. When the openings become filled, however, the solutions are quite capable of replacing the adjacent wall rock. If the wall rock is out of equilibrium with the quicksilver mineralizing solutions, the adjustment of equilibrium and consequent precipitation of mercuric sulphide will be quite rapid.

Precipitation of cinnabar is caused primarily by relief of pressure, evaporation of solvent, and wall rock reaction. Except in ammoniacal solutions, a decrease in temperature will not cause precipitation. Dilution of solutions causes the precipitation of metacinnabar and colloidal mercury. Such dilution is probably responsible for the native mercury which is a common, minor component of many quicksilver deposits. Acidification will likewise precipitate metacinnabar, but not cinnabar. The infrequent occurrences of metacinnabar can best be explained by near-surface dilution or acidification of hypogene solutions. Insofar as temperature and alkalinity are concerned, pyrite or both pyrite and marcasite could be formed simultaneously with cinnabar or metacinnabar or both. However, where marcasite occurs with cinnabar alone (as is quite commonly the case), the marcasite has probably been deposited separately from the cinnabar. Since cinnabar (rather than metacinnabar) is deposited only from hot alkaline solutions and since oxidized mercury minerals are very rare, supergene deposition of cinnabar must be a very local and a very uncommon occurrence.

Some cinnabar darkens rapidly on exposure to sunlight and it is suggested that this darkening may involve the formation of a surficial layer of colloidal mercury in solid solution in the cinnabar.

THE GEOCHEMISTRY OF QUICKSILVER MINERALIZATION

INTRODUCTION

Purpose of Investigation

The investigation of the geochemistry of quicksilver mineralization was undertaken with the hope that it would be possible to ascertain the chemical character and behavior of the mineralizing solutions which have deposited mercury-bearing ores. The geological occurrence and the mineralogical associations of quicksilver ores suggest deposition under surface or near-surface conditions where temperatures and pressures approach those conveniently obtainable in the laboratory. Moreover, the mineralogy of quicksilver deposits is markedly simple and uniform in contrast to the complexity and variability of many other types of ore deposits. These facts made it appear practical to attempt to ascertain the factors involved in the geochemistry of quicksilver mineralization.

The investigation was pursued along three lines. The first line of investigation consisted of a study of the chemical aspects of quicksilver mineralization with especial emphasis on the significance of such chemical data in relation to the occurrence and genesis of quicksilver ores. Much of the chemical literature has been overlooked in previous geological investigations and few of the investigations have correlated chemical and geological aspects of the genesis of quicksilver deposits. There are likewise discrepencies in the available data and an attempt has been made to ascertain experimentally the veracity of the data and the validity of the conclusions derived therefrom. A number of chemical experiments have been performed on the chemical aspects of certain significant geologic problems. The second part of the problem is a general petrographic study of typical California quicksilver ores in an attempt to correlate chemical and petrographic data on certain significant petrographic problems. The third portion of the investigation consists of a spectrographic study of cinnabar and cinnabar ores and involves a new approach to the study of metallogenesis.

Acknowledgements

The writer wishes to acknowledge the assistance of Professor H. J. Fraser, without whose advice and encouragement this project could not have been completed. Professor Ian Campbell and other members of the staff of the Division of the Geological Sciences, California Institute of Technology, have been most generous with their advice and assistance. The writer likewise acknowledges the financial assistance of the Division of the Geological Sciences in connection with the spectroscopic analyses used for this investigation. Professor J. H. Sturdivant of the Division of Chemistry, California Institute of Technology, has given the writer a great deal of invaluable data on the crystallographic properties of mercuric sulphide.

Mr. H. W. Gould and Mr. C. N. Schuette of San Francisco have, on numerous occasions, generously given the writer the benefit of their long experience in the production of quicksilver.

The U. S. Geological Survey has kindly permitted the writer to use unpublished data on the occurrence and genesis of the Goldbanks(Nevada) quicksilver deposit, the investigation of which was made by the writer during the fall of 1938. Mr. W. T. Schaller and Mr. E. B. Eckel of the U. S. Geological Survey have assisted the writer in an attempt to ascertain the cause of the darkening of some cinnabar on exposure to sunlight.

The spectrographic analyses accompanying this paper were performed by Dr. M. F. Hasler, Applied Research Laboratories, Los Angeles. Much credit is due Dr. Hasler for perfecting techniques whereby large scale

spectrographic correlations could be obtained with a maximum of validity and with a minimum expenditure of time and money.

During the course of this investigation, the writer has had occasion to visit most of the operating quicksilver mines in the United States. During these collecting trips, the finest type of cooperation was shown by most of the mine operators and superintendents. This assistance is here gratefully acknowledged and it is hoped that some of the data here assembled will prove to be of practical value in solving problems in the mining and treatment of quicksilver ores.

Location of Deposits

Of a world production of 91,625 flasks (of 76 pounds each) of mercury during 1935, 17,518 were produced in the United States. Of this amount, 9,271 flasks were produced in California and 3,456 flasks in Oregon.[1] For many years, a great portion of the foreign production has come from Almaden in central Spain and from Idria and Monte Amiata in Italy.

Of the American production, a small amount comes from the Arkansas deposits in Pike County in the southwestern corner of the state.[2] The Terlingua mines in Brewster County, Texas have, in the past, been large producers.[3] A very small amount of quicksilver is produced in Arizona, mainly in the Mazatzal Mountains about seventy miles northwest of Globe.[4] A number of small quicksilver mines are scattered throughout Nevada and are sporadically operated to furnish a small annual production.[5]

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[1] Meyer, H. M., Quicksilver: In Minerals Yearbook for 1936, U. S. Bureau of Mines, pp. 689, 693, 1937.

[2] Reed, J. C., and Wells, F. G., Geology and ore deposits of the southwestern Arkansas quicksilver district: U. S. Geol. Survey Bull. 886-C, 1938.

[3] Philips, W. B., The quicksilver deposits of Brewster County, Texas: Econ. Geology, vol. 1, pp. 155-62, 1905.
Turner, H. W., The Terlingua quicksilver deposits: Econ. Geology, vol. 1, pp. 265-81, 1905.

[4] Ransome, F. L., Quicksilver deposits of the Mazatzal Range, Arizona: U. S. Geol. Survey Bull. 620, pp. 111-128, 1915.
Lausen, Carl and Gardner, E. D., Quicksilver resources of Arizona: Ariz. Bureau of Mines Bull. 122, 1927.

[5] Knopf, Adolph, Some cinnabar deposits in western Nevada: U. S. Geol. Survey Bull. 620, pp. 59-68, 1915.
Foshag, W. F., Quicksilver deposits of the Pilot Mountains, Mineral County, Nevada: U. S. Geol. Survey Bull. 795-E, 1927.
Schuette, C. N., Occurrence of quicksilver orebodies: Trans. Am. Inst. Min and Met Engineers, pp. 438-43, 1931.
Dreyer, R. M., Geology of the Goldbanks mining district, Pershing County, Nevada: U. S. Geol. Survey Unpublished manuscript.

Quicksilver is produced on a large scale in the southwestern,[1] central and southeastern[2] portions of Oregon. In the southwestern portion of the state the largest producers are the Black Butte (fifteen miles south of Cottage Grove) and the Bonanza (six miles east of Sutherlin). Each of these mines as well as the smaller War Eagle (twenty six miles north of Medford) were visited by the writer. In southeastern Oregon, the Opalite on the Nevada border just north of McDermitt is an old producer. More recently a number of mines have been opened in the Ochoco district, notably the Horse Heaven (about forty miles east of Ashwood), which was visited by the writer.

A very large number of quicksilver deposits are known in California and those discovered prior to 1918 are listed in State Mining Bureau Bulletin 78.[3] The general geology of several of the California mines was studied a number of years ago.[4] The largest producer in the state, at the present time, is the New Idria mine. Most of the producing mines in California were visited by the writer during 1937 and 1938, and representative suites were collected from all of the mines visited.

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[1] Wells, F. G., and Waters, A. C., Quicksilver deposits of southwestern Oregon: U. S. Geol. Survey Bull. 850, 1934.

[2] Schuette, C. N., Quicksilver in Oregon: Oregon Dept. of Geology and Mineral Industry, Bull. 4, 1938.

[3] Bradley, W.W., Quicksilver resources of California Min. Bureau Bull. 78, 1918. Many of the properties listed in this bulletin are little more than prospects and some are large producers no longer active - as, for example, New Almaden.

[4] Becker, G. F., Quicksilver deposits of the Pacific slope: U.S. Geol. Survey Mon. 13, 1888.

Following is a list of the mines visited in California:

Inyo County

Coso Hot Springs - three miles southwest of the Coso Hot Springs Resort.

Kern County

Cuddeback - one half mile north of the Tehachapi Loop.

San Luis Obsipo County

Klau - sixteen miles west of Paso Robles.

Oceanic - five miles southeast of New Idria.

San Benito County

New Idria - forty miles south by west of Mendota.

Aurora - five miles southeast of New Idria.

Contra Costa County

Mount Diablo - five miles east of Clayton.

Napa County

Aetna - nine miles northeast of Calistoga.

Oat Hill - two miles northwest of Aetna.

Sonoma County

Cloverdale - twelve miles east of the town of Cloverdale.

Lake County

Great Western - four miles southwest of Middletown.

Bradford - two miles southeast of Great Western.

Sulphur Bank - five miles north of the town of Lower Lake on the shore of Clear Lake.

GEOLOGICAL CHARACTERISTICS AND ENVIRONMENT OF QUICKSILVER MINERALIZATION

Mineralogy of Quicksilver Deposits

Following is a list of the known mercury bearing minerals:

Native mercury	Hg
Cinnabar	HgS
Metacinnabar	HgS
Guadalcazarite	Metacinnabar with up to 4% Zn
Tiemannite	HgSe
Coloradoite	HgTe
Onofrite	Hg(S,Se)
Lehrbachite	HgSe·PbSe
Livingstonite	$HgSb_4S_7$
Montroydite	HgO
Calomel	Hg_2Cl_2
Terlinguaite	HgClO
Eglestonite	Hg_4Cl_2O
Kleinite	Mercury ammonium chloride
Mosesite	Mercury ammonium chloride with SO_3 and H_2O
Ammiolite	Mercuric antimonite
Barcenite	Mercuric antimonite
Schwatzite	Tetrahedrite with 6-17% Hg
Leviglianite	Iron bearing guadalazarite
Magnolite	$HgTe_2O_4$
Coccinite	HgI
Tocornalite	Iodide of Hg and Ag.

Of the aforementioned minerals all but three are rare. Most quicksilver deposits have as their principal sulphide cinnabar. Many have small amounts of native mercury. Some few deposits have local concentrations of metacinnabar. The remainder of the minerals are characteristic of certain unusual occurrences as, for example, the chlorides and oxide at Terlingua, Texas[1], livingstonite, barcenite,

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[1] Cf. Hillebrand, W. F. and Schaller, W. T., The mercury minerals from Terlingua, Texas: U. S. Geol. Survey Bull. 405, 1909.

and guadalcazarite at Huitzuco, Guerrero, Mexico[1] and schwatzite in the Blue Mountains of Oregon.[2]

Marcasite and pyrite are frequently associated with cinnabar. Some of the California deposits contain small amounts of millerite (NiS) and local concentrations of hydrocarbons. Silicification is the predominant type of wall rock alteration. Carbonatization is not uncommon and, in a few deposits like Sulphur Bank, native sulphur is associated with the ore. The simple, common, uniform association of cinnabar, pyrite, marcasite, and silica is characteristic of many cinnabar deposits in the western United States. It is this simplicity of mineralization that permits the study of quicksilver geochemistry under controlled conditions which cannot be simulated in types of deposits where the presence of a number of complex sulphides renders necessary the consideration of the effect of a number of metallic ions in solution at the same time.

A study of the geochemistry of quicksilver mineralization is thus essentially a study of the geochemistry of mercuric sulphide. In this study, the following factors have been investigated: (1) The chemical and geological relationships of cinnabar and metacinnabar (2) The reasons for the not uncommon disseminations of native mercury in many deposits (3) The relation of pyrite and marcasite to the

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[1] Cf. Vaupell, C. W., Mercury deposits of Huitzuco, Guerrero, Mexico: Am. Inst of Min and Met. Engineers Technical Paper 842, 1937.

[2] Cf. Lindgren, Waldemar, The gold belt of the Blue Mountains of Oregon: U. S. Geol. Survey 22nd Ann. Rept., pt. 2, p.664, 1901.

quicksilver mineralizing solutions (4) The relationship of silicification and carbonatization to the quicksilver mineralizing solutions and (5) The significance of minor amounts of antimony and arsenic trisulphides in some quicksilver ores.

Geological Environment of Quicksilver Mineralization

Although the mineralogy of quicksilver deposits is both uniform and simple, the geological environment of deposition is highly varied. However, a number of the deposits occur in the same type of rock - namely, chalcedonized serpentine, an association so common that the silicified serpentine has long been given the name "quicksilver rock" in the northern California districts where this association is most characteristic. Since, in the early days, many more deposits were mined in serpentine than is now the case, the erroneous impression has been created that cinnabar deposits in the California Coast Ranges are confined to serpentine. Such is certainly not the case. At the Klau mine the wall rock is shale. Nearby at the Oceanic the cinnabar is disseminated through sandstone as is also a part of the ore at New Idria and Oat Hill. A large part of the ore at New Idria is in slate. At the Cuddeback mine and at the Coso Hot Spring deposit, the cinnabar is disseminated through kaolinized intrusives. At Sulphur Bank, the ore occurs in basalt and lacustrine gravels. The Aurora, Aetna, Bradford, Great Western, and Mount Diablo mines are confined to serpentine. In Oregon, the Black Butte and Horse Heaven mines occur in volcanics. The Bonanza is in sandstone and the War Eagle is in coal. The fact that a number of the deposits occur in different rock types and that several are confined to serpentine makes it possible to study the effect on mineralizing solutions of both similarities and differences in the country rock.

The structure of California quicksilver deposits has not been studied in detail since Becker's[1] monumental work was completed in 1888. Since 1888, many of the mines that Becker mapped have closed down and those mines that are still operating have long since exhausted the portions of the properties that were mapped for Monograph 13. Therefore only the broadest features of the structural geology presented in Monograph 13 are of significance today. This situation is unfortunate since it has rendered it impossible to correlate the petrographic work accompanying this investigation with the detailed geologic structure of each district. Nevertheless, it is possible to fulfill the purpose of this investigation by correlating petrographic and geochemical data. It is, of course, obvious, moreover, that a geochemical study of mineralization presents only one aspect of the problem of quicksilver concentration since the structural control is of equal importance in determining the course of mineralization.

Of significance, however, in the light of geochemical data to be presented, is the hypothesis formulated by Schuette[2] concerning structural control of quicksilver mineralization. After a study of the published reports on most of the important quicksilver deposits of the world - a study supplemented by long experience and personal observation - Schuette has advanced the theory that the large, high-grade quicksilver deposits are those which have been deposited against some type of geologic trap and that, where no such trap is present,

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[1] Becker, G. F., Op. cit.

[2] Schuette, C. N., Occurrence of quicksilver orebodies, pp. 403-88.

the deposits are always small and ephemeral in character. Such a hypothesis applies, to a certain extent, to any hydrothermally formed ore deposit, but, as will be noted, it is of particular significance in quicksilver mineralization.

Physical Environment of Quicksilver Mineralization

No geologically significant study of mineralization can be pursued under ordinary laboratory conditions without making the assumption that the natural processes of mineralization occur in a physical environment which can be simulated closely in the laboratory. The entire validity of the interpretation of experimental work on any type of mineralization is dependent on the validity of the assumptions that are made concerning physical conditions under which mineralization occurs. In reference to quicksilver mineralization, there is an abundance of evidence that by far the greater number of deposits are formed by hydrothermal solutions at temperatures varying between 100 and 150°C and at pressures approaching atmospheric. Such physical conditions can be simulated easily in the laboratory. Following is the evidence suggesting shallow deposition by hydrothermal solutions in a physical environment similar to that obtainable under surface conditions:

(1) Mercuric sulphides can be formed easily in the laboratory at atmospheric pressures and at temperatures below the boiling point of water.

(2) Small amounts of native mercury occur in many quicksilver deposits. At room temperature, mercury has a small, but perceptible, vapor pressure. At 260°C, the vapor pressure is 100 mm. and, at 357°, the volatilization point (760 mm.) is reached. Thus, without evidence of containing pressures (and, at most quicksilver deposits, the rocks are markedly porous and fractured), native mercury would not be stable

at high temperatures.

(3) Cinnabar occurs in the sinter of active hot springs as at Steamboat Springs[1] and at the Great Geyser of Iceland.[2]

(4) Cinnabar occurs in the sinter of springs or in the tubes of geysers no longer active as, for example, (a) the occurrence of cinnabar in the old sinter at Steamboat Springs[3] (b) the occurrence, in the Goldbanks district, Nevada, of a commercially productive cinnabar deposit that was formed syngenetically with a silica apron deposited by thermal springs[4] and (c) the occurrence of a quicksilver deposit in old geyser tubes at Huitzuco, Guerrero, Mexico.[5]

(5) Quicksilver deposits are commonly associated with areas of recent volcanism and active thermal springs. The presence of thermal springs at or in close proximity to quicksilver deposits in the California Coast Ranges is a common rather than an uncommon feature. For example, hot springs flow at Sulphur Bank. A short distance from the Cloverdale mine and from a number of adjacent, smaller quicksilver deposits is a group of silica bearing hot springs incorrectly known as "The Geysers". The entire northern California district is an area where large flows of basalt have only recently been extruded and, throughout the area, thermal springs are extremely common. Near the Coso Hot Springs deposit are a series of active

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[1] Becker, G. F. Op. cit., pp. 25-6.
[2] Ibid., p. 344.
[3] Ibid., p. 350.
[4] Dreyer, R. M., Op. cit.
[5] Vaupell, C. W., Op. cit.

thermal springs and the deposit itself is the site of fumarolic activity. Six miles north of the Goldbanks deposit is a group of hot springs which have deposited a siliceous sinter strikingly similar to that with which the cinnabar deposits are associated. A great many other examples could be cited.

(6) The near-surface ephemeral character of most quicksilver deposits suggests near-surface deposition. There are, of course, several notable exceptions to this generalization probably representing deposits where uniform physical and chemical conditions prevailed over a wide vertical range, but bay far the greater number of quicksilver deposits are not only confined to a range of within one or two hundred feet from the surface, but are exhausted after only a relatively small production.

(7) Chalcedonization, common in quicksilver deposits, is generally associated with low temperature types of mineralization.

(8) The common presence, in quicksilver deposits, of open, often crustified veins is another indication of low temperatures and pressures.

In direct contrast to all of the evidence indicating deposition under low temperatures and pressures is the absence of any evidence which would make it necessary to postulate either high temperatures or high pressures. Although no single line of evidence presented above is sufficient in itself to prove low temperature, low pressure, near surface deposition, the cumulative value of all lines of evidence makes it appear valid to assume that physical conditions which are readily obtainable in the laboratory simulate closely the natural environment of quicksilver mineralization.

CHEMICAL STUDIES OF QUICKSILVER MINERALIZATION

Introduction

It has been mentioned that, on account of the extreme simplicity of quicksilver mineralization, the study of quicksilver geochemistry involves essentially a study of mercuric sulphide and of the relation of mercuric sulphide to the few minerals with which it is commonly associated.

Because of the early desire to produce a satisfactory vermilion pigment, the preparation of mercuric sulphide has been studied since the dawn of alchemy and the various formulae for the preparation of vermilion were highly prized by the early alchemists. Most of the papers on the subject are, unfortunately, very old and many were published before the development of modern chemical theories so that they involve little more than a description of isolated experiments and preparations without furnishing any real information as to the chemical principles underlying the results obtained. Of 104 papers on the chemistry of mercuric sulphide listed by Mellor[1], 84 were published before 1899, 16 between 1899 and 1909, and 4 since 1909. It has been over twenty years since any work has been published on quicksilver geochemistry. Fortunately, however, there are several papers which, taken together, furnish a good basis for further investigations of the geochemistry of mercuric sulphide.

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[1] Mellor, J. W., A comprehensive treatise on inorganic and theoretical chemistry, vol. 4, pp. 957-61, 1923.

The Solution of Mercuric Sulphide

The mode of preparation and the chemical properties of mercuric sulphide have been studied for many centuries. It was learned at an early date that, whereas the black sulphide can be prepared by the reaction of an acid solution of any mercuric salt with hydrogen sulphide or even by the trituration of mercury with sulphur, the formation of the red sulphide can occur only under very definite chemical conditions. The production of the normal red mercuric sulphide (cinnabar) can be resolved into two general processes - the wet and the dry preparations. The dry preparation has long been used for the commercial production of vermilion since it involves the use of no material other than the two integral components of mercuric sulphide. Mercury and sulphur are triturated together and gently heated to form the black sulphide. The black sulphide is then sublimed in the absence of air and vermilion is condensed. In the presence of air, the sulphur is oxidized to sulphur dioxide and the mercury is reduced to the elemental state. This latter procedure is used in the recovery of mercury from its ores. The wet process depends on the solubility of mercuric sulphide in alkaline solutions of the alkaline sulphides. When these solutions are concentrated, the mercuric sulphide is precipitated.

S. B. Christy[1] was the first scientist to correlate the wet process of chemical preparation with the natural deposition of

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[1] Christy, S. B., On the genesis of quicksilver deposits: Am. Jour. Sci., 3rd series, vol. 17, pp. 453-63, 1879.

cinnabar. Christy was much impressed by the widespread hydrothermal alteration associated with the California quicksilver deposits (and more especially by the intense silicification) and concluded that the deposits must be formed by hydrothermal deposition from the same type of solutions from which red mercuric sulphide can be precipitated in the laboratory - namely alkaline sulphide solutions. Such solutions would also be capable of dissolving silica. This hypothesis was a marked departure from the early concept that natural cinnabar was formed by the condensation of a sublimate and Christy found it necessary to state several reasons why the sublimation hypothesis seemed impossible; viz.:

(1) Cinnabar does not volatilize below 500°C and, with a normal geothermal gradient, such a temperature would not be achieved (according to Christy) unless the cinnabar were deposited at a far greater depth than is indicated geologically. Since Christy's time, the low temperature, near surface character of much quicksilver mineralization has been established by more sound geologic reasoning.

(2) The second point in Christy's argument was that cinnabar is definitely associated with hydrothermal alteration (silicification and carbonatization) of a type that cannot have been formed by sublimation. More recent work has emphasized the marked syngenesis of cinnabar with silica in many of the deposits - a relationship so marked that, in many cases, the cinnabar is actually dispersed through the silica.

(3) The deposition of bitumens (found in several of the California

quicksilver mines) seemed to Christy to be difficultly explicable by the volatilization hypothesis.

(4) Lastly, the similarity in composition of the thermal spring waters, flowing near many of the quicksilver mines, to the solutions from which cinnabar can be precipitated in the laboratory led Christy to believe that the wet method of preparing cinnabar (by the concentration of alkaline sulphide solutions) was a more suitable explanation than the condensation of gaseous sublimates.

Christy's work was ingenious, but it lacked detailed chemical and geological investigations to support the hypotheses advanced. It remained for Becker,[1] several years later, to show that Christy's hypothesis was not only adequate, but is the only one by which quicksilver mineralization can be explained.

After mapping a large number of quicksilver deposits, Becker realized that any theory explaining quicksilver mineralization must likewise explain a number of other features characteristic of quicksilver deposits. Like Christy, Becker noted the marked hydrothermal alteration and also the association of quicksilver deposits with areas of recent volcanism and thermal activity and quickly realized that such an association must indicate hydrothermal mineralization. Since the only type of solution from which cinnabar can be precipitated is an alkaline sulphide solution, Becker sought to ascertain if mineralization by such solutions could explain not only the occurrence

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[1] Becker, G. F., Op. cit. Page citations to this work in the ensuing geochemical discussion will be made as follows: (B, pp.).

of cinnabar, but also the occurrence of other sulphides and wall rock alteration products characteristic of quicksilver deposits.

Becker determined experimentally that the sulphides of mercury (which would be the compound of mercury formed from any mercury salt in a sulphide solution) as well as the trisulphides of arsenic and antimony are readily soluble in alkaline sulphide solutions(B, pp. 423-4, 434). Becker likewise stated that pyrite is soluble in sodium sulphide solutions; that the solubility increases with an increase in temperature; and that marcasite is more readily soluble than pyrite (B, pp. 432-3). Foreman,[1] however, has made a detailed study of the solubility of iron disulphide in sodium sulphide solutions and has found that pyrite is insoluble even in concentrated sodium sulphide solutions. Experiments by the writer have substantiated Foreman's findings. Gold, which Becker reports in small amounts from several quicksilver mines, is likewise soluble in alkaline sulphide solutions to the extent of 1:843 (B, p. 433). Since these solubilities probably depend on equilibria, Becker's quantitative determinations, except as showing an order of magnitude, are of little significance. As will be shown, such solutions as are under consideration must be alkaline and silica is known to be soluble in alkaline solutions.[2] It might also be mentioned that germanium disulphide (M, vol. 7, p. 275) and stannic sulphide (M, vol. 7, p. 472) are likewise readily soluble in alkaline

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1 Foreman, Fred, Hydrothermal experiments on solubility, hydrolysis, and and oxidation of iron and copper sulphides: Econ. Geology, vol. 24, pp. 811-37, 1929.

2 Mellor, J. W., Op. cit., vol. 6, pp. 282-4. Hereafter references to Mellor will be written "M" followed by volume and page citations.

sulphide solutions. Nickel sulphide is also soluble in alkaline sulphide solutions (M, vol. 15, p. 441). Lead sulphide is very slightly soluble (M, vol. 7, pp. 790-1) and silver sulphide is still more insoluble (M, vol. 3, p. 445). Becker's work was published long before the theories of ionic equilibria had received general acceptance and, hence, much of the chemistry of alkaline sulphide solutions that troubled him now seems quite clear. For example, Becker did not understand the relation between sodium sulphydrate (NaHS) and sodium sulphide (Na_2S) in reference to the solubility of mercuric sulphide or the function of alkaline hydroxide in increasing the solubility. A large portion of his geochemical discussion consists of unsuccessful attempts to explain the numerous contradictions that had arisen regarding the function of these compounds. It was not until some years later that the solution of mercuric sulphide in alkaline sulphide solutions was explained in the light of ionic equilibria by Knox.[1]

Knox (K, p. 477) showed that the solubility of mercuric sulphide in alkaline sulphide solutions involves the formation of a soluble sulphide complex, R_2HgS_2 (where R is an alkali metal). The equilibrium involved is then

$$HgS + Na_2S \rightleftarrows Na_2HgS_2$$

or, more generally,

$$HgS + S^{=} \rightleftarrows HgS_2^{=}.$$

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[1] Knox, Joseph, Zur Kenntnis der Ionenbildungen des Schwefels und der komplex Ionen des Quecksilbers: Zeit. fur Elektrochemie, Bd. 12, pp. 477-81, 1906. References to this paper will be marked (K, pp.).

The shifting of this equilibrium is caused by a variation in the concentration of sulphide ion in solution. When the equation is shifted to the right, mercuric sulphide is dissolved. When the equation is shifted to the left, mercuric sulphide is precipitated. The ionization of an alkaline sulphide such as sodium sulphide is given by the following reaction:

$$Na_2S + 2H_2O \rightleftarrows NaHS + NaOH + H_2O \rightleftarrows H_2S + 2NaOH$$

or, more generally,

$$S'' + 2H_2O \rightleftarrows HS' + OH' + H_2O \rightleftarrows H_2S + 2OH'.$$

Since it is only the sulphide ion which combines with the mercuric sulphide to produce the soluble sulphide complex, it is necessary to shift the equilibrium in such a way that the sulphide ion (S'') forms instead of the sulphydrate ion (HS') or hydrogen sulphide (H_2S). From the equation for the ionization equilibrium of an alkaline sulphide, it can be seen that the sulphide ion concentration can be increased by increasing the alkalinity of the solution. Some mercuric sulphide will be dissolved by alkaline sulphide, however, even in neutral solution since in neutral solutions some sulphide ions are likewise present. In acid solution, however, the hydrolysis of the sodium sulphide is accelerated and the solution of mercuric sulphide is halted. The concentration of sulphide ion is thus determined by (a) the original concentration of alkaline sulphide and (b) the alkalinity of the solution. Table 1 (K, p. 477) shows the decrease in solubility of red and black mercuric sulphide with a decreasing concentration of sodium sulphide in the absence of sodium hydroxide. This, of course,

Table 1

Relation of Solubility of HgS to the Concentration of Na_2S

Conc. Na_2S Mole/liter	Red HgS dissolved Mole/liter	Ratio red HgS: Na_2S	HgS black dissolved	Ratio HgS black: HgS red
2.030	1.144	0.5635	-	-
1.52	0.7832	0.5153	0.8561	1.09
1.015	0.4425	0.4328	0.5002	1.13
0.755	0.2878	0.3812	0.3336	1.16
0.50	0.1500	0.3006	0.1805	1.20
0.25	0.04544	0.1818	0.05622	1.24
0.10	0.008241	0.0824	0.01085	1.32

results from the increased hydrolysis of the alkaline sulphide on dilution and a corresponding decrease in sulphide ion concentration. The table also shows that the black sulphide is more soluble in dilute solutions and hence is the less stable form. Table 2 (K,p.478) shows that the solubility of mercuric sulphide in alkaline sulphide solutions decreases slightly with an increase in temperature. As Knox notes (K, pp. 478-9), the factors that cause a decrease in solubility are the decrease in ionization of the sulphide complex and an increased hydrolysis of the sodium sulphide with increased temperature. Counteracting this effect and reducing the size of the negative temperature coefficient is the fact that the solubility of mercuric sulphide varies

Table 2

Decrease in Solubility of HgS with an Increase in Temperature

Conc. Na_2S Mole/liter	Cinnabar dissolved (in mole/liter) at 33°	25°
0.755	0.2828	0.2878
0.5	0.1465	0.1500
0.25	0.04360	0.04544
0.10	0.007887	0.00824

directly with temperature. Table 3 (K, p. 478) shows the effect of

Table 3

Variation in Solubility of HgS with an Increase in Alkalinity

Conc. Na_2S Mole/liter	HgS dissolved (in moles/liter) in Na_2S with Pure Na_2S	0.5N NaOH	1.0N NaOH	4.48N NaOH	4.67N NaOH	7.7N NaOH	Ratio HgS:Na_2S in solution with 7.7N NaOH added
1.015	0.4423	-	0.673	-	-	0.9167	0.903
0.755	0.2878	-	0.485	-	-	-	-
0.50	0.1500	0.2483	0.302	0.435	-	0.4637	0.927
0.25	0.4544	0.1106	0.148	-	0.225	0.2369	0.948
0.10	0.008241	0.0396	0.056	-	0.090	0.09634	0.963

alkali hydroxide in increasing the solubility of mercuric sulphide by decreasing the hydrolysis of the sulphide ion. However, a very strongly alkaline solution is needed before the hydrolysis is anywhere nearly completely halted.

The significance of these features of ionic equilibria in the geochemistry of quicksilver mineralization has been completely overlooked. Following are some of the significant features to be noted:

(1) Decreased temperature actually causes an increased solubility of the mercuric sulphide.

(2) Any hydrogen sulphide solution which is alkaline will have the ionization equilibrium displaced in such a manner that the hydrogen sulphide is largely dissociated. Thus there will be an abundance of sulphide ions capable of entering into the soluble mercuric sulphide complex.

(3) Alkaline solutions are capable of dissolving silica. Hence, the common occurrence of silicification around quicksilver deposits is to be expected.

(4) By the equilibrium equation for carbonic acid

$$CO_3'' + 2H_2O \rightleftarrows HCO_3' + OH' + H_2O \rightleftarrows H_2CO_3 + 2OH' ,$$

in any alkaline solution the equation must be shifted to the left so that an abundance of carbonate ions are formed. The fact that carbonate ions are present in solution means that alkaline earth ions (as calcium and magnesium) cannot exist in the same solution otherwise they would combine with the carbonate ions to form a precipitate of a mineral carbonate. The carbonatization associated with some quicksilver ores must thus have been accomplished at a time when the mineralizing solutions were slightly acid and must thus be distinct from the period of cinnabar deposition.

(5) Except that they are somewhat more soluble, the trisulphides of arsenic and antimony form sulphide complexes in the presence of an excess of sulphide ion. These complexes are exactly analogous to that of mercury. The common association of small amounts of arsenic and antimony with quicksilver ores is thus to be expected.

Precipitation of Mercuric Sulphide

By the equilibrium equation

$$HgS + S^{''} \rightleftharpoons HgS^{''}_{2},$$

any factor which tends to decrease the sulphide ion concentration relative to the total concentration of mercuric sulphide or to increase the concentration of mercuric sulphide relative to the total sulphide ion concentration or relative to the total volume of solvent will cause some of the mercuric sulphide to be precipitated until the solution is again in equilibrium. The precipitate resulting from such an adjustment to equilibrium is not, in all cases, the same. Therefore, it is desirable to examine each of the factors which may displace the equilibrium of any mineralizing solution and see which of these agencies can be responsible for the deposition of quicksilver ores. The factors which can possibly cause a displacement of equilibrium in any mineralizing solutions are listed below:

(1) Decrease of temperature as the mineralizing solutions approach either the surface or some other cool horizon.

(2) Relief of pressure as a result of escape of gases at the surface or through fractures connecting with the surface.

(3) Increase in acidity of solutions on reaching surficial oxidizing zones.

(4) Dilution of solutions by ground water or by undersaturated juvenile waters.

(5) Reaction of the mineralizing solutions with components of the wall rock which are not in equilibrium with the solutions.

(6) Concentration of solutions as a result of a gradual evaporation of the solvent.

Each of these factors which may tend to displace the equilibrium of the solutions will be examined separately in an attempt to ascertain which factors are competent to explain the precipitation of quicksilver ores in their usual form.

A. Effect of a Decrease in Temperature.

The solubility of mercuric sulphide has been shown (in Table 2) to increase slightly with a decrease in temperature. Assuming that the increased solubility bears a linear relationship to the increase shown in Table 2, the increased solubility corresponding to a decreased temperature is very small. That the relationship is essentially linear is shown by the fact that a saturated alkaline mercuric sulphide complex solution, when heated to boiling, precipitates only a very small portion of the contained cinnabar. It is important to note, however, that a decreasing temperature is not in itself an agency capable of precipitating cinnabar. In fact, some other precipitating agency must overcome the slight increase in solubility caused by a decreasing temperature. This increase in solubility with decreasing temperature is more marked, however, than would be indicated by the figures in Table 2 since such a decreased temperature will likewise decrease the rate of evaporation and thus decrease the effect of concentration by evaporation.

Indirectly, however, there is one way in which a decrease in temperature can serve as a precipitant of cinnabar. Becker (B, p. 260) noted the presence of ammonia in the thermal waters at Sulphur Bank as has also the writer. Becker determined empirically that, at normal temperatures, ammonium salts would cause the precipitation of mercuric sulphide from alkaline sulphide solutions, but that, when the temperature was raised, the sulphide was re-dissolved (B, pp. 269-70). By the principles of ionic equilibria, this reaction is easily explained. At low temperatures, ammonium ion combines with any excess of hydroxyl ion to form the weakly ionized ammonium hydroxide. The consequent removal of hydroxyl ions from solution permits the partial hydrolysis of the sulphide ion and hence causes a decreased solubilty of mercuric sulphide. When the solution is heated, ammonia is volatilized. Ammonium ions are thus removed from the system and there is an increased hydroxyl ion concentration resulting in a decreased hydrolysis of the sulphide ion and a correspondingly increased solubility of mercuric sulphide. Conversely, a decrease in temperature will cause a decrease in the solubility of mercuric sulphide in such ammoniacal solutions.

How common ammonia is in quicksilver mineralizing solutions at the time of mineralization is not known. Suffice it to say that ammonia has been detected in the thermal springs flowing near quicksilver deposits at few localities besides Sulphur Bank. At any rate, except in the presence of ammonia, a decrease in temperature will increase rather than decrease the solubility of mercuric sulphide. A decreasing temperature is not, therefore, in itself a precipitating agency.

B. Effect of a Decrease in Pressure.

The principal result of a decrease of pressure in alkaline sulphide solutions is to allow more of the liquid to enter the vapor phase. The rate of evaporation and concentration of the solution is thus accelerated. When the concentration exceeds the solubility of the mercuric sulphide, precipitation of the sulphide will occur. When mineralizing solutions gain access to the surface, the decrease in pressure may be sufficiently abrupt to cause the precipitation of large amounts of cinnabar. In solutions containing ammonia, the increased volatility of the ammonia resulting from decreased pressure will tend to counteract this concentration of solution resulting from an increased rate of evaporation since, as has been shown, an increased volatility of ammonia causes an increased solubility of mercuric sulphide. Judging by active thermal springs, probably the majority of quicksilver mineralizing solutions contained no ammonia. For these solutions, a decrease in pressure, but not a decrease in temperature, would be a predominating precipitating agency. In mineralizing solutions containing ammonia, a decrease in temperature rather than a decrease in pressure would be a predominating precipitating agency. In mineralizing solutions containing no ammonia, the decrease in pressure necessary to cause a precipitation of mercuric sulphide must be sufficient to counteract any increased solubility resulting from decreased temperature . Similarly, in ammoniacal solutions, before precipitation can begin, the decreased solubility of mercuric sulphide due to decreased temperature must be sufficient to counteract any increased solubility that may result from a decrease of pressure.

C. Effect of Increased Acidity.

Any reduction of the alkalinity of an alkaline sulphide solution will accelerate the hydrolysis of the sulphide ion and hence will decrease the solubility of the mercuric sulphide. In acid solutions, the hydrolysis goes nearly to completion and the mercuric sulphide is almost completely precipitated. However, when alkaline sulphide solutions containing dissolved mercuric sulphide are acidified at temperatures below 200°, only the black mercuric sulphide (metacinnabar) is precipitated.[1] That metacinnabar is a monotropic form of mercuric sulphide in contrast to the stable cinnabar is shown by the fact that, in acid solutions above 200° and in alkaline solutions above 100°, metacinnabar is converted to cinnabar (AC, p. 378). Conversely, once cinnabar has been precipitated, it is stable in all solutions up to the volatilization point (AC, p. 377).

Allen and Crenshaw likewise experimented with the precipitation of mercuric sulphide in sodium thiosulphate solutions (AC, pp. 369-73). Sodium thiosulphate and sodium chloride were dissolved with an excess of mercuric chloride in water. When precipitation is induced, the first precipitate is the white $HgCl_2 \cdot 2HgS$. This precipitate continues to form until the ratio of $HgCl_2 : Na_2S_2O_3$ falls to 3:2. At this concentration, metacinnabar begins to precipitate until the ratio falls to 1:4 at which point a red mercuric sulphide begins to precipitate.

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[1] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline form and genetic conditions: Am. Jour. Sci., 4th series, vol. 34, pp. 341-96, 1912. References to this paper will be made (AC, pp.).

This red mercuric sulphide is said to have a lower specific gravity and lower indices of refraction than ordinary cinnabar (AC, p. 377). This third form (named b-HgS) is likewise monotropic and inverts to cinnabar at 100° in alkaline sulphide solution (AC, p. 377).

The writer prepared the three forms of mercuric sulphide following the directions given by Allen and Crenshaw. Professor J. H. Sturdivant, Division of Chemistry, California Institute of Technology, obtained X-ray powder diffraction patterns for artificial metacinnabar, b-HgS, and natural cinnabar(from the Klau mine). The metacinnabar was found to be isometric as previously determined (AC, p. 374) and the b-HgS and natural cinnabar were both found to be hexagonal as reported (AC, p. 393) although a preliminary study has led Dr. Sturdivant to believe that the crystal structure of cinnabar has been interpreted incorrectly. Further work on this problem is in progress. The significant point, however, is that the powder diffraction patterns of cinnabar and b-HgS are identical. The minimum specific gravity given for cinnabar is 8.176 (AC, p. 369) whereas the maximum specific gravity of b-HgS is stated to be 7.221 (AC, p. 377). This is a difference of over 11% whereas any difference in gravity of over 3% (and probably of over 1%) will be revealed by differences in X-ray pattern. The X-ray diffraction patterns of these two compounds are identical and this identity raises the question as to whether b-HgS is actually a distinct form of mercuric sulphide or whether the published gravity and index determinations are in error so that, as appears probable, cinnabar and b-HgS are identical.

Metacinnabar is an uncommon mineral in quicksilver deposits. For this reason, the relation of metacinnabar to cinnabar has been only slightly studied. Becker mentioned the occurrence of metacinnabar at the Knoxville mine (B, p. 285). Unfortunately, the portions of this property containing metacinnabar were inaccessible at the time of Becker's visit although he stated that "Specimens show that it (metacinnabar) was accompanied by opal and marcasite and that it was, in some cases, coated by cinnabar as if in the process of conversion". Metacinnabar also occurred in some of the old workings at New Idria (B, p. 302). The occurrence of metacinnabar at the Culver-Baer, Hastings, and Redd mines has also been noted,[1] but the relationship of metacinnabar to cinnabar in the ore from these mines is not known. The petrographic relationships of metacinnabar and cinnabar in ore from the Mount Diablo mine will be described subsequently.

The scarcity of metacinnabar suggests that increased acidity is not an important factor in the precipitation of most quicksilver ores. It has been noted that, in acid solutions below 200°, only metacinnabar is precipitated. In acid solutions above 200°, metacinnabar will be the first precipitate, but will be slowly converted to cinnabar. Similarly, metacinnabar is converted to cinnabar in alkaline sulphide solutions at about 100°. Were increased acidity an important precipitating agency, despite the absence of metacinnabar in most deposits, one of the following changes must have occurred: (1) A temperature above 200° must have existed. It is doubtful whether aqueous solutions

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[1] Bradley, W. W., Op. cit., pp. 172, 185, 205.

near the surface could attain so high a temperature in the porous fractured country rocks in which cinnabar ores commonly occur and many reasons have been cited for believing that the temperatures of such quicksilver mineralizing solutions are quite low. Even granting such high temperatures, the slow rate of conversion of metacinnabar to cinnabar in acid solutions makes it unlikely that the metacinnabar would be completely converted to cinnabar. Metacinnabar, however, is notably absent in many deposits. (2) A new influx of alkaline sulphide solutions would be needed. Metacinnabar is easily converted to cinnabar in such solutions. However, if physical conditions are such as to oxidize and hence acidify the solutions during one stage of the period of mineralization, it is difficult to see why, during a later stage of the mineralization, similar solutions should not be acidified likewise.

For these reasons, it is believed that increased acidity is not generally a common cause for the precipitation of mercuric sulphide although it may account for the local concentrations of metacinnabar that have been reported. It is to be noted, moreover, that wherever metacinnabar occurs it could easily have been deposited, merely by acidification, from the same type of hypogene solutions that deposited the associated cinnabar.

D. Effect of Dilution.

It is possible that mineralizing solutions may come in contact with ground water or that there may be an influx of dilute juvenile waters. The admixture of ground water or dilute juvenile water may effect a dilution and neutralization of solution sufficient to cause precipitation. Hence, it is desirable to note the effect of dilution on quicksilver mineralizing solutions.

By the fundamental equations

$$HgS + S'' \rightleftarrows HgS_2''$$

$$S'' + 2H_2O \rightleftarrows HS' + OH' + H_2O \rightleftarrows H_2S + 2OH',$$

whenever the hydroxyl ion concentration drops sufficiently to allow the hydrolysis of the sulphide ion to proceed to a point where there is a deficiency of sulphide ion in relation to mercuric sulphide, some of the mercuric sulphide will be precipitated. However, if the alkalinity of the solution is maintained so as to largely inhibit hydrolysis, no precipitation will occur regardless of the volume of alkaline solution in which the sulphide complex is dissolved. Therefore the problem of dilution is very similar to that of acidification except that, with an increased acidity, the hydrolysis goes immediately nearly to completion whereas, with dilution, the hydrolysis and hence the precipitation are most gradual. Becker gave quantitative estimates of the amount of dilution necessary to cause precipitation. Quantitative estimates of the amount of dilution necessary to effect precipitation are of little significance since the reaction depends on equilibrium relations. Such estimates, however, do show the extreme dilution that is necessary before precipitation will occur. Becker (B, pp. 429-30) placed Na_2S, NaOH, and HgS in solution in a ratio of 2.04:1.38:1 so that 0.3349 g. of HgS were present in 3.9 cc. of solution or 86 g. per liter. This solution would contain, in moles per liter, 0.37 HgS, 2.8 NaOH, and 2.6 Na_2S. Precipitation began when 25 cc. of water had been added to the 3.9 cc. or when the solution was 0.13 of its original concentration and continued until 100 cc. of water had been added. The writer prepared a solution containing 0.42 moles Na_2S, 1.8 moles KOH, and 0.17 moles HgS per liter. No precipitation occurred until the solution was diluted to 1/30 of its original concentration. This is a large dilution, but the dilution needed to effect precipitation is dependent only on the available sulphide ion concentration which is, in turn, dependent on the alkalinity of the solution.

The precipitate formed by dilution is metacinnabar, not cinnabar. Becker stated that metallic mercury was precipitated with the black sulphide (B, p. 431), but the writer could not confirm this statement since visual examination of the precipitate resulting from dilution showed no free mercury. Moreover, after the precipitate was washed with nitric acid, the filtrate gave no test for mercury. However, it was found that, after filtering the precipitated metacinnabar, the filtrate still remained brown. If this filtrate is boiled, a mercury mirror is deposited indicating that colloidal mercury is formed at the same time that the metacinnabar is precipitated. If the alkaline mercuric sulphide complex solution is boiled and diluted with boiling water, the resulting solution is colorless and no mercury mirror is formed by further boiling the filtrate. Thus, in boiling water, the mercury is coagulated and precipitated with the metacinnabar.

Native mercury is commonly disseminated in small amounts through many quicksilver deposits. At some mines, native mercury is present in relatively large amounts. Although Becker (B, p. 431) noted the effect of dilution as a precipitant of native mercury, the presence of native mercury is generally attributed to reduction by organic matter or other reducing agencies in the wall rock.[1] It is probably true that organic compounds can be found which will reduce the mercuric sulphide complex to native mercury. Nevertheless, the writer feels, for the following reasons, that such organic reduction is only a minor cause of the precipitation of native mercury: (1) Solutions containing mercuric sulphide dissolved in alkaline sulphide were placed in contact with coal and charcoal for a considerable period of time and no native mercury was precipitated. (2) At the War Eagle mine in southwestern Oregon, cinnabar has been mined from coal beds. Were organic material a potent reducer of quicksilver mineralizing solutions, it is difficult to see why cinnabar rather than native mercury should have been precipitated on the coal. (3) The writer has found globules of native quicksilver in basalt at Sulphur Bank. It would be difficult to explain the presence of organic matter in basalt.

It is to be expected that, during the course of mineralization, ground waters should occasionally dilute the mineralizing solutions to such an extent as to precipitate mercuric sulphide and native mercury. Since the flow of ground waters and of thermal solutions is a most variable factor over a long period of time, there is no reason to believe that, after one epoch of dilution, the quantity of ground water

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[1] Cf. Emmons, W. H., Enrichment of ore deposits: U. S. Geol. Survey Bull. 625, p. 394, 1917.

relative to the mineralizing solutions should not decrease. The mineralizing solutions would then be strong enough to convert the metacinnabar formed during dilution into cinnabar. It is notable, moreover, that alkaline sulphide solutions have no effect on metallic mercury. The writer has found that it is only when the solutions are acid so that abundant hydrogen sulphide is produced that a coating of metacinnabar is formed on the metallic mercury. The fact that native mercury is not tarnished,even where it is found in cavities (as at Sulphur Bank) in which it could not have been disturbed, indicates that the solutions must have been alkaline as previously postulated and that the hydrogen sulphide vapors found around many thermal springs are often the result only of oxidation (and attendant acidification) at the surface. Since metacinnabar is readily converted to cinnabar in alkaline sulphide solutions whereas metallic mercury is unaffected, it is believed that the periodic dilution and reconcentration of solutions furnishes the best means of explaining the occurrence of native mercury. However, since (1) a marked dilution is necessary to precipitate mercuric sulphide and (2) the quantity of native mercury in most deposits is small, it appears that dilution is probably not a major factor in the formation of most cinnabar concentrations.

Mention is frequently made of the possibility of native mercury having been deposited as a sublimate. A number of reasons have been given for believing that quicksilver deposits are formed at very low temperatures and pressures - the temperature probably not exceeding

150°. At 150°, the vapor pressure of mercury is negligible and it is not until 260° that the vapor pressure reaches 100 mm. It is, therefore, possible, but not probable, that native mercury has been deposited as a sublimate. However, if mercury vapors were present during mineralization, they must have been carried along with the solution as vapor and cannot have resulted from any decomposition of the solutions by heat since high temperatures will serve only to evaporate the solutions and precipitate cinnabar. Cinnabar is stable up to its volatilization point and has no appreciable vapor pressure below 300°. Thus, native mercury could not result from a decomposition of the mineralizing solutions, but could, conceivably be carried in as a vapor accompanying the solutions. Whether such a situation is possible would involve a study of the stability relations of mercury vapor in the presence of alkaline sulphide solutions at temperatures above 150°. In any case, deposition as a sublimate is not a postulate necessary to explain the presence of native mercury in a deposit.

E. Effect of Wall Rock.

The effect of the wall rock in causing precipitation from mineralizing solutions is the integrated effect of all individual components of the rock which are out of equilibrium with the solutions and which, in an attempt to restore equilibrium, cause precipitation. The complexity of wall rocks and the wide variability in type renders it impossible to predict what precipitative effect each wall rock will have. However, in order to ascertain empirically what effect wall rock has in causing precipitation, the following experiment was performed: A solution was prepared containing 0.42 moles Na_2S, 1.8 moles KOH, and 0.15 moles HgS per liter. Into 15 cc. portions of this solution were put two rock slices from each of a number of deposits containing different types of wall rock. A second standard solution was prepared containing the aforementioned components plus 200 cc. of water glass per liter. (The water glass was 40° Be, S.G. 1.381 and had a molecular ratio SiO_2:Na_2O of 3.12. There was thus 24.6% silica in the water glass or 49 grams of SiO_2 per liter.) Into 15 cc. portions of this second standard solution were placed two slices of the same rocks from the same districts. All of the solutions were sealed with paraffin. The solutions were examined at the end of two, four, and eleven days and again at the end of four months. The mercuric sulphide precipitates were classified quantitatively as light, medium, and heavy. The two end members of the classification were reserved for extreme cases. The results of the experiment are tabulated in Table 4. Many of the precipitates classified as light consist of only a few scattered grains. Although such wall rock precipitation would undoubtedly vary with variations in a given rock type and would depend, to a certain extent, on variations in temperature and pressure, nevertheless, certain generalizations can be drawn from the results presented in Table 4. These generalizations are listed below:

(1) The precipitation was practically complete after two days. The amount of precipitate was practically the same after four months as after two days. Hence, the amount of precipitate is listed as the

Effect of Wall Rock in Precipitating Mercuric Sulphide

Rock	Volume of precipitate after two days			Slight precipitate after four months
	Light	Medium	Heavy	
Basalt Sulphur Bank	X			X
Kaolinized rhyolite Cuddeback	X			X
Silicified tuff Horse Heaven	X			X
Agglomerate Black Butte			X	
Sandstone Skagg Springs		X		
Sandstone Bonanza		X		
Coarse agglomerate Black Butte		X		
Coarse sandstone Oat Hill			X	
Coal War Eagle	X			X
Unaltered serpentine Bradford	X			X
Chert Cloverdale	X			X
Slate New Idria	X			X
Sandstone Oceanic		X		
Shale Klau		X		
Granite Coso Hot Springs	X			X

result after two days, but it is essentially the same as the precipitate after four months. Wall rock reaction is thus a rapid process and increased temperature and pressure probably would accelerate the reactions.

(2) In all cases, the solutions containing water glass gave about the same amount of precipitate as those without water glass.

(3) Although some of the rocks are notably out of equilibrium with the solutions (notably the Oat Hill sandstone and Black Butte agglomerate) a very great number of the rocks caused only a small amount of precipitation. Some of the wall rocks causing the least precipitation were from among the largest mercury deposits. However, there is no relation between degree of reactivity and size of the quicksilver deposit. These results indicate that, in some places, some factor other than wall rock reaction must often play a large part in controlling the loci and intensity of quicksilver mineralization.

F. Effect of Evaporation of the Solvent.

All of the factors which can effect precipitation involve a relative concentration of the solute in relation to the solvent beyond the maximum solubility of the solute under the particular chemical and physical conditions. Of the factors already studied, relief of pressure and wall rock reaction are the most probable causes of the precipitation of cinnabar. Relief of pressure involves precipitation by an accelerated evaporation. However, even without a relief of pressure, evaporation can occur so long as the liberated vapors can escape from the mineralizing solutions through pores and fractures. Actually, both vapor and liquid must penetrate out through any permeable media, but, because the viscosity of gases is less than that of liquids, the escape of the vapors will be more rapid than that of the liquid. The solutions will thus be gradually concentrated. As evaporation and concentration proceed, precipitation of cinnabar will begin for it is exactly by such an evaporation of solvent that cinnabar is most easily precipitated in the laboratory. If the mineralizing solutions are made to follow certain definite paths as a result of fractures and structural traps, the precipitate will form along the path followed by the solutions. The cinnabar concentrations will then form along the available openings and beneath whatever trap may be present. Such evaporation must play an important part in the precipitation of cinnabar ores for it is known not only that the loci of cinnabar deposition follow closely openings in the country rock, but also that the great cinnabar concentrations are often found beneath some form of structural trap.[1]

Cf. Schuette, C. N., Occurrence of quicksilver orebodies.

Relation of Pyrite and Marcasite to Quicksilver Mineralization

Reasons have been indicated for believing that cinnabar, metacinnabar, and native mercury are generally deposited from the same type of mineralizing solutions under varying chemical and physical conditions. Silica can be deposited by these same solutions and petrographic evidence will indicate a frequent syngenesis of silica with cinnabar. The relationship of pyrite and marcasite to the quicksilver mineralization is not, however, so clear. Since iron disulphide is a ubiquitous precipitate from many types of hydrothermal solutions, there is no reason to believe that it is always deposited syngenetically with the cinnabar - especially not since the period of cinnabar deposition probably comprises only one small portion of the total mineralizing epoch and since it has been noted that iron disulphide is not soluble in alkaline sulphide solutions. It is most difficult to determine paragenetic relations of pyrite and marcasite to cinnabar and metacinnabar. However, the chemical relations of pyrite and marcasite have been studied in detail. For this reason, it might be well to attempt to ascertain under what chemical and physical conditions pyrite and marcasite could be (but not necessarily are) deposited from the same solutions as cinnabar and metacinnabar.

Allen, Crenshaw, Johnston, and Larsen[1] have determined that

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[1] Allen, E. T., Crenshaw, J. L., Johnston, John, and Larsen, E. S., The mineral sulphides of iron: Am. Jour. Sci., 4th series, vol. 33, pp. 188-90, 1912. References to this article will be made (ACJL, pp.).

marcasite is a monotropic form of pyrite just as metacinnabar is a monotropic form of cinnabar. Unlike the change of metacinnabar to cinnabar, the irreversible change of marcasite to pyrite does not occur below 450° at any pressures (ACJL, pp. 187-90). Therefore, insofar as the study of quicksilver mineralization is concerned, marcasite, like pyrite, is stable over the entire range of possible physical conditions. Thus, once marcasite or pyrite has formed, later quicksilver mineralizing solutions could effect no changes.

The original conditions of formation of marcasite and pyrite are, however, somewhat different than the conditions under which metacinnabar and cinnabar are formed. Cinnabar will be deposited only from markedly alkaline solutions. An increase in acidity or a dilution of solution will immediately cause the precipitation of metacinnabar. Metacinnabar, however, is readily re-converted to cinnabar by a new influx of more concentrated alkaline sulphide solutions. Unlike the relation of metacinnabar to cinnabar, it has been found that, whereas marcasite is the predominant form deposited at low temperatures from acid solutions, some pyrite is deposited along with the marcasite in such solutions (ACJL, pp. 179-81). The amount of pyrite increases with a decrease in acidity and an increase in temperature (ACJL, pp. 179-81). Thus, the occurrence of metacinnabar with both pyrite and marcasite could be expected. Since later alkaline sulphide solutions will convert a part of the metacinnabar to cinnabar, but will not effect the marcasite (ACJL, p. 184), the occurrence of metacinnabar, cinnabar, pyrite, and marcasite together is not anomalous. In alkaline solutions, pyrite, not marcasite, is deposited, but once marcasite has been formed it is not changed by later alkaline sulphide solutions (ACJL, p. 184). Thus, unless the cinnabar in a given area has resulted from metacinnabar that was deposited in neutral or acid solutions and has since been completely converted to cinnabar by alkaline sulphide solutions, the occurrence of marcasite with cinnabar alone is an anomaly that must indicate that the marcasite was not deposited contemporaneously with the cinnabar. Since the occurrence of marcasite with cinnabar in deposits containing no metacinnabar or pyrite is not uncommon, there is good reason for believing that, at least in some cases, the iron disulphide deposition is not strictly contemporaneous with the deposition of mercuric sulphide.

The Problem of Supergene Enrichment of Quicksilver Deposits

The possibility of supergene enrichment of quicksilver deposits has been studied by Broderick.[1] By experiment, Broderick determined the following facts regarding solution and deposition of mercuric sulphide by acid waters:

(1) Cinnabar is somewhat soluble in chloride waters or in a solution in which nascent chlorine is generated by the action of manganese dioxide on chlorides.

(2) Sulphate waters do not dissolve cinnabar.

(3) Since cinnabar is somewhat soluble in hydrochloric acid, but not in sulphuric acid, the assumption is that supergene solution of cinnabar can occur only where supergene waters are chloride in character - thus probably only in arid climates.

(4) Of the sulphides which commonly occur with cinnabar, only stibnite will precipitate mercuric sulphide from chloride solution.

(5) Illuminating gas was found to reduce mercuric chloride to the mercurous form producing a precipitate of calomel.

(6) The action of hydrogen sulphide on calomel gives mercuric sulphide and metallic mercury.

(7) Calcite and ferrous sulphate cause mercuric chloride solutions to precipitate the oxychloride, chloride, and oxide.

(8) In all cases, the mercuric sulphide precipitated from chloride solutions is the black sulphide, metacinnabar.

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[1] Broderick, T. M., Some experiments bearing on the secondary enrichment of mercury deposits: Econ. Geology, vol. 11, pp. 645-51, 1916.

The most recent investigation of the solubility of mercuric sulphide in pure water (pH 7) has shown the solubility, at 25°, to be 1×10^{-17} grams/liter and, at 400°, 3×10^{-15} grams/liter.[1] This fact together with the not infrequent occurrence of cinnabar in placers[2] indicates that pure waters is incapable of transporting mercuric sulphide in solution.

Broderick's experiments show a possible means by which metacinnabar and native mercury can be formed (namely, by reaction of mercuric chloride solutions with stibnite or with organic and hydrogen sulphide gases). Following are some of the reasons for believing that little if any of the naturally occurring metacinnabar or native mercury has resulted from reactions with supergene mercuric chloride solutions:

(1) Of the large number of quicksilver mines in the California Coast Ranges existing under essentially the same climatic conditions (which are certainly not arid) an outcropping at or near the surface, only a very few have metacinnabar.

(2) Many of the deposits which contain native mercury have no metacinnabar although decomposition of the chloride by hydrogen sulphide should produce both compounds.

(3) In all of the deposits which contain metacinnabar or native mercury, the chlorides, oxychloride, and oxide are very rare or absent.

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[1] Verhoogen, Jean, Thermodynamical calculations of the solubility of some important sulphides up to 400°C: Econ. Geology, vol. 33, p. 776, 1938.

[2] Bradley, W. W., Op. cit., pp. 82, 169, 201.

In many of these deposits, insofar as the writer is aware, secondary mercury minerals have never been found.

(4) Of all of the sulphides commonly associated with cinnabar only stibnite will cause the precipitation of metacinnabar from chloride solutions and antimony, although common, is generally present in only very small amounts. The precipitation cannot, therefore, be effected to any appreciable extent by stibnite. According to Broderick's experiments, in the presence of organic matter only the highly insoluble calomel is precipitated. In the presence of carbonates and ferrous sulphates, only chlorides, the oxychloride, and oxide will form. It is not until the hydrogen sulphide zone is reached that the chloride could be converted into metallic mercury and metacinnabar. If supergene transportation of mercury were common, there should, therefore, be found near the surface of some of the deposits containing native mercury and metacinnabar an oxidized zone containing the chlorides, oxychloride, and oxide. Below this zone should occur the metacinnabar and native mercury. Not only are no such oxidized zones found, but there are many cinnabar deposits at or near the surface which show no metacinnabar, but contain native mercury disseminated throughout. Moreover, where native mercury is found, it is often disseminated uniformily in small amounts throughout a deposit and no evidence is at hand for believing that there is any definite native mercury zone.

(5) The occurrence of cinnabar in placers proves that supergene solution of cinnabar must be negligible. The unusual oxidized mineral

assemblage found at Terlingua must be the result of conditions not commonly found at most other quicksilver deposits.

In contrast to the foregoing, is the evidence that, on dilution (or acidification in the case of metacinnabar) of hypogene alkaline sulphide solutions, both metacinnabar and native mercury can be deposited from the hypogene solutions. All of the features of the occurrence of metacinnabar and native mercury can be explained easily by deposition from hypogene solutions.

A few occurrences of supergene cinnabar have been reported. Some of these occurrences are listed below:

(1) Lindgren[1] reported cinnabar in the oxidized ore of some of the mines in the Blue Mountains of Oregon. He believes that the cinnabar results from the decomposition of schwatzite (mercurial tetrahedrite) found in the primary ore.

(2) Hewett[2] has noted the occurrence of cinnabar as a coating over the carbonate or sulphate of lead formed by the alteration of galena.

(3) Becker (B, p. 436) reported a veinlet of cinnabar in an encrustation of secondary salts in an abandoned drift at New Idria.

The deposition of supergene cinnabar could have occurred in one of two ways:

(1) From chloride waters - deposition from chloride waters by

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[1] Lindgren, Waldemar, Mineral deposits, 4th ed., p. 869, 1933.

[2] Hewett, D. F., Geology and ore deposits of the Goodsprings quadrangle, Nevada: U. S. Geol. Survey Prof. Paper 162, pp. 81-2, 1931.

any means would give metacinnabar. Metacinnabar could be converted to cinnabar only by the action of hot alkaline sulphide solutions.

(2) By deposition from supergene alkaline sulphide waters. The formation of supergene cinnabar (rather than metacinnabar) in either case necessitates the presence of hot supergene alkaline sulphide waters. It is conceivable that such supergene solutions could be formed on a small scale. However, since supergene waters are not commonly either hot or alkaline, especially in the presence of pyrite or marcasite which are common sulphides in many cinnabar deposits, it is most difficult to see how supergene cinnabar can be formed to any large degree. Therefore, cinnabar should not be classed as supergene unless field relations permit no other possible interpretation.

The Darkening of Cinnabar in Sunlight

During the course of this investigation, it was found that some cinnabar ores show the peculiar tendency to turn surfisially black relatively rapidly on exposure to sunlight. Insofar as the writer is aware, this rapid darkening is shown by cinnabar from only the following four localities: (1) The Opalite mine and associated deposits located in southeastern Oregon a few miles north of the town of McDermitt on the northwestern Nevada-Oregon border. (2) The Goldbanks deposit located about thirty five miles south of Winnemucca, Nevada. (3) Some of the cinnabar in siliceous sinter at Steamboat Springs, Nevada and (4) Ore from the B and B mine in Esmeralda County, Nevada. The darkening of cinnabar at the third locality is known to the writer only through conversation with Professor V. P. Gianella and that at the fourth locality, through conversation with Dr. R. W. Webb. At all four of these localities, the cinnabar occurs as a dispersion through hydrothermal silica formed at or near the surface. At least in the Goldbanks deposit, the cinnabar and silica have been deposited syngenetically and the intermixture is so intimate that it is impossible to effect a complete separation of cinnabar from silica. Ransome[1] has stated that all cinnabar darkens on exposure to sunlight. Over a great number of years, this may be true since it likewise has been noted that cinnabar vermilion used in painting darkens after a number of

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[1] Ransome, F. L., Quicksilver: U. S. Geol. Survey Mineral Resources 1917, pt I, p. 392, 1921.

years (M, vol. 4, p. 951). However, within a period of months or several years this darkening is not characteristic of all cinnabar since the writer has seen a number of museum specimens and open pit exposures which are still bright red after exposure to sunlight for many years. A specimen of cinnabar from the Aurora mine in San Benito County, California as well as cinnabar concentrated from a specimen collected by Ransome in the Mazatzal Mountains of Arizona were exposed to sunlight for six months and were not darkened.

Table 5 tabulates the results of experiments on natural and artificial mercuric sulphide. After exposure to sunlight for one month, mercuric sulphide prepared by either sublimation or the wet method failed to turn black when exposed to sunlight in air, water, or KOH. The b-HgS prepared according to directions given by Allen and Crenshaw (AC, pp. 375-6) has not darkened after exposure to sunlight for eight weeks in air and ten weeks in water, but turned black in ten days in 10% KOH whereas the same b-HgS has not darkened after exposure to KOH for one month in the dark.

At the Goldbanks mine, the walls of the open pit are composed mainly of low grade ore - below ten pounds - and the walls of the pit have been so darkened that no red coloration is seen unless a fresh surface is broken. The writer exposed fresh surfaces of several different specimens of this low grade ore to sunlight in Winnemucca, Nevada, and found that all specimens were considerably darkened after exposure to sunlight for five days whereas such darkening did not occur in the absence of sunlight. The higher grade ore was not darkened

Table 5

Experiments on the Darkening of Red Mercuric Sulphide in Sunlight

Sample	In air	In water	In 10% KOH	In darkness
Mercuric sulphide prepared by sublimation	Not darkened in 10 weeks	Not darkened in 10 weeks	Not darkened in 10 weeks	
Mercuric sulphide prepared by wet method	Not darkened in 10 weeks	Not darkened in 10 weeks	Not darkened in 10 weeks	
b-HgS	Not darkened in 8 weeks	Not darkened in 10 weeks	Darkened in 8 days	Not darkened in 10 weeks in 10% KOH or in 1 year in air
Cinnabar ore from Aurora mine	Not darkened in 8 months	Not darkened in 10 weeks		
Concentrates of cinnabar ore from Mazatzal Mts.	Not darkened in 8 months	Not darkened in 10 weeks	Darkened in 2 weeks	
Low grade Goldbanks ore	Darkened in Winnemucca and Washington in 5 days Darkened in Pasadena in 8 weeks	Not darkened in 10 weeks in Pasadena	Darkened in 8 weeks in Pasadena	Not darkened in 5 months
High grade Goldbanks ore	Not darkened in 10 weeks in Pasadena nor in 2 weeks in Winnemucca	Not darkened in 10 weeks in Pasadena	Not darkened in 8 weeks in Pasadena	Not darkened in 5 months
Low grade Opalite ore	Darkened in 2 days	Darkened in 2 days	Darkened in 1/2 hour	Not darkened in 6 months in air, but darkened in 1/2 hour in KOH.
High grade Opalite ore	Darkened in 4 weeks	Not darkened in 10 weeks	Darkened in 2 days	Not darkened in 6 months in air nor in 2 weeks in KOH.

after an exposure of two weeks. Since it was assumed that all of the low grade ore would darken well anywhere, some of the typical low grade ore was sent in to Mr. W. T. Schaller in Washington, D. C. for experimental work. Mr. Schaller[1] likewise noted considerable darkening after five days. However, several specimens of the same type of ore darkened only after an exposure of eight weeks in air and KOH in Pasadena and have not darkened after exposure for ten weeks in water. Nevertheless, all of the Opalite ore darkens very rapidly under exactly the same conditions in Pasadena. The low grade Opalite ore darkened after exposure to sunlight for two days in air and water, but has not darkened in six months in the absence of light. The same low grade Opalite ore darkened in one half hour in KOH, but the same darkening occurred in KOH in the dark and, in this case alone, the darkened layer was not surficial. High grade Opalite ore darkened after four weeks exposure to sunlight in air; was not darkened after exposure to sunlight for ten weeks in water; but was greatly darkened after exposure to sunlight for two days in KOH. The high grade ore when exposed to KOH in the darkness was not darkened after two weeks and the darkening of the high grade ore in sunlight is only surficial.

A specimen of the low grade Opalite ore was mounted in Bakelite and polished. The section was then exposed to sunlight in air and the decrease in internal reflection noted every three hours. The internal reflection decreased gradually until none remained after two

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[1] Schaller, W. T., Personal communication.

days. Since the cinnabar itself is dispersed through silica, the character of the darkened compound could not be determined from the polished section.

The experimentally determined relationships are rather confusing, but can be summarized as follows:

(1) Cinnabar in low grade ore darkens on exposure to sunlight more rapidly than that in high grade ore.

(2) When the darkening occurs, alkali seems to accelerate the rate of darkening.

(3) Water appears to decrease slightly the rate of darkening.

(4) The rate of darkening varies greatly for mercuric sulphide prepared in various ways.

(5) All known naturally occurring cinnabar that darkens rapidly occurs in a matrix of hydrothermal silica.

The darkening under discussion involves a change in the color of a very thin surficial layer of cinnabar from red to black. Longer exposure, as noted at the Goldbanks mine, intensifies the darkening, but does not cause a thickening of the darkened layer. Heumann[1] states that acids inhibit the darkening; that under pure water the change is very slow; but that under alkali the darkening occurs in a few minutes and that cinnabar prepared by the wet method darkens more rapidly than that prepared by sublimation. The writer has been unable to duplicate Heumann's results. Allen and Crenshaw (AC, p. 379)

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[1] Heumann, Karl, Veranderung des Zinnobers durch das Licht: Berichte der deutsche chemische Gesellschafte, Bd. 7, pp. 750-51, 1874.

observed that, when cinnabar is heated to 325°, the surface turns black, but that the red color returns when the cinnabar is cooled. If the cinnabar is heated to 445° the darkening is permanent. The surficial change in the color of cinnabar from red to black in sunlight always has been assumed tacitly to be a change from metacinnabar to cinnabar. However, the fact that the same surficial darkening is observed when cinnabar is heated (although metacinnabar is a monotropic form which, at high temperatures, is converted to cinnabar) casts doubt on the validity of this assumption. Mr. W. T. Schaller[1] has reminded the writer that some metals such as platinum, when precipitated in a very finely divided state, are black. The writer prepared a solution of colloidal mercury by dilution of an alkaline mercuric sulphide complex solution. When this solution is poured over a porcelain surface, a mercury mirror is deposited. When the mercury mirror is wiped off with a rag, the deposit on the rag is black. There is, therefore, no reason why the darkening of cinnabar could not be the result of the formation of a surficial layer of colloidal mercury in solid solution in the cinnabar. The darkened layer is not removed by nitric acid as it should be were it mercury. However, silver halides, covered with a solution of nitric acid in which metallic silver is soluble, darken on exposure to sunlight. The current theory explaining the darkening of silver halides, therefore, likewise postulates a surficial dispersion of silver as a solid solution in the silver halide (M,vol.3,p.414);

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[1] Schaller, W. T., Personal communication.

since metallic silver in solid solution would not be removed by nitric acid. Despite the long use of photographic emulsions, the exact cause and character of the darkening of silver halides still is not known definitely. One of the difficulties in studying photosynthetic compounds is not only the small amount of the synthesized substance which is formed, but also the fact that very small differences in the medium in which the compound is imbedded cause a wide variation in the photosensitivity of the compound. Although it has long been known that variations in the emulsion cause a great variation in the sensitivity of silver halides to light, the fact was only recently discovered that the sensitivity of the halides is greatly increased by the presence in the emulsion of minute amounts (1:300,000 to 1:1,000,000) of allyl isothiocyanate (C_3H_5CNS - allyl mustard oil).[1] By analogy, it is possible that some minute impurity in the cinnabar or adjacent wall rock might greatly effect the photosensitivity of the cinnabar and explain some of the observed anomalies.

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[1] Wall, E. J., Photographic emulsions, pp. 25-7, 1929.

PETROGRAPHIC ASPECTS OF THE GEOCHEMISTRY OF QUICKSILVER MINERALIZATION

Introduction

Suites of typical ores and associated wall rocks were collected for petrographic study from each of the mines visited. It is obviously beyond the scope and purpose of this paper to attempt a complete petrographic description of ores from every quicksilver deposit. Instead, studies have been made of a large number of thin and polished sections of rocks from typical quicksilver deposits for the purpose of obtaining evidence pertaining to each of the fundamental problems of quicksilver mineralization listed below:

(1) The relation of the various types of wall rock alteration to the quicksilver mineralizing solutions.

(2) The relation of metacinnabar to cinnabar and the type of iron disulphide associated with metacinnabar- and cinnabar-bearing ores.

(3) The mode of access of quicksilver mineralizing solutions into the various types of country rock.

Petrographic evidence pertaining to each of these problems will be discussed in the following pages.

Relation of Wall Rock Alteration to Quicksilver Mineralization

The degree of wall rock alteration accompanying quicksilver mineralization varies within wide limits. Some of the deposits occurring in sandstone show notably little alteration. Conversely, the silicification accompanying cinnabar deposition in serpentine is so marked that the silicified serpentines have been given the name "quicksilver rock". In other deposits, the predominant alteration is carbonatization and some deposits exhibit intense kaolinization. Since both cinnabar and silica are soluble in alkaline sulphide solutions, it would be expected that there would be a close genetic relationship between cinnabar and silica deposition. Conversely, alkaline earth and carbonate ions cannot exist together in alkaline solutions and hence carbonate vein filling must be related to acid rather than to alkaline solutions. Thus the presence of carbonatization would seem to necessitate a temporary change in the character of the mineralizing solutions and a temporary cessation of cinnabar deposition during the course of mineralization.

Probably nowhere is the relation between cinnabar and silica deposition shown more clearly than in the Goldbanks deposit. A prominent feature of this district is a series of silica hot spring deposits forming a linear, northward-trending zone about two and one half miles in length and averaging about one half mile in width. The silica deposits occur near the contact of Quaternary (?) basalt with Permian (?) coarse clastics and volcanics. The mineralization is believed th be very recent and to be directly related to the period of basaltic extrusion. The silica deposits form a gently westward dipping cover (never more than one hundred feet in thickness) over a mature topography. On account of this mode of occurrence, the deposits have been given the descriptive name "silica apron".

Near the southern end of the apron zone, cinnabar is disseminated through the silica. The cinnabar occurs in two zones about three feet apart and varying up to seven feet in thickness. The two cinnabar-bearing zones follow the gentle, westward dipping stratification of the silica apron. Nowhere has the cinnabar been found below these zones. In many places, the cinnabar occurs in a very dense silica beneath more porous layers of the apron. The field relations thus indicate a syngenetic deposition of cinnabar and silica. The cinnabar, however, occurs in only one small portion of the total silica apron zone and there in only two horizons in the apron. In other words, from only one of a series of closely related thermal springs was cinnabar deposited and there during only two stages of the hydrothermal activity.

The material of the apron consists essentially of quartz and chalcedony. Minor amounts of opal form the linings of a few microscopic vugs. The apron has a highly fragmental appearance, but, in only one area, where the siliceous waters flowed out over rounded, fluvial gravels, is there any considerable amount of exotic material in the apron. In the remainder of the apron, the fragments consist entirely of re-worked hydrothermal silica distinguishable by differences in color. These fragments have been formed by continued de-hydration, cracking, weathering, re-working, and re-cementation of the hydrothermal silica. Microscopically, the cinnabar occurs as dispersions through silica cement and through colloformally banded silica veinlets. The maximum concentrations of cinnabar usually occur along the contacts of the corroded silica fragments. The cinnabar-silica cement has been re-fractured and re-cemented by more cinnabar-silica cement. The net result of this process of continued cracking, re-working, and re-cementation is the cinnabar ore as it is now found consisting of silica fragments in a matrix through which is dispersed abundant cinnabar the whole being cut by still later silica containing more dispersed cinnabar.

In summarizing the mode of formation of the Goldbanks ore, the following stages are separated with the understanding that the entire process occurred simultaneously in various portions of the deposit. (1) Deposition of silica by a number of thermal springs,(2) Dehydration and crystallization of the silica with consequent cracking, (3) Accentuation of the brecciation by weathering and re-working of the fragmental material by the spring waters, (4) Cementation of the fragmental silica by solutions carrying silica and, locally, mercuric sulphide. The cinnabar was probably precipitated as a result of decreased solubility resulting from a relief of pressure and evaporation at the surface. (5) Repeated cracking and brecciation and subsequent re-cementation of the rock by cinnabar-silica cement resulting in the formation of an ore containing barren silica fragments in a silica cement through which is dispersed much cinnabar the whole being cut by many later veinlets containing silica and more of such dispersed cinnabar.

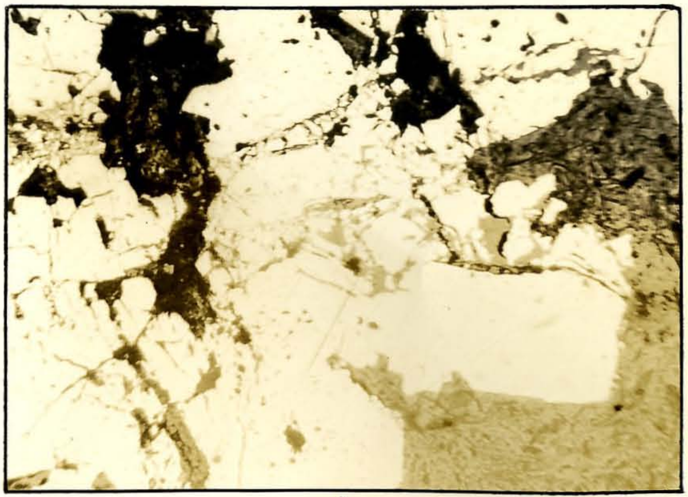
Another evidence of the marked syngenesis of cinnabar with silica is the fact that the cinnabar is not merely a dissemination, but rather is actually a dispersion through the silica. Thin sections of cinnabar ore tend to over-emphasize the size of the cinnabar aggregates because the thinness of the section and the fact that the section is examined in transmitted light make it impossible to see any third dimension of the individual grains. On the other hand, a study of polished sections in reflected light gives some idea of the three dimensional size of the cinnabar grains since the individual grains will not take a polish unless they are above some definite size. Ordinary cinnabar when polished shows a soft, metallic surface (Plate 1-A). Goldbanks cinnabar, however, characteristically shows no such metallic surface (Plate 1-B). Ore above 2% shows small metallic areas although by far the greater portion of the cinnabar in the section has a non-metallic surface (Plate 1-C). Megascopically, and under obliquely reflected light, such cinnabar ore that shows a non-metallic surface appears bright red and often appears to be nearly pure cinnabar. The polished surface, however, is not only non-metallic, but is also hard. The surface polished is thus a silica surface and the cinnabar is dispersed through the silica in so fine a state of subdivision that, except in the very highest grade ore, none of the cinnabar is in aggregates large enough to show a polish. This state of dispersion has given to an ore, the maximum cinnabar content of which is not over 7%, the appearance of being nearly pure cinnabar. The color of the cinnabar is most pervading

Plate 1

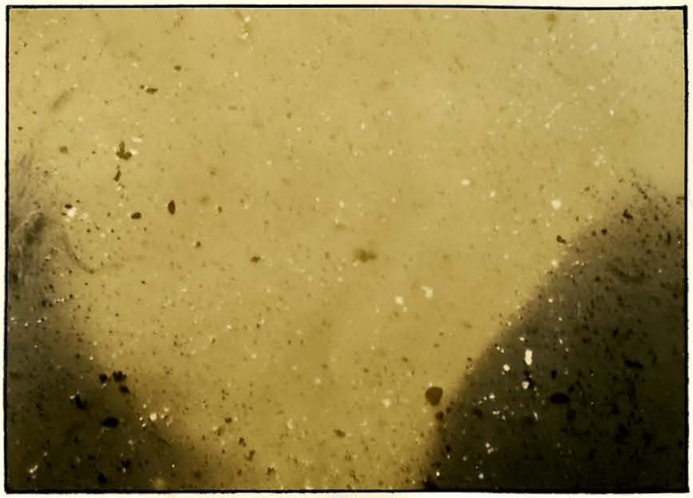
A. Polished section of cinnabar from Klau mine showing typical metallic surface. X 105.

B. Polished section of high grade Goldbanks ore (about 1%) showing hard, non-metallic silica surface with only a few small cinnabar aggregates sufficiently large to polish with a metallic surface. The entire field is bright red megascopically and in obliquely reflected light. X 105.

C. Polished section of very high grade Goldbanks ore (about 4%) showing small metallic areas throughout a field which is largely non-metallic and hard. The entire field is bright red megascopically and in obliquely reflected light. X 105.



A



B

C

and, for this reason, it is necessary to use the utmost care in megascopic estimations of cinnabar concentrations since the color of a hand specimen depends not only on the total cinnabar content, but also on the state of subdivision and degree of dispersion of the cinnabar through the ore. Some of the Goldbanks ore was crushed to -125 mesh and concentrated. The concentrate appeared to be nearly pure cinnabar. The concentrate was mounted in an immersion oil of index 1.620. This liquid was chosen so that its index would be far from the indices of the minerals that might be present in the concentrate - namely, cinnabar, quartz, and chalcedony. Although all of the concentrate was bright red and appeared to be nearly pure cinnabar, nearly all of the grains showed an index below 1.620. The cinnabar is thus again shown to be clearly a dispersion through the silica and the pervading color of the cinnabar has caused the cinnabar-silica dispersion to appear like pure cinnabar. In order to ascertain the order of magnitude of particles that would not polish with a metallic surface, cinnabar powder prepared by sublimation and chemically precipitated cinnabar were mounted in separate bakelite mounts and polished. The powder was nearly all finer than 200 mesh. In spite of the difficulties inherent in the polishing of soft powders, both of the cinnabars polished with metallic surfaces. The size of the cinnabar particles dispersed through the silica must thus be considerably less than 200 mesh. This extremely fine state of cinnabar subdivision must indicate a very marked change in the physical environment of the solutions on reaching the surface. Only a very marked change in the physical environment could account for the rapid precipitation necessary to produce so high a degree of dispersion. Schuette[1] has noted a similar dispersion of cinnabar through silica in ore from the Opalite mine in southeastern Oregon.

The cinnabar deposits occurring in serpentine have been highly silicified. In these deposits, there has also been some carbonatization so that it is here possible to study the relation of cinnabar mineralization not only to silicification, but also to carbonatization. In polished sections, it is possible to recognize two types of gangue - the soft gangue minerals which are carbonate and serpentine and the hard gangue minerals which are silica - quartz and chalcedony. Here again, much of the bright red cinnabar polished with a hard, non-metallic surface although megascopically, under obliquely reflected light, and in transmitted light the ore can be seen to contain abundant cinnabar. The cinnabar is here again dispersed in a very finely divided state through the silica. Notable, however, is the fact that such dispersed cinnabar occurs only in the cinnabar and not in the carbonate or serpentine. In fact, it is often possible in polished section to distinguish areas of hard gangue from those of soft gangue merely by noting where the cinnabar is wholly or partly dispersed and where all of the cinnabar polishes with the typical soft, metallic surface. All of the cinnabar in carbonate or serpentine is in aggregates coarse enough to show a metallic surface. It is only in the silica that some - but not all - of the cinnabar occurs in dispersions

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[1] Schuette, C. N., Quicksilver in Oregon, pp. 151-2.

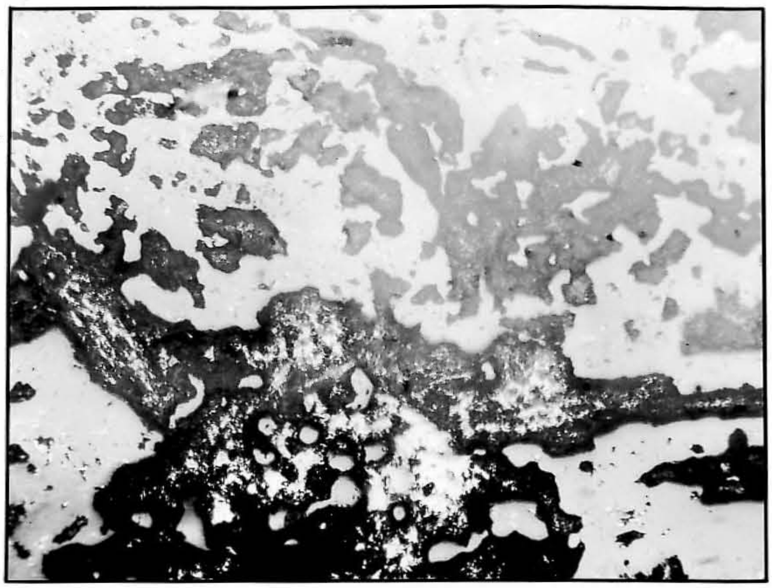
too fine-grained to show a metallic surface. The cinnabar is, of course, known not to be syngenetic with the serpentine and the evidence here presented corroborates the evidence obtained by geochemical experimentation - namely, that cinnabar may be deposited syngenetically with silica, but cannot be deposited syngenetically with carbonate. The presence of carbonate in quicksilver deposits must indicate a temporary cessation of quicksilver mineralization and an influx of acidic carbonate waters during the period of hydrothermal activity.

In polished section Aurora 20, all of the cinnabar occurs dispersed through silica which has replaced the serpentine. None of the cinnabar shows a metallic polish and the cinnabar is thus detectable only megascopically or in obliquely reflected light. Most of the cinnabar of polished section Aetna 14 is dispersed through the silica and a large part of the section shows a non-metallic (silica) surface although locally there are cinnabar aggregates in the silica which are sufficiently coarse to polish with a metallic surface. Polished sections Aurora 12, 15, 16, Bradford 5, 11, 13, and Aetna 5 and 14 all show cinnabar with both metallic and non-metallic surfaces - the latter confined to silica areas. So marked is this relationship in polished section Aetna 5 that silica and non-silica areas can be dilineated visually merely by noting the presence or absence of dispersed cinnabar (See Plate 2).

Many interesting features of wall rock alteration are likewise apparent in thin section. Thin section Aurora 18 shows clearly the close relationship of cinnabar with silica in contrast to the carbonate.

Plate 2

Polished section of cinnabar ore in silicified serpentine from open pit at Aetna mines. Metallic cinnabar replacing unaltered serpentine (black) and non-metallic cinnabar dispersed through silica (light grey). All of the light grey silica areas are bright red both megascopically and in obliquely reflected light. X 105.



Here all of the cinnabar is confined to the chalcedony (quartzine) which is replacing the serpentine. Thin sections Aurora 15 and 20 show especially well both spherulitic chalcedony and fibrous chalcedony veinlets. Thin section Aetna 5 shows a heavy dissemination of cinnabar through unaltered serpentine. Silicification is thus not necessary to provide a means of access for the mineralizing solutions. The cinnabar in thin section Bradford 5 occurs in partly silicified serpentine. Note here the delicate chalcedonic vug linings. The cinnabar of thin section Bradford 11 is disseminated through carbonate. The cinnabar of thin section Aurora 16 is largely confined to the silicified portions of the serpentine although there is also some cinnabar disseminated through the carbonate. The close association of cinnabar and silica is especially well shown in thin section Aetna 14 in which each of the small chalcedony replacement blebs is associated with cinnabar which commonly forms a halo around the bleb and which often occurs likewise within the bleb.

Cinnabar which is in so fine a state of subdivision that it will not show a metallic surface when polished is not confined wholly to silicified rocks, but may also be the result of a very lean, fine-grained dissemination. Polished section Cuddeback 12 shows a cinnabar streak cutting highly kaolinized rhyolite. The cinnabar streak is distinctly visible both megascopically and in oblique illumination, but only a very small portion of the streak gives a metallic polished surface. An examination of a concentrate of the ore reveals that the cinnabar is only a very thin coating over the kaolin grains. In ore from the Coso Hot Springs deposit, the cinnabar coating over kaolin grains is so thin that it is virtually impossible to obtain a gangue-free concentrate and the color of any concentrate obtained is far more red than the cinnabar content warrants merely because the cinnabar is only a very thin coating over the kaolin grains. Since the cinnabar is a coating over the kaolin in both the Cuddeback and Coso Hot Springs deposits, the kaolinization has apparently preceded the quicksilver mineralization.

The close relationship of cinnabar and silica deposition is quite apparent in many deposits. It would seem,however, that carbonatization and kaolinization are not so closely related to the deposition of cinnabar and, at least insofar as concerns carbonatization, it is deductively most difficult to see how cinnabar and carbonate could be deposited from the same solutions. The presence of cinnabar in only one small portion of a series of strikingly similar silica hot spring deposits in the Goldbanks district indicates that the heavy metal content of thermal springs varies widely during any given period of mineralization. Similarly, there is no reason to believe that the alkalinity and general elemental content of thermal waters should likewise not vary widely during a period of mineralization and that the various mineral components should not be deposited at different times.

Type of Iron Disulphide Associated With Quicksilver Deposits

The type of iron disulphide which can be deposited from quicksilver mineralizing solutions is directly related to the temperature and acidity of the solutions and these factors, in turn, determine the type of mercuric sulphide which is deposited. Cinnabar is deposited only from alkaline solutions and metacinnabar only from neutral or acid solutions at low temperatures. Marcasite is deposited only from acid solutions at low temperatures, but some pyrite is deposited in acid as well as alkaline solutions. At the temperatures of quicksilver mineralization, both pyrite and marcasite are stable in any solutions after once having been formed. In a new influx of alkaline sulphide solutions, metacinnabar will be wholly or partly converted to cinnabar. Thus the occurrence of cinnabar, metacinnabar, pyrite, and marcasite together is not anomalous. However, unless all of the cinnabar has been converted from metacinnabar, the association of marcasite and cinnabar alone must indicate that the two sulphides were deposited at different times. If the cinnabar has been converted from metacinnabar, it would be expected that some metacinnabar remnants would be visible in the ore. Metacinnabar, however, is notably absent from most quicksilver ores. The paragenetic relations of iron disulphide to mercuric sulphide are difficult to determine petrographically not only because of the relative scarcity of metacinnabar, but also on account of the strong crystallizing power of the iron disulphides which makes it difficult to ascertain whether euhedral crystals are earlier or later than the adjacent ore and alteration minerals.

The writer was fortunate to visit the Mount Diablo mine at a time when much of the ore consisted of a mixture of metacinnabar and cinnabar with much pyrite and marcasite. Much of the pyrite and marcasite occurs as vein fillings cutting the mercuric sulphides and as crustifications over the mercuric sulphides. It would thus appear that at least a portion of the iron disulphide is post-mercuric sulphide. The paragenetic relations of iron disulphide to mercuric sulphide are well shown in polished sections Mount Diablo 1, 1A, 5, 5A, and 6. The iron disulphides are very intimately related and must have been deposited at essentially the same time. Polished sections 1, 1A, 5, and 5A all show beautifully banded iron disulphide. Such colloform bands often consist of both pyrite and marcasite and the intimate association of the two minerals is likewise shown by the occurrence of either one of the iron disulphides enclosed within areas of the other. The relationship of cinnabar to metacinnabar is likewise most intimate - metacinnabar occurs within cinnabar and cinnabar occurs within metacinnabar to give a most intimate mixture. Cinnabar and metacinnabar, unlike pyrite and marcasite cannot be deposited from the same solutions except at very low temperatures so that this intimate relationship must indicate a partial conversion of the monotropic metacinnabar to cinnabar by later alkaline sulphide solutions. That such an inversion has occurred is indicated by the anomalous anisotropism of much of the metacinnabar. This anisotropism must be attributed to the incipient inversion of some of the isometric metacinnabar. A remarkable feature of polished sections of metacinnabar and cinnabar is that polished surfaces of the former are much smoother than those of the latter. This effect has been noted by Short[1] and is so pronounced in the Mount Diablo polished sections that it is possible to distinguish the two mercuric sulphides solely by the character of the polish. In the Mount Diablo deposit, then, although the mineral assemblage is of a type that chemically might indicate simultaneous deposition of the iron and mercuric sulphides, nevertheless, the crustifications and veins of the iron disulphide through mercuric sulphide would indicate that at least a portion of the iron disulphide is later than the mercuric sulphide.

All of the iron disulphide in specimens from the Aurora mine is marcasite although no metacinnabar is present in the ore. Unless the cinnabar has been derived from a complete conversion of the metacinnabar that has not left a trace of metacinnabar, this association must mean that the marcasite and cinnabar have not been deposited simultaneously from the same mineralizing solutions. The cinnabar in the Aurora mine is largely dispersed through syngenetic chalcedony which has replaced the serpentine. The marcasite replaces this cinnabar-silica mixture as shown in polished sections Aurora 12, 15, and 16. The marcasite in polished section Aurora 15 is largely in well-formed euhedral crystals scattered through the silica. The fact that euhedral marcasite crystals are found scattered through highly

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[1] Short, M. N., Microscopic determination of the ore minerals: U. S. Geol. Survey Bull. 825, p. 96, 1931.

silicified country rock through which is dispersed much cinnabar makes it appear certain that the marcasite deposition was distinctly separate and later than the syngenetic deposition of cinnabar and silica.

Cinnabar occurs with marcasite in polished sections Great Western 1 and 2. Cinnabar occurs with both pyrite and marcasite in polished sections Bradford 5, Oceanic 12, New Idria 2, and Sulphur Bank 1 and 2. Cinnabar occurs only with pyrite in polished sections New Idria 4, Sulphur Bank 6 and 5 (This specimen shows well developed colloform banding in cinnabar.) and Klau 21 and 26. The common occurrence of cinnabar with marcasite (in the absence of metacinnabar) makes it appear that much of the iron disulphide deposition has been accomplished at a period of the mineralization distinct from the period of quicksilver deposition and often at times when the mineralizing solutions were somewhat acid and thus capable of depositing marcasite. Like carbonatization and perhaps kaolinization (but unlike silicification), the deposition of iron disulphide apparently has not been accomplished by the same solutions that deposited the mercuric sulphide although the entire mineralization is undoubtedly related to one period of hydrothermal activity during which the character of the mineralizing solutions varied considerably.

Mode of Access of Quicksilver Mineralizing Solutions

Becker[1] has stated that all cinnabar in sandstone occurs as impregnations of intergranular voids and that, in other types of rocks, the cinnabar occurs filling fractures or other types of openings. Becker denied the existence of any replacement of wall rock by the quicksilver mineralizing solutions. An examination of Becker's reasoning shows that he was influenced more by erroneous deductions than by actual petrographic evidence. Becker could not understand how solutions which, in some places, themselves deposited silica could likewise be capable of dissolving silica to provide new depositional loci for the cinnabar. In the light of theories of chemical equilibrium such as are now recognized, but which were not understood in Becker's time, it is known that a solution which may be undersaturated with respect to silica at one time may later become saturated with silica and re-deposit the silica at another point. One and the same solution is thus capable both of dissolving silica and thus providing depositional loci for the cinnabar and, at the same time, of silicifying the country rock. Even saturated solutions in equilibrium continually dissolve and re-precipitate to maintain the necessary equilibrium. In Becker's time, replacement was believed to consist in the solution of a molecule of one substance and the corresponding deposition of a molecule of the second substance rather than the present concept of large scale solution and re-deposition. Since Becker regarded replacement as a process of

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[1] Becker, G. F., Op. cit., pp. 30, 315, 394-401.

molecular interchange, he believed that cinnabar should be pseudomorphous after any wall rock constituents that were replaced. In the absence of pseudomorphs of cinnabar after rock-forming minerals, Becker felt that replacement could not have occurred. The absence of such pseudomorphs is no proof of the absence of replacement and many quicksilver deposits show evidence of abundant replacement.

One of the ores in which Becker stated that no replacement had occurred is that of the Almaden mine in Spain. Becker stated that the Almaden occurrence was solely an impregnation of the intergranular voids of the sandstone and that there was no replacement of the sandstone grains. Ransome[1] undertook a study of the occurrence of cinnabar in sandstone at Almaden. By showing that the Almaden ore grades all the way from lean specimens in which the cinnabar is only an impregnation of the sandstone voids into specimens in which there are large areas of nearly pure cinnabar in the sandstone with only occasional sandstone residues, Ransome proved that there had been abundant replacement of the sandstone in those portions of the sandstone where there is an excess of cinnabar. Similarly, the writer has studied a large number of occurrences of cinnabar in sandstone and other types of wall rock. There is some replacement in all types of wall rock and, in high grade ore occurring in sandstone, there often is a large scale replacement of the component sand grains. A notable feature of quicksilver mineralization, however, is that the first stages of

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[1] Ransome, F. L., The ore of the Almaden mine: Econ Geology, vol. 16, pp. 313-21, 1921.

mineralization always involve a filling of fractures or, in sandstones, of the intergranular voids. It is only when the cinnabar is locally in excess that the cinnabar begins to replace the wall rock constituents. Nevertheless, in the examination of occurrences of cinnabar in various types of wall rock, the writer has yet to see a quicksilver deposit in which there has not been some replacement and often the amount of replacement is very considerable.

The ore of the Oceanic mine is particularly indicative of considerable replacement of the sandstone grains by cinnabar. A peculiarity of the occurrence of cinnabar in the Oceanic ore is that the cinnabar is not a fine-grained dissemination through the sandstone such as could be attributed to the impregnation of intergranular voids, but occurs rather as sparsely scattered aggregates most of which are several times the size of the component sandstone grains and of the intergranular voids. For such cinnabar aggregates to have attained their present size, there must have been some replacement and the ragged outlines of the sandstone grains adjacent to the cinnabar likewise attest to such replacement. Such relatively large cinnabar aggregates are well shown in polished section Oceanic 12 and thin sections Oceanic 6 and 12. Polished section Oceanic 4 is of interest since it illustrates exactly what Ransome noted in the Almaden ore - namely, that in the same sandstone, the lean disseminations of cinnabar occur as impregnations and cement replacements, but that, in the portions of the sandstone in which there is a large concentration of cinnabar, there has been much replacement of the sandstone grains. One portion of polished section Oceanic 4 is a lean impregnation and replacement of the sandstone cement, but the other portion of the same section shows large areas of the sandstone almost completely replaced by cinnabar. Likewise, there are areas where much - but not all - of the sandstone has been replaced and there are many ragged sandstone grains as well as isolated sandstone remnants within the cinnabar. Plate 3A shows one of the relatively large aggregates of thin section Oceanic 6. High grade ore shows a much larger degree of replacement.

A portion of the ore at the New Idria mine occurs disseminated through sandstone. Polished section New Idria 19 shows that, in the low grade portions of the ore, the cinnabar has gained access by impregnation and by a replacement of the cement and that there has been corrosion and replacement of the individual grains only in the portions of the section in which there is a relatively great concentration of cinnabar. Thin section New Idria 19 shows the same low-grade impregnation. Thin section New Idria 2 shows a high grade dissemination in sandstone. In this section, there is considerable corrosion. One edge of the section shows a surficial crustification of cinnabar and the replacement of the sandstone beneath the crustification is of interest.

A large portion of the ore at New Idria occurs in apparently sharp-walled veins in a dense slate. Thin sections New Idria 10 and 32 show that there has been much dissemination through and hence replacement of the dense slate.

Some of the ore at Sulphur Bank occurs as a dissemination through lacustrine gravels. In the higher grade ore, there has been much inward corrosion and replacement of the gravel pebbles by the cinnabar. Polished sections Sulphur Bank 1, 8, and 8A all show ragged pebbles and residual grains in cinnabar as well as cinnabar aggregates very much larger than the gravel grains or than the intergranular voids. In the higher grade ore, there has been much corrosion of the gravel pebbles by the cinnabar, but it is noteworthy that, here again, the cinnabar has first gained access by impregnation and by a replacement of the cement. Corrosion and replacement are features only of those portions of the ore that have a relatively large cinnabar content and where the cinnabar content thus exceeds the capacity of the available intergranular spaces. Thin sections Sulphur Bank 1 and 15 (Plate 3B) also show large scale corrosion and replacement of the gravel pebbles.

A large portion of the ore at Sulphur Bank occurs in a dense basalt. The cinnabar occurs as fracture fillings and, megascopically, the veins appear very sharp walled. Thin section Sulphur Bank 100 shows a main fracture filled with cinnabar. From this main fracture branch a number of thin, straight veinlets. If the loci of these small veinlets was originally controlled by fracturing, the fractures are no longer apparent. In detail, the outlines of the veinlets are most ragged and there has been an amount of replacement by the veinlets which is large relative to the size of the veinlets. There is likewise evidence of replacement along the walls of the main vein which obviously has followed a fracture. Here again it is to be noted that the solutions have followed fractures until such fractures have been filled. The cinnabar is then forced to corrode and replace the country rock. Thin sections Sulphur

Bank 100A and 100B (Plate 4) show more straight, narrow veinlets the boundaries of which, in detail, are markedly ragged and the cinnabar in which must have replaced the basalt wall rock.

Mention has already been made of the occurrence of cinnabar in serpentine. Such cinnabar is by no means confined to fractures. The greater part of the cinnabar is confined to portions of the serpentine which have been silicified, but some cinnabar is likewise disseminated through unaltered serpentine.

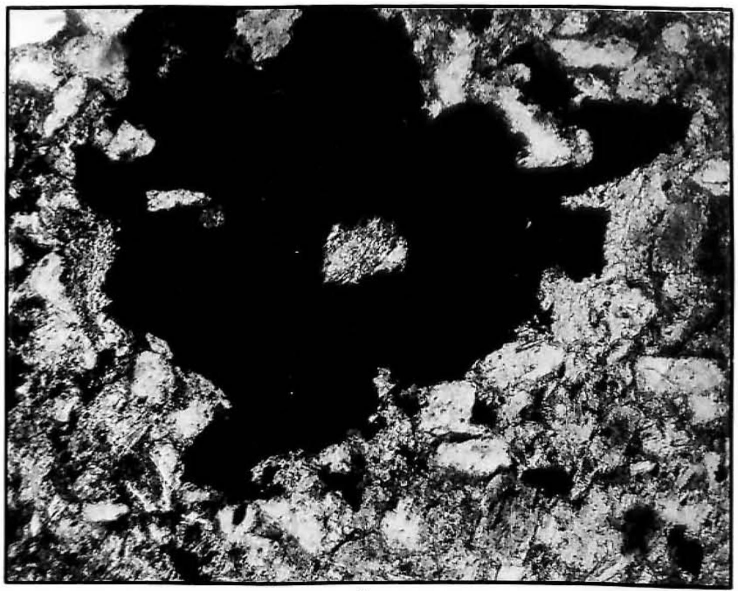
The wall rock at the Klau mine is a dense shale. Most of the cinnabar occurs as crustifications and fracture fillings, but dissemination and replacement are present on a small scale. Thin section Klau 22 shows cinnabar disseminated through a shale so dense that the cinnabar grains must have replaced some of the wall rock. Similarly, the ore at the Cuddeback mine occurs in a highly kaolinized rhyolite - so highly kaolinized that only the quartz blebs of the original rock remain. Thin section Cuddeback 12 shows a vein of cinnabar cutting the kaolin. Only locally is the vein sharp-walled. Generally, there has been abundant wall rock replacement. Thin section Cuddeback 11 likewise illustrates the common dissemination of cinnabar through kaolin at the Cuddeback mine.

There can be no doubt that, in the first instance, quicksilver mineralizing solutions have gained access into the country rock through intergranular openings and fractures. The occurrence of cinnabar in such openings and fractures commonly accounts for by far the greater percentage of cinnabar in the ordinary quicksilver ore.

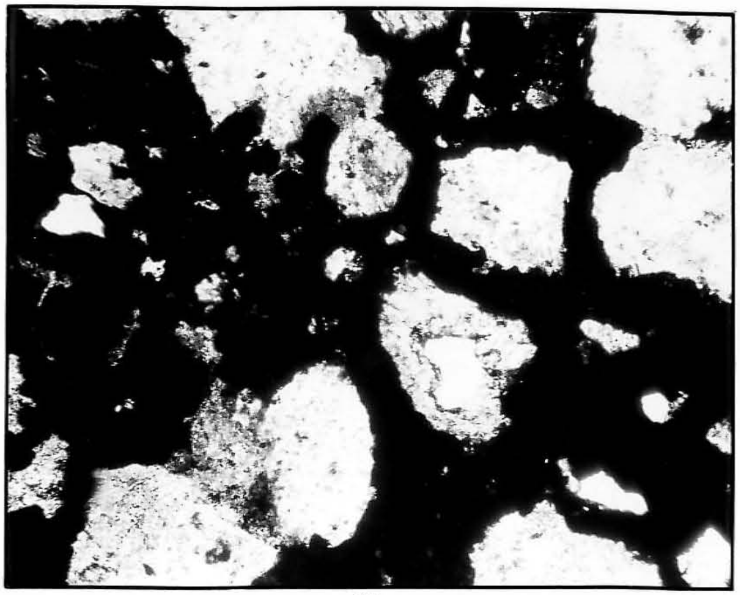
Plate 3

A. Thin section of ore from Oceanic mine showing relatively large cinnabar aggregate replacing fine sandstone grains. Such large cinnabar aggregates are characteristic of the Oceanic ore. X 120. Plain light.

B. Thin section of ore from open pit of Sulphur Bank mine showing large cinnabar aggregates replacing lacustrine gravel pebbles. Note the ragged, corroded pebbles and the residual grains in the cinnabar. X 120. Plain light.



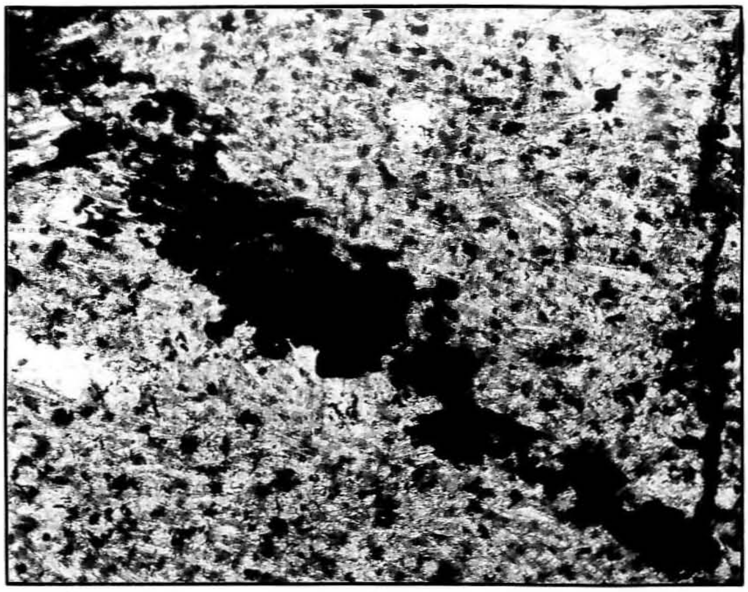
A



B

Plate 4

Thin section of ore from open pit of Sulphur Bank mine showing straight replacement veinlets cutting basalt. Note the ragged boundaries of the veinlets. X 120. Plain light.



However, whenever the concentration of cinnabar in any small area becomes so great that the available openings are filled, the cinnabar-bearing solutions are quite capable of replacing components of the wall rock and such replacement is by no means an uncommon feature of quicksilver ores. Replacement of grains and pebbles of sandstone is particularly common and, even in the densest rocks such as basalt, slate, and serpentine, there has been some replacement of the wall rock components by the cinnabar.

SPECTROGRAPHIC STUDY OF CINNABAR MINERALIZATION

Purpose

A spectrographic study of cinnabar and cinnabar ores from a number of representative quicksilver deposits has been undertaken for the purpose of obtaining a more accurate quantitative picture of the exact chemical character of quicksilver mineralizing solutions. By such a study of impurities concentrated in the cinnabar and the relations of such concentrations to wall rock impurities, it was hoped that some of the following general metallogenetic problems could be answered; viz.:

(1) Are there any elements which are always concentrated in the cinnabar regardless of geological or geographical occurrence?

(2) Are there any significant differences in elemental composition that distinguish quicksilver deposits of one district or of one type of geological occurrence from those of another?

(3) Are there any elements which are unique to individual deposits?

(4) Does the character and composition of the wall rock cause a quantitative variation of elements concentrated in the cinnabar? Do differences in wall rock in the same deposit cause a quantitative or qualitative variation in the elemental assemblage?

(5) What portion of the impurities found in natural crystals is due to inclusions of wall rock and what portions represent a concentration of certain elements in solid solution in the crystals?

(6) Can the varying shades of cinnabar coloration be attributed to any specific elements concentrated in the cinnabar?

Methods for effecting a large-scale spectrographic study are presented and the significance of the results obtained from such a study is discussed in the following pages.

Selection and Preparation of Samples

Cinnabar ores from a number of quicksilver deposits throughout the United States were chosen for spectrographic analysis. The list of specimens is given in Table 6. Care was taken to choose ore not only from geographically diverse districts, but also ores that occur in a number of diverse rock types. Among the samples are specimens from five deposits in various parts of California which occur in serpentine. Thus the effect of similarities as well as differences in wall rock can be studied. One sample each was analyzed from the Bradford and Great Western mines both of which occur in serpentine only a few miles apart. A specimen of ore in basalt as well as one in lacustrine gravel at Sulphur Bank was submitted for analysis. These two specimens were chosen to show the effect on the elemental content of cinnabar of various rock types in the same deposit. The ore specimens taken for analysis were average, representative ores from each district.

The ore was crushed as finely as possible with a porcelain mortar and pestle. Any porcelain contaminating the ore as a result of crushing was easily removed by the subsequent gravity separation. The cinnabar was concentrated by gravity on a super-panner.[1] The heavy minerals commonly occurring with cinnabar (S.G. 7.6-8.1) are pyrite (S.G. 5.0-5.1), marcasite (S.G. 4.8-4.9), chromite (from the serpentine) (S.G. 4.1-4.9) and native mercury (S.G. 13.6). With the exception of native

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[1] For a description of the super-panner see Haultain, H.E.T., Splitting the minus 200 with the super-panner and infra-sizer: Can. Inst. Min. Metallurgy Bull. 301, pp. 229-40, 1937.

Table 6

Ores Used For Spectrographic Analyses

1. Cuddeback mine, Kern County, California. Cinnabar disseminated through kaolinized rhyolite.
2. Klau mine, San Luis Obsipo County, California. Clusters of dark cinnabar crystals from a shale fracture plane.
3. Oceanic mine, San Luis Obispo County, California. Cinnabar disseminated through sandstone.
4. New Idria mine, San Benito County, California. Cinnabar veins in slate.
5. Aurora mine, San Benito County, California. Cinnabar in veins through silicified serpentine.
6. Bradford mine, Lake County, California. Cinnabar associated with carbonate as veins in silicified serpentine.
7. Great Western mine, Lake County, California. Cinnabar veins in serpentine.
8. Aetna mine, Napa County, California. Cinnabar with a little metacinnabar from silicified and limonitized serpentine.
9. Cloverdale mine, Sonoma County, California. Cinnabar in veins through chert.
10. Mount Diablo mine, Contra Costa County, California. Cinnabar and much metacinnabar as veins and disseminations through serpentine.
11. Sulphur Bank mine, Lake County, California. Cinnabar in veins in basalt.
12. Sulphur Bank mine, Lake County, California. Cinnabar disseminated through lacustrine gravels.
13. Bonanza mine, Douglas County, Oregon. Cinnabar disseminated through sandstone.
14. Black Butte mine, Lane County, Oregon. Cinnabar disseminated through highly altered volcanics.
15. Horse Heaven mine, Jefferson County, Oregon. Cinnabar disseminated through altered agglomerate.
16. Maury Mountain mine,Crook County, Oregon. Cinnabar disseminated through altered volcanic. (Collected by C. N. Schuette)
17. Cardinal mine, Mineral County, Nevada. Cinnabar veins in chert. (Collected by C. N. Schuette)
18. Mazatzal Mountains, Arizona. Cinnabar veins in schist. (Collected by F. L. Ransome)
19. Terlingua deposit, Brewster County, Texas. Cinnabar veins in shale. (Collected by J. B. Stone)
20. Southwestern Arkansas deposit. Cinnabar encrustations on sandstone. (Collected by C. N. Schuette)

mercury which is much heavier than the cinnabar, all of the other minerals are much lighter and no difficulty was experience in effecting a clean separation of the cinnabar. In specimens in which the cinnabar was very finely disseminated through the gangue, repeated grinding and re-concentration of the concentrate was necessary to effect a satisfactory separation of cinnabar. It is not possible to separate cinnabar and metacinnabar (S.G. 7.7) by gravity, but, since only two of the samples (Mount Diablo and Aetna) had any metacinnabar, this was not a serious difficulty. Each cinnabar concentrate was then re-concentrated several times to effect a maximum purification of the sample and the purified concentrate was examined very carefully with binoculars to make certain that there was no differential concentration of other heavy minerals with the cinnabar. Further evidence will be submitted subsequently to prove that actually no such differential concentration occurred.

Wall rock from the same specimens from which the cinnabar was concentrated was crushed and diluted with CP red mercuric sulphide to the extent of 3% wall rock in the mercuric sulphide. The small amount of cinnabar in the wall rock samples (always less than 0.5%) was not separated from the wall rock samples since differential flotation of some of the lighter constituents of the rock during gravity concentration was feared. However, since the amount of cinnabar in the wall rock was always very small, the impurities in the wall rock resulting from the cinnabar are negligible. The cinnabar concentrates and the wall rock samples (3% wall rock in spectrographically analyzed CP HgS) were then submitted to the analyst, Dr. M. F. Hasler, Applied Research Laboratories, Los Angeles.

The Spectrographic Method

The prime purpose of the spectrographic investigation was to ascertain quantitatively the elements which are actually differentially concentrated in the cinnabar with respect to the adjacent wall rock. It was necessary, therefore, to devise some method whereby the amount of wall rock contamination of the cinnabar concentrates could be determined so that the amount of such contamination could be subtracted from the total impurity of the cinnabar thus revealing the amount of each element actually concentrated in the cinnabar. For this purpose, there were prepared cinnabar concentrates and corresponding samples of the crushed wall rock from which each cinnabar concentrate was obtained. The wall rock was then used as a diluent of CP HgS so that, in both the natural cinnabar and the wall rock samples, any extraneous elements existed as impurities of mercuric sulphide. The amount of wall rock to be mixed with the mercuric sulphide was determined empirically by determining the order of magnitude of the gravity purification of cinnabar. It was found that, in most cases without undue difficulty, cinnabar samples could be concentrated until they contained less than 3% impurity. Therefore, corresponding to each natural cinnabar concentrate, wall rock was mixed to the extent of 3% with the spectrographically analyzed CP HgS, the analysis of which follows:

Spectrographic Analysis of CP Mercuric Sulphide Red (Merck 3934)

Used as a Wall Rock Diluent

SiO_2	0.02%	ZnO	0.005%
Fe_2O_3	0.012%	CaO	0.005%
Al_2O_3	0.01%	CuO	0.0012%
MgO	0.013%	MnO	0.0016%

A sample to be studied spectrographically is placed on carbon electrodes and volatilized. The spectrum of the resulting vapor is then photographed and, since each element emits characteristic spectral lines, the elements can be identified on the spectrogram by the position and character of the spectral lines. By visual examination of the density of the spectral lines, a semi-quantitative determination of elemental concentration can be obtained. However, since concentration of an element is not a linear function of spectral intensity (except within certain narrow limits to be noted), it is necessary, in order to ascertain the exact quantitative concentration of each element, to follow the procedure outlined below.

For quantitative determination of an element spectrographically, the approximate concentration is determined from a preliminary qualitative analysis. Then, for each element, a known concentration of the element in approximately the amount present in the unknown sample is placed in a medium similar to that in which it occurs in the unknown sample and the spectrum of the particular element is obtained. By varying the known amount of an element until the spectral lines are of approximately the same intensity as in the unknown, a first approximation of the actual quantitative concentration of the element in the unknown is obtained. Subsequently, by means of a photo-electric cell, small variations in the density of the spectral lines can be plotted as a function of known variations in concentration of an element and then, by determining similar variations in spectral intensity in the unknown, it is possible to calculate the exact composition of the unknown. This procedure must be repeated for each element in each sample in order to obtain an exact quantitative analysis.

Since, for this problem, it was necessary to run more than forty samples, it was obviously impossible to make separate quantitative estimates for each element in each sample. It was therefore necessary to submit the samples in a form such that exact quantitative analyses could be prepared for all samples from one set of standard spectral lines of determined intensity and of determined variation of elemental concentration with variation in spectral intensity. It is known that, if a number of samples have about the same amount of total impurity and if the individual elements are present in approximately the same order of magnitude, it is necessary to obtain only one set of standard spectral lines to which all spectrograms can be referred. Such a procedure is valid insofar as it can be shown empirically that, within the range of concentrations observed in the samples, the intensity is a linear function of concentration. In order to ascertain whether such a linear relation existed over the range of impurity present in the cinnabar concentrates, sandstone from the Oceanic mine was mixed with the aforementioned analyzed CP HgS to the extent of three percent. The exact quantitative concentration of each element in the diluted wall rock sample was then determined. Then, using the same standard spectral lines as were used in quantitative determination of the 3% sample, the impurity in samples containing 1% and 6% was determined. Table 7 shows that, at least within a range of 1-6%, the relation is linear and the procedure is valid. In other words, in Table 7, it can be noted

Table 7

Determination of the Range of Linearity of Elemental Concentration as a Function of Spectral Density

Samples used are all CP HgS diluted, to the extent indicated, by sandstone from the Oceanic mine.

	1%	3%	6%
SiO_2	0.53%	1.70%	3.34%
Al_2O_3	0.22	0.83	1.45
Fe_2O_3	0.03	0.098	0.20
CaO	0.03	0.105	0.20
MgO	0.04	0.113	0.23
NiO	0.0004	0.0013	0.0022
TiO_2	0.01	0.028	0.05
CuO	0.005	0.012	0.025
ZnO	0.011	0.026	0.045
MnO	0.003	0.0094	0.020
Na_2O	0.07	0.227	0.50
BaO	0.001	0.0024	0.004

that, by using the same set of standard spectral lines as was used for quantitative determination of the 3% sample, the 6% sample was found to have twice as much of each element and the 1% sample was found to have 1/3 as much of each element, which is as it should be. Since it was necessary to refer not only all of the cinnabar samples to standard spectral lines, but likewise all of the wall rock, the wall rock samples were submitted as 3% wall rock in spectrographically analyzed CP HgS. The cinnabar samples and diluted wall rock samples were thus referable to one set of spectral lines and were strictly comparable with each other.

Dilution of the wall rock by the same medium as that in which the impurities of the cinnabar occur (namely HgS) is necessary for the following reason. Density of the spectral lines is in part a function of the volatility of the medium with which the element is volatilized. The observed spectral densities will not be the same when an element is volatilized with a highly volatile substance such as mercuric sulphide as when the element is present in some less volatile medium. Since the quantitative concentration is determined by reference to standard spectral lines for known concentrations of the elements in the same medium, this difference in spectral intensity with varying volatility makes no difference if the impurities of all of the samples are present in the same medium. However, if some impurities are present in a highly volatile medium and others in a refractory medium, the results cannot be referred to one set of standard spectral lines. For this reason, it was necessary to submit the wall rocks for analysis as diluents of analyzed mercuric sulphide.

Each spectrogram obtained was the product of exposure during arcing for 10 seconds for each of three portions of 15 mg. each. The total exposure was thus 30 seconds and the total sample was 45 mg. The current used was 5 amperes. For each sample, two spectrograms were made and the quantitative determinations averaged. It was thus necessary to submit samples of at least 100 mg. in weight. For all analyses, the quantitative concentrations of all elements shown in the portion of the spectrum from 2380 to 4600 Å were determined.

Determinable Elements, Sensitivity, and Possible Error

Table 8 gives the spectrographic analyses of cinnabar concentrates and of the corresponding wall rocks from each of twenty typical quicksilver deposits. The first column of each analysis gives the elements present as impurities in the cinnabar concentrate. The second column gives the composition of the three percent of wall rock diluted in CP HgS (from which have been subtracted the impurities of the CP HgS). The third column lists the elements of the wall rock in column two multiplied by some factor such that the total of the third column is 100%. The third column thus gives (within limits to be noted) the actual composition of the wall rock from which the cinnabar was concentrated. The spectral lines show only the elemental concentrations. The elemental concentrations were converted into the oxide form so as to be comparable with other rock analyses.

Actual quantitative concentrations of all elements shown in the portion of the spectrum between 2380 and 4600 Å were determined. Certain elements are notably absent from this portion of the spectrum; namely, the inert gases, oxygen, the halogens, sulphur, and selenium. The halogens, inert gases, oxygen, and sulphur can be determined only by arcing in a vacuum. The determination of selenium necessitates the use of specially sensitized plates. Carbon was not determined since the electrodes used were of carbon. Strontium was not determined because the strontium lines in the portion of the spectrum photographed coincide with the cyanogen band spectra and hence cannot be studied easily. A study of the visible spectrum would have given quantitative determinations of strontium, but

Table 8

Analyses of Cinnabar Concentrates and Corresponding Wall Rocks

Oxides	Cinnabar Concentrate	Cuddeback 3% Diluted Wall Rock	Wall Rock Calculated to 100%	Cinnabar Concentrate	Klau 3% Diluted Wall Rock	Wall Rock Calculated to 100%	Cinnabar Concentrate	Oceanic 3% Diluted Wall Rock	Wall Rock Calculated to 100%
SiO_2	6.34%	2.31%	72.05%	0.069%	1.80%	58.50%	2.95%	1.68%	54.00%
Al_2O_3	1.28	0.566	17.75	0.13	0.561	18.30	2.28	0.82	26.40
Fe_2O_3	0.20	0.023	0.72	0.13	0.298	9.69	0.42	0.086	2.76
CaO	0.037	0.017	0.53	0.012	0.0273	0.89	0.15	0.1	3.21
MgO	0.056	0.03	0.62	0.023	0.147	4.78	0.205	0.1	3.21
Cr_2O_3	<0.016	<0.013	<0.41	<0.005	<0.018	<0.58	0.09	<0.016	<0.51
NiO	<0.002	<0.002	<0.063	0.0018	0.0062	0.20	0.0059	0.0013	0.04
TiO_2	<0.024	<0.021	<0.65	<0.004	0.0415	1.13	0.125	0.028	0.9
CuO	0.042	0.0055	0.17	0.038	0.0124	0.40	0.037	0.0108	0.32
GeO	<0.007	<0.006	<0.19	0.01	<0.004	<0.13	0.0042	<0.004	<0.03
ZnO	<0.032	<0.022	<0.69	0.124	0.0225	0.73	<0.012	0.021	0.675
MnO	0.034	<0.0024	<0.08	<0.0009	0.0125	0.41	0.023	0.0078	0.25
Na_2O	<0.21	<0.18	<5.66	<0.034	<0.12	<3.99	0.276	0.227	7.29
BaO	<0.026	<0.002	<0.062	<0.0004	<0.0015	<0.047	0.005	0.0024	0.083
Co_2O_3	<0.004	<0.0035	<0.11	<0.0007	<0.003	<0.06	<0.0015	<0.002	<0.06
PbO	0.013	<0.0077	<0.24	0.0021	<0.005	<0.16	<0.0033	<0.005	<0.16
Ag2O	0.0021	<0.0001	<0.003	0.00013	<0.00008	<0.003	<0.00002	<0.00007	<0.002
Trace Elements									
TOTAL	8.3251	3.2012	100.00	0.58503	3.07898	100.00	6.58592	3.11137	100.00

Table 8

Analyses of Cinnabar Concentrates and Corresponding Wall Rocks

Oxides	New Idria Cinnabar Concentrate	New Idria 3% Diluted Wall Rock	New Idria Wall Rock Calculated to 100%	Aurora Cinnabar Concentrate	Aurora 3% Diluted Wall Rock	Aurora Wall Rock Calculated to 100%	Bradford Cinnabar Concentrate	Bradford 3% Diluted Wall Rock	Bradford Wall Rock Calculated to 100%
SiO_2	0.474%	1.71%	58.20%	0.135%	0.495%	16.30%	0.300%	0.374%	12.60%
Al_2O_3	0.134	0.745	25.40	0.099	0.126	4.14	0.083	0.101	3.44
Fe_2O_3	0.033	0.084	2.88	0.043	0.218	7.16	0.09	0.073	2.48
CaO	0.017	0.037	1.26	0.02	0.143	4.69	0.0256	1.435	48.70
MgO	0.019	0.05	1.71	0.087	1.707	56.00	0.302	0.772	26.23
Cr_2O_3	0.003	0.0173	0.59	0.022	0.122	4.01	0.045	0.128	4.35
NiO	0.0003	0.0013	0.04	0.018	0.018	0.59	0.019	0.0061	0.21
TiO_2	0.01	0.0472	1.61	0.0047	0.013	0.43	0.018	0.005	0.17
CuO	0.014	0.0076	0.26	0.020	0.0068	0.22	0.015	0.0023	0.08
GeO	<0.0006	<0.003	<0.1	0.0024	<0.0016	<0.05	0.0013	<0.00065	<0.029
ZnO	0.25	0.0122	0.428	<0.0086	0.022	0.72	0.0077	0.005	0.17
MnO	<0.0005	0.005	0.17	0.005	0.0534	1.75	0.0124	0.019	0.65
Na_2O	<0.018	0.207	7.05	<0.057	0.11	3.66	<0.026	<0.019	<0.65
BaO	0.0006	0.003	0.10	0.0012	0.0013	0.04	0.005	0.0052	0.18
Co_2O_3	<0.0004	<0.002	<0.07	0.0023	0.005	0.169	0.003	0.001	0.03
PbO	<0.0008	<0.004	<0.13	<0.0025	<0.002	<0.07	0.0013	<0.00083	<0.03
Ag_2O	0.0002	<0.00005	<0.002	<0.00004	<0.00003	<0.001	0.00016	<0.00002	<0.001
Trace Elements				B					
Total	0.97540	2.93565	100.00	0.52774	3.04413	100.00	0.95446	2.9471	100.00

Table 8

Analyses of Cinnabar Concentrates and Corresponding Wall Rocks

Oxides	Great Western			Aetna			Cloverdale		
	Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%	Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%	Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%
SiO_2	1.37%	2.07%	69.60%	5.90%	2.10%	71.20%	0.72%	2.53%	86.10%
Al_2O_3	0.104	0.145	4.90	0.20	0.226	7.64	0.23	0.093	3.20
Fe_2O_3	0.110	0.237	7.98	0.29	0.102	3.46	0.125	0.0743	2.57
CaO	0.021	0.029	0.98	0.015	0.053	1.79	0.032	0.006	0.20
MgO	0.081	0.146	4.82	0.025	0.098	3.33	0.034	0.043	1.46
Cr_2O_3	0.068	0.240	8.08	1.33	0.116	3.93	<0.004	<0.003	<0.10
NiO	0.0046	0.018	0.61	0.055	0.022	0.75	0.0028	0.0009	0.03
TiO_2	<0.006	0.012	0.40	0.034	<0.014	<0.48	0.01	0.008	0.27
CuO	0.041	0.0053	0.18	0.091	0.0098	0.33	0.044	0.0081	0.28
GeO	0.037	<0.0014	<0.049	0.0044	<0.004	<0.14	<0.002	<0.001	<0.03
ZnO	<0.008	0.015	0.51	0.065	0.037	1.25	<0.008	0.0126	0.439
MnO	<0.0013	0.0094	0.32	0.060	0.0117	0.40	0.102	0.0699	2.38
Na_2O	<0.051	<0.042	<1.41	0.26	0.147	4.98	<0.054	0.0845	2.88
BaO	<0.0007	<0.0005	<0.02	<0.001	<0.0014	<0.05	0.0032	0.0006	0.02
Co_2O_3	<0.001	0.0022	0.07	0.01	0.0027	0.098	0.002	<0.0007	<0.02
PbO	<0.002	<0.002	<0.07	<0.0031	<0.005	<0.17	<0.002	<0.002	<0.07
Ag_2O	0.00045	<0.00003	<0.001	<0.00005	<0.00007	<0.002	0.0001	<0.00002	<0.001
Trace Elements									
TOTAL	1.90705	2.97483	100.00	8.34355	2.94967	100.00	1.37510	2.93762	100.00

Table 8

Analyses of Cinnabar Concentrates and Corresponding Wall Rocks

Oxides	Mount Diablo Cinnabar Concentrate	Mount Diablo 3% Diluted Wall Rock	Mount Diablo Wall Rock Calculated to 100%	Sulphur Bank (Basalt) Cinnabar Concentrate	Sulphur Bank (Basalt) 3% Diluted Wall Rock	Sulphur Bank (Basalt) Wall Rock Calculated to 100%	Sulphur Bank (Gravel) Cinnabar Concentrate	Sulphur Bank (Gravel) 3% Diluted Wall Rock	Sulphur Bank (Gravel) Wall Rock Calculated to 100%
SiO_2	0.286%	2.21%	74.30%	3.00%	1.11%	37.63%	3.80%	2.40%	82.10%
Al_2O_3	0.124	0.132	4.44	1.17	1.09	37.13	1.17	0.26	8.90
Fe_2O_3	0.352	0.248	8.33	0.65	0.081	2.76	0.31	0.08	2.80
CaO	0.027	0.031	1.04	0.63	0.24	8.17	0.049	0.019	0.65
MgO	0.042	0.0598	2.02	0.023	0.114	3.89	0.15	0.065	2.24
Cr_2O_3	0.018	0.21	7.06	0.058	0.014	0.48	0.032	0.0084	0.29
NiO	0.0009	0.001	0.03	<0.001	<0.0009	<0.03	0.002	0.001	0.03
TiO_2	<0.005	0.0185	0.62	0.043	0.053	1.82	0.053	0.02	0.68
CuO	0.017	0.0049	0.17	0.064	0.0069	0.23	0.073	0.0062	0.21
CeO	0.006	<0.0013	<0.04	0.006	0.003	0.10	<0.002	<0.001	<0.03
ZnO	<0.0054	0.0115	0.39	0.02	0.012	0.41	0.014	0.011	0.38
MnO	<0.0014	0.004	0.13	0.32	0.0134	0.46	0.028	0.0144	0.49
Na_2O	<0.041	<0.038	<1.28	0.175	0.193	6.57	<0.067	<0.032	<1.09
BaO	0.0012	0.0021	0.069	0.0041	0.0031	0.11	0.0043	0.001	0.03
Co_2O_3	<0.0008	<0.00075	<0.03	<0.002	<0.002	<0.067	<0.0013	<0.0006	<0.02
PbO	0.0024	<0.0016	<0.05	<0.0045	<0.004	<0.14	0.004	<0.0014	<0.059
Ag_2O	0.00004	<0.00002	<0.001	0.00015	0.00009	0,003	0.00026	<0.00002	<0.001
Trace Elements	Sb						Sb		
TOTAL	0.93114	2.96727	100.00	6.17075	2.94039	100.00	5.75986	2.92102	100.00

Table 8

Analyses of Cinnabar Concentrates and Corresponding Wall Rocks

	Bonanza			Black Butte			Horse Heaven		
Oxides	Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%	Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%	Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%
SiO_2	3.36%	2.11%	71.90%	1.58%	2.28%	76.20%	2.20%	2.22%	73.30%
Al_2O_3	2.12	0.535	18.20	0.71	0.44	14.80	0.095	0.486	16.00
Fe_2O_3	0.315	0.073	2.40	0.230	0.076	2.50	0.047	0.144	4.75
CaO	0.027	0.0082	0.28	0.026	0.0055	0.18	0.0060	0.0143	0.472
MgO	0.086	0.029	0.98	0.032	0.021	0.70	0.009	0.0275	0.91
Cr_2O_3	0.115	0.0114	0.39	0.091	<0.004	<0.13	<0.002	<0.0025	<0.08
NiO	0.0015	0.0005	0.02	0.0097	0.0016	0.05	0.0005	0.0005	0.02
TiO_2	0.156	0.0368	1.22	0.042	0.068	2.30	<0.0034	0.0103	0.34
CuO	0.109	0.0075	0.26	0.073	0.0088	0.29	0.054	0.0056	0.18
GeO	<0.002	<0.0014	<0.05	<0.0016	<0.002	<0.07	0.018	<0.001	<0.03
ZnO	1.56	0.019	0.65	0.530	0.019	0.64	0.0123	0.013	0.43
MnO	0.006	0.0031	0.11	0.0085	0.004	0.13	<0.0007	0.0042	0.14
Na_2O	<0.067	0.100	3.41	<0.054	<0.056	<1.87	<0.028	0.098	3.23
BaO	0.0016	0.0008	0.03	<0.0007	<0.0007	<0.02	<0.0003	0.0013	0.048
Co_2O_3	<0.0013	<0.0008	<0.03	0.0064	<0.0011	<0.049	<0.0005	<0.0007	<0.02
PbO	0.0069	<0.002	<0.069	0.0104	<0.002	<0.07	0.0027	<0.001	<0.03
Ag_2O	0.0007	<0.00002	<0.001	0.0003	0.00004	0.001	0.00005	<0.00005	<0.002
Trace Elements	Sb			Sn, Sb			Sb, As		
TOTAL	7.9350	2.93752	100.00	3.4056	2.98974	100.00	2.47945	3.02995	100.00

Table 8

Analyses of Cinnabar Concentrates and Corresponding Wall Rocks

Oxides	Maury Mountain Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%	Cardinal Cinnabar Concentrate	3 % Diluted Wall Rock	Wall Rock Calculated to 100%	Mazatzal Cinnabar Concentrate	3% Diluted Wall Rock	Wall Rock Calculated to 100%
SiO_2	0.91%	1.95%	65.30%	0.055%	1.59%	52.50%	1.07%	2.00%	67.10%
Al_2O_3	0.88	0.678	22.70	0.0105	0.965	31.90	0.765	0.642	21.60
Fe_2O_3	0.154	0.129	4.31	0.035	0.079	2.70	0.325	0.071	2.40
CaO	0.025	0.0171	0.57	0.021	0.055	1.84	0.235	0.0194	0.659
MgO	0.053	0.03	1.00	0.015	0.104	3.40	0.04	0.032	1.00
Cr_2O_3	0.053	0.048	1.61	0.0107	0.0168	0.56	0.074	0.0381	1.28
NiO	0.006	0.0015	0.05	0.0004	0.002	0.06	0.0013	0.0015	0.05
TiO_2	0.147	0.034	1.14	0.006	0.0316	1.04	0.09	0.076	2.57
CuO	0.029	0.0074	0.25	0.006	0.0094	0.31	0.0214	0.0184	0.64
GeO	<0.0009	<0.002	<0.07	<0.001	<0.0032	<0.01	<0.0006	<0.002	<0.06
ZnO	0.18	0.0147	0.488	0.004	0.0178	0.598	0.005	0.0092	0.31
MnO	0.006	0.0038	0.13	<0.0007	0.0088	0.29	0.004	0.0112	0.38
Na_2O	<0.026	<0.066	<2.21	<0.029	<0.095	<3.10	<0.019	<0.053	<1.80
BaO	0.001	<0.0008	<0.03	0.060	0.045	1.49	0.0004	0.0011	0.04
Co_2O_3	0.0026	<0.0013	<0.04	<0.0006	<0.002	<0.07	<0.0004	<0.001	<0.04
PbO	0.0012	<0.003	<0.10	<0.0013	<0.004	<0.13	0.0013	<0.002	<0.07
Ag_2O	0.00004	<0.00006	<0.002	0.00016	<0.00006	<0.002	0.00007	<0.00003	<0.001
Trace Elements	B						B		
TOTAL	2.47844	2.98666	100. 00	0.25636	3.02866	100.00	2.65347	2.97793	100.00

Table 8

Analyses of Cinnabar Concentrates and Corresponding Wall Rocks

Oxides	Terlingua Cinnabar Concentrate	Terlingua 3% Diluted Wall Rock	Terlingua Wall Rock Calculated to 100%	Arkansas Cinnabar Concentrate	Arkansas 3% Diluted Wall Rock	Arkansas Wall Rock Calculated to 100%
SiO_2	0.247%	1.45%	46.30%	0.64%	2.69%	90.30%
Al_2O_3	0.286	1.14	36.50	0.103	0.148	4.50
Fe_2O_3	0.162	0.115	3.70	0.06	0.029	0.98
CaO	0.276	0.0545	1.74	0.016	0.003	0.10
MgO	0.071	0.070	2.24	0.018	0.022	0.77
Cr_2O_3	0.0107	0.015	0.48	<0.003	<0.003	<0.10
NiO	<0.0002	0.0016	0.059	0.0007	0.0016	0.05
TiO_2	0.014	0.037	1.18	0.007	0.017	0.57
CuO	0.018	0.0098	0.32	0.028	0.0099	0.34
GeO	<0.0008	<0.002	<0.06	<0.0013	<0.0013	<0.039
ZnO	0.0075	0.008	0.26	0.008	0.007	0.24
MnO	0.0106	0.0056	0.18	0.0034	0.0020	0.06
Na_2O	<0.02	0.21	6.72	<0.036	<0.04	<1.35
BaO	0.0036	0.004	0.13	<0.0005	<0.0005	<0.02
Co_2O_3	<0.0004	<0.001	<0.03	<0.0008	<0.0007	<0.02
PbO	<0.0009	<0.003	<0.10	<0.0016	<0.0017	<0.06
Ag_2O	0.00007	<0.00004	<0.001	0.00003	<0.00002	<0.001
Trace Elements	Sb					
TOTAL	1.13077	3.12654	100.00	0.9273%	2.97662	100.00

this would have necessitated an unjustifiably large increase in the cost of the analyses. Table 9 lists all of the common elements that could have been determined if present and the spectral sensitivity of each element. This tabulation shows the wide variation in sensitivity of the common elements. The second column of Table 9 is the first column multiplied by approximately 33. The second column thus gives the minimum amount of a wall rock element that will appear in the synthetic HgS-wall rock sample in which the wall rock is diluted with 33 times its weight of HgS. Conversely, the second column of Table 9 indicates the minimum amount of an element that must have been present in the original wall rock in order that the element will appear in the analysis of the 3% diluted samples. The differences in sensitivity explain the absence of certain elements from the analyses of the 3% samples. Thus, silver is present in all of the samples, but no gold is recorded. Gold, however, is found in small amounts in several of the deposits. An examination of the sensitivity of silver shows that the lines have a sensitivity of 0.00002% (0.0034% equals 1 troy ounce. Therefore, 0.00002% equals 0.006 oz.). Thus 0.006 oz. of silver must be present in the cinnabar concentrate or 0.2 oz. in the wall rock to appear in the analyses. On the other hand, the sensitivity of gold is only 0.001%. Thus 0.3 oz. of gold must be present in the cinnabar concentrate or 10 oz. in the wall rock to appear in the analyses. Obviously, no such quantities of gold are present and hence no gold appears in the analyses although gold may very well be present in nearly as large amounts as silver. Many quicksilver deposits contain small amounts of arsenic and antimony and the

Table 9

Spectral Sensitivity of the Common Elements

Element	Sensitivity (In percent)	Amount of element necessary in wall rock so that element will appear in analysis after dilution to 3% (Equals first column times 33 ca.) (In percent)
Al	0.001	0.03
Sb	0.003	0.1
As	0.01	0.3
Ba	0.0003	0.01
Bi	0.001	0.03
B	0.001	0.03
Cd	0.002	0.07
Ca	0.001	0.03
Cr	0.002	0.07
Co	0.0003	0.01
Cu	0.0001	0.003
Ge	0.0005	0.02
Au	0.001	0.03
Fe	0.001	0.03
Pb	0.0008	0.03
Mg	0.001	0.03
Mn	0.0004	0.01
Hg	0.03	1.0
Mo	0.001	0.03
Ni	0.0002	0.007
P	0.1	3.3
K	0.05	1.7
Si	0.005	0.2
Ag	0.00002	0.0007
Na	0.02	0.7
Te	0.01	0.3
Sn	0.001	0.03
Ti	0.002	0.7
W	0.005	0.2
U	0.1	3.3
V	0.002	0.7
Zn	0.005	0.2
Zr	0.01	0.3

general absence of these elements in the analyses is likewise understandable from the sensitivity tables since more than 0.33% arsenic must be present to appear in the analyses of wall rock. Similarly, for antimony to appear in the 3% diluted wall rock samples, 0.1% must be present. Neither arsenic nor antimony is generally present in such large amounts; in fact, the presence of either arsenic or antimony in such quantities would seriously lower the value of the ore as a source of quicksilver. On account of their low sensitivities, potassium and phosphorous are likewise not recorded although they are probably present in the wall rock in small amounts. The elements gold, arsenic, antimony, phosphorous, and potassium are the only common elements that are missing on account of their low sensitivities. In order to have the samples comparable so that the actual concentration of elements in the cinnabar could be determined, it was necessary to sacrifice the higher sensitivity that would result were the wall rocks analyzed without dilution. The total wall rock composition as shown in the third column of each of the analyses of Table 8 is thus slightly in error for the following reasons:

(1) Sulphur has not been determined. In most cases the sulphur content would not exceed 1%.

(2) The mercury present in the cinnabar in the wall rock cannot be distinguished from the mercury of the mercuric sulphide diluent. The mercury of the cinnabar would not exceed 0.5%.

(3) The phosphorous and potassium content falls below the spectrographic sensitivity when the sample is diluted to 3%. Then, when the

sample is re-calculated to 100%, neither the potassium nor the phosphorous appears in the analyses although both probably are often present. This could not involve an error of more than 3%. In re-calculating the total wall rock composition, the error resulting from low sensitivities of certain elements, therefore, could not exceed 5% although, as has been shown, certain elements of especial interest (such as gold, arsenic, and antimony) do not appear in the analyses.

The possible error for each element in the analyses of the natural and synthetic samples has been determined empirically to be less than 30% of the amount of the element present. When the data are plotted as the ratio of the difference between the amount of element in excess in the cinnabar or wall rock to the amount that was originally present in the cinnabar or wall rock (as has been done for this investigation), the error is less than 15% of the percentage of the element present. (Thus, for example, if a sample is said to contain 10% of a particular element, the possible error is 1.5%.) Thus 15% is taken as the maximum analytical error involved in the ratios to be presented subsequently. This is the maximum possible error - the probable error is considerably less.

Computation and Tabulation of Differential Elemental Concentrations

In order to subtract the wall rock contamination from the cinnabar concentrates and thus find which elements are differentially concentrated in the cinnabar and which are differentially concentrated in the wall rock during mineralization, it is necessary first to determine in some way how much of the impurity in the cinnabar concentrates is attributable to wall rock contamination (wall rock not completely removed during gravity separation) and how much of the impurity involves a differential concentration of elements in either the cinnabar or the wall rock during mineralization. The three percent diluted wall rock samples give the correct ratios of elements to one another in the wall rock. It is, therefore, necessary only to ascertain which elements or groups of elements are stable during mineralization and then to convert the entire wall rock sample by some factor such that the selected element or group of elements is equal in both wall rock and cinnabar. Any excess of an element in either wall rock or cinnabar is then attributable to differential concentration during mineralization. Therefore, it is necessary to ascertain certain elements or groups of elements which are stable during mineralization.

The term "stable during mineralization" here implies elements that are not carried by the mineralizing solutions; elements which, if present in the wall rock, would effect no preferential precipitation of cinnabar; and elements which are not soluble in the mineralizing solutions and hence would not be preferentially leached during mineralization. Any of the heavy metals might conceivable be carried in small amounts by the mineralizing solutions or, if present in the wall rock, might cause preferential precipitation of cinnabar. Thus, of the elements present in the analyses, the following cannot be used to re-calculate the diluted wall rock samples: iron, chromium, nickel, copper, germanium, zinc, manganese, cobalt, lead, and silver. Because of their solubility in mineralizing solutions and the possibility that they may have been transported in solution, the alkali and alkaline earth metals (in the analyses, sodium, calcium, magnesium, and barium) cannot be used for re-calculation. Silicification is so common a process in connection with quicksilver mineralization and silica is so markedly soluble in hot alkaline solutions that silica is likewise of no value in determining wall rock contamination in the cinnabar. Of the individual elements that are most likely to be stable, only aluminum and titanium are present in the analyses. Three methods of adjusting the diluted wall rock samples to determine wall rock contamination in the cinnabar concentrates have been used:

Method I - Alumina Method: All of the constituents of the diluted wall rock sample are multiplied by some factor such that the alumina in the diluted wall rock sample is equal to that of the corresponding cinnabar concentrate. Table 10 lists the factors used and the re-calculated values of the elements in the wall rock samples. Since each element in an analysis is multiplied by the same factor, the ratio of elements to one another is constant - only the ratio of an element in the wall rock to that in the corresponding cinnabar concentrate is varied. This method assumes that, during mineralization, the alumina has been neither (1) carried in by the mineralizing solutions (2) preferentially replaced by cinnabar (3) preferentially reactive to the mineralizing solutions nor (4) differentially leached by the mineralizing solutions. Thus, if these assumptions are correct, by multiplying the wall rock by some factor such that the alumina of the wall rock and cinnabar are equal, the resulting wall rock values represent the actual amount of wall rock elements in the cinnabar and any excess or deficiency of an element in the cinnabar beyond that present in the corrected wall rock must represent differential concentration during mineralization. Although no such assumption can be entirely valid in every case, nevertheless, the character of the quicksilver mineralizing solutions is such that, during mineralization, the alumina would most probably be highly stable. A comparison of the alumina content of typical serpentines with the alumina content of the five serpentines analyzed (Aetna, Aurora, Bradford, Great Western, and Mount Diablo) will show that, at least in these five cases, the alumina has been quite stable.

Method II - Titania Method: All of the constituents of the diluted wall rock samples are multiplied by some factor such that the titania in the diluted wall rock sample is equal to that of the corresponding cinnabar concentrate. Table 10 lists the factors used and the recalculated wall rock values. This method operates on the assumption that the titania is stable during mineralization. This assumption probably has the greatest validity,[1] but the low sensitivity of titania and the small amounts of titania present renders this method less satisfactory than the alumina method. However, in connection with the analyses with which it can be used, the titania method serves as a check on the alumina method.

Method III - Total Impurity Method: All of the constituents of the diluted wall rock sample are multiplied by some factor such that the total content of the diluted wall rock sample is equal to the total impurity content of the corresponding cinnabar concentrate. Table 10 lists the factors used and the re-calculated wall rock values. This method operates on the assumption that, since the ratio of elements to one another in the diluted wall rock sample is the same before and after re-calculation, if the total impurity of the cinnabar and wall rock are made equal, any excess of an element in the cinnabar represents a concentration above the relative amount present in the wall rock and any deficiency in the cinnabar represents a relative deficiency below that present in the wall rock.

Any disparity in the results obtained by the three methods of wall rock re-calculation indicates that, in the particular case, one or more of these assumptions is invalid. However, only those generalities that appear as the result of all three methods of re-calculation will

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[1] Cf. Schwartz, G. M., Hydrothermal alteration of igneous rocks: Geol. Soc. America Bull. vol. 50, pp. 217-19, 231-2, 1939. The study of a number of analyses of hydrothermally altered igneous rocks has here shown the relative stability of alumina and, more especially, of titania during hydrothermal alteration.

be regarded as significant. Since certain of the general results obtained by all three methods of re-calculation are very similar, it is believed that the general validity of the assumptions is established.

The relation of the concentrations or deficiencies in the cinnabar to the amount originally present in the cinnabar or wall rock was determined by the following procedure.

Where A equals the amount of an element in the cinnabar and B equals the amount of an element in the re-calculated diluted wall rock sample (re-calculated by one of the three methods outlined above) then A-B (equals C) equals the actual differential concentration, in percent, of an element in the cinnabar. Where the element is in excess in the wall rock, B-A (equals D) equals the actual differential concentration, in percent, of an element in the wall rock. Table 11 shows the actual differential concentrations when the wall rock is re-calculated by each of the three methods. In all cases, parentheses around any figure in the tables indicates a concentration in the wall rock rather than in the cinnabar. (In other words, the value C has no parentheses; the value D is parenthesized.)

Then the value C/A (equals E) equals the ratio of the actual differential concentration of an element in the cinnabar to the original concentration of the element in the cinnabar and D/B (equals F) equals the ratio of the actual differential concentration of an element in the wall rock to the amount originally present in the re-calculated wall rock. These ratios, as computed by the three methods, are tabulated in Table 12. (Relative concentrations in the wall rock (F) are

Table 10

Recalculated Wall Rock Values*
(In percent)

Mines	Recalculation factors			SiO_2			Al_2O_3		
	A	B	C	A	B	C	A	B	C
Cuddeback	2.26	-	2.57	5.23	-	5.94	1.28	-	1.45
Klau	1/4.52	-	1/5.85	.416	-	.343	.130	-	.107
Oceanic	2.79	4.4	2.12	4.7	7.4	3.56	2.28	3.6	1.74
New Idria	1/5.56	1/4.72	1/3.01	.308	.362	.564	.134	.158	.245
Aurora	1/1.27	1/2.76	1/5.76	.389	.179	.0859	.0981	.0456	.028
Bradford	1/1.22	3.6	1/3.11	.306	1.35	.120	.083	.364	.0323
Great Western	1/1.39	-	.64	1.49	-	1.33	.104	-	.093
Aetna	1/1.13	-	2.83	1.86	-	5.94	.20	-	.64
Cloverdale	2.46	1.25	1/2.14	6.28	3.16	1.18	.23	.106	.0434
Mount Diablo	1/1.06	-	1/3.19	2.08	-	.692	.124	-	.0414
Sulphur Bank(Basalt)	1.07	1/1.23	2.10	1.19	.90	2.33	1.17	.884	2.29
Sulphur Bank(Gravel)	4.5	2.65	1.97	10.80	6.36	4.74	1.17	.69	.512
Bonanza	3.96	4.36	2.7	8.35	9.21	5.7	2.12	2.34	1.44
Black Butte	1.61	1/1.62	1.14	3.67	1.41	2.60	.71	2.72	.502
Horse Heaven	1/5.13	-	1/1.22	.433	-	1.82	.433	-	.398
Maury Mountain	1.3	4.325	1/1.21	2.54	8.43	1.61	.881	2.93	.56
Cardinal	1/92	1/5.27	1/11.8	.0173	.3015	.135	.0105	.1831	.0816
Mazatzal	1.19	1.183	1/1.12	2.38	2.37	1.78	.765	.76	.574
Terlingua	1/5	1/2.68	1/2.76	.29	.541	.525	.228	.426	.413
Arkansas	1/1.44	1/2.42	1/3.21	1.87	1.11	.838	.103	.061	.0461

*All elements of the 3% diluted wall rock samples multiplies by some factor such that:

Column A - the alumina of the wall rock is equal to that of the cinnabar.

Column B - the titania of the wall rock is equal to that of the cinnabar.

Column C - the total impurity of the wall rock sample is equal to that of the cinnabar.

Table 10

Re-calculated Wall Rock Values*
(In percent)

Mines	Fe_2O_3			CaO			MgO		
	A	B	C	A	B	C	A	B	C
Cuddeback	.052	-	.0591	.036	-	.0437	.045	-	.0514
Klau	.069	-	.567	.0063	-	.0052	.034	-	.028
Oceanic	.24	.378	.182	.279	.44	.212	.279	.44	.212
New Idria	.015	.0178	.0276	.0066	.0078	.0122	.0090	.0106	.0164
Aurora	.172	.079	.0378	.113	.0518	.0248	1.34	.6187	.296
Bradford	.0598	.263	.0235	1.175	5.16	.46	.633	2.78	.248
Great Western	.171	-	.152	.028	-	.0186	.105	-	.094
Aetna	.090	-	.289	.046	-	.15	.087	-	.277
Cloverdale	.184	.0929	.0347	.0149	.0075	.00281	.109	.054	.0201
Mount Diablo	.234	-	.0776	.0292	-	.00971	.0564	-	.0187
Sulphur Bank(Basalt)	.087	.066	.171	.257	.195	.505	.122	.0925	.241
Sulphur Bank(Gravel)	.36	.212	.158	.0855	.05	.0374	.293	.172	.128
Bonanza	2.89	.328	.197	3.24	.0358	.0221	.115	.127	.0784
Black Butte	.122	.047	.0866	.00865	.0034	.00626	.0338	.013	.0239
Horse Heaven	.028	-	.118	.0028	-	.0117	.0054	-	.0325
Maury Mountain	.168	.557	.106	.0222	.0739	.0141	.039	.1297	.0258
Cardinal	.000858	.015	.0067	.000598	.0105	.00466	.00113	.018	.00801
Mazatzal	.0845	.084	.0634	.0231	.023	.0173	.0381	.0379	.0286
Terlingua	.023	.0429	.0416	.019	.0203	.0197	.014	.0261	.0264
Arkansas	.0202	.012	.00904	.00208	.00124	.000935	.00208	.0091	.00635

*All elements of the 3% diluted wall rock samples multiplied by some factor such that:
Column A- The alumina of the wall rock is equal to that of the cinnabar.
Column B- The titania of the wall rock is equal to that of the cinnabar.
Column C- The total impurity of the wall rock sample is equal to that of the cinnabar.

Table 10

Re-calculated Wall Rock Values*
(In percent)

Mines	Cr_2O_3			NiO			TiO_2		
	A	B	C	A	B	C	A	B	C
Cuddeback	<.029	-	<.0334	<.0045	-	<.0514	<.047	-	<.054
Klau	<.00416	-	<.00343	.00143	-	.00118	.00959	-	.0078
Oceanic	<.0448	<.0704	<.0339	.00364	.0057	.00275	.0785	.123	.0593
New Idria	.0031	.00366	.00568	.00023	.00028	.000428	.0085	.01	.0155
Aurora	.0968	.0442	.0212	.0142	.0065	.00302	.0102	.0047	.00216
Bradford	.105	.461	.041	.005	.022	.00196	.0041	.018	.00161
Great Western	.172	-	.154	.0129	-	.012	.00875	-	.077
Aetna	.103	-	.328	.019	-	.0643	<.012	-	<.0396
Cloverdale	<.00744	<.0038	<.0014	.00223	.0011	.000421	.1080	.01	.00374
Mount Diablo	.198	-	.0658	.00095	-	.000313	.0175	-	.00578
Sulphur Bank(Basalt)	.015	.011	.0286	<.00096	<.00073	<.0019	.057	.043	.112
Sulphur Bank(Gravel)	.0378	.0223	.0165	.0045	.0027	.00197	.090	.053	.0394
Bonanza	.045	.0497	.0308	.0020	.0022	.00135	.144	.156	.0967
Black Butte	<.00645	<.0025	<.00456	.00258	.00099	.00183	.110	.042	.0775
Horse Heaven	<.00049	-	<.00205	.0001	-	.000408	.002	-	.0082
Maury Mountain	.0624	.2075	.0396	.00195	.0065	.00134	.0442	.147	.0281
Cardinal	.000183	.00319	.00142	.0000217	.00038	.00017	.000344	.006	.00268
Mazatzal	.0453	.0451	.034	.00179	.00178	.00134	.0905	.09	.0676
Terlingua	.0030	.0056	.00543	.00052	.0006	.000578	.0054	.014	.0134
Arkansas	.00208	.00124	.000935	.00111	.00066	.000623	.00118	.007	.00498

*All elements of the 3% diluted wall rock samples multiplied by some factor such that:
Column A - The alumina of the wall rock is equal to that of the cinnabar.
Column B - The titania of the wall rock is equal to that of the cinnabar.
Column C - The total impurity of the wall rock sample is equal to that of the cinnabar.

Table 10

Re-calculated Wall Rock Values*
(In percent)

Mines	CuO			GeO			ZnO		
	A	B	C	A	B	C	A	B	C
Cuddeback	.012	-	.0141	<.014	-	<.0154	<.050	-	<.0566
Klau	.00286	-	.00236	<.000925	-	<.000762	.0052	-	.00428
Oceanic	.0302	.0475	.0229	<.0112	<.0176	<.00848	.0588	.092	.0445
New Idria	.0014	.0016	.0025	<.00054	<.00064	<.000987	.0022	.0026	.00401
Aurora	.00535	.0025	.00118	<.00126	<.00058	<.000277	.0173	.008	.00382
Bradford	.00188	.0083	.00074	<.00053	<.00234	<.000209	.0041	.018	.00161
Great Western	.0038	-	.00339	<.00101	-	<.00089	.0108	-	.0096
Aetna	.0087	-	.277	<.0035	-	<.0113	.032	-	.105
Cloverdale	.0201	.0101	.00378	<.00248	<.0013	<.000466	.0312	.0157	.00588
Mount Diablo	.00462	-	.00153	<.00123	-	<.000407	.0109	-	.0036
Sulphur Bank(Basalt)	.0074	.0056	.0146	<.0032	<.0024	<.00633	.013	.0097	.0254
Sulphur Bank(Gravel)	.0279	.0164	.0122	<.0045	<.0027	<.00197	.0495	.029	.0217
Bonanza	.030	.033	.0203	<.0055	<.0061	<.00378	.075	.083	.0322
Black Butte	.0142	.0054	.0105	<.00322	<.0012	<.00228	.0306	.0117	.0217
Horse Heaven	.0011	-	.00458	<.00019	-	<.00082	.0025	-	.0106
Maury Mountain	.00961	.032	.00611	<.0026	<.00865	<.00165	.0191	.0635	.0121
Cardinal	.000102	.00178	.000796	<.0000348	<.00061	<.000271	.0001	.00338	.00151
Mazatzal	.0219	.0218	.0164	<.00238	<.0024	<.00178	.0101	.0108	.0082
Terlingua	.00196	.00366	.00354	<.0004	<.00075	<.0724	.0016	.00298	.0029
Arkansas	.0068	.00404	.00305	<.0009	<.00054	<.000405	.0004	.0029	.00218

*All elements of the 3% diluted wall rock samples multiplied by some factor such that:
Column A The alumina of the wall rock is equal to that of the cinnabar.
Column B - The titania of the wall rock is equal to that of the cinnabar.
Column C - The total impurity of the wall rock sample is equal to that of the cinnabar.

Table 10

Re-calculated Wall Rock Values*
(In percent)

Mines	MnO			Na_2O			BaO		
	A	B	C	A	B	C	A	B	C
Cuddeback	<.054	-	<.00618	<.41	-	<.463	<.0045	-	<.00514
Klau	.00289	-	.00238	<.0277	-	<.00228	<.000346	-	<.000285
Oceanic	.028	.034	.0165	.635	1.00	.481	.0067	.0106	.00504
New Idria	.0009	.0011	.00164	.027	.0438	.0681	.00054	.00064	.000987
Aurora	.042	.0193	.00927	.086	.04	.0191	.00102	.00047	.000226
Bradford	.0156	.0684	.00608	<.0156	<.068	<.00608	.00425	.0187	.00167
Great Western	.0068	-	.006	<.0302	-	<.0269	<.00036	-	<.00032
Aetna	.010	-	.0334	.130	-	.416	<.0012	-	<.00396
Cloverdale	.173	.087	.0326	.209	.106	.0395	.0015	.00075	.000281
Mount Diablo	.00378	-	.00125	<.0358	-	<.0119	.00198	-	.000658
Sulphur Bank(Basalt)	.0143	.0109	.0283	.206	.157	.407	.0033	.0024	.0065
Sulphur Bank(Gravel)	.065	.0382	.0284	<.144	<.085	<.0631	.0045	.0027	.00197
Bonanza	.012	.0135	.00838	.396	.436	.27	.0032	.0035	.00216
Black Butte	.00644	.0025	.00406	<.0901	<.0346	<.0639	<.0013	<.00048	<.000798
Horse Heaven	.00082	-	.00344	.019	-	.0802	.00025	-	.00106
Maury Mountain	.00494	.0164	.00314	<.0858	<.286	<.0545	<.00104	<.0035	<.00066
Cardinal	.0000956	.00167	.000745	<.00103	<.0184	<.00805	.000489	.0078	.00381
Mazatzal	.0113	.0133	.01	<.0631	<.0627	<.0473	.00131	.0013	.00098
Terlingua	.00112	.00205	.00203	.042	.0784	.076	.0008	.00149	.00145
Arkansas	.00139	.00083	.000623	<.0278	<.0165	<.0125	<.000347	<.00021	<.000156

*All elements of the 3% diluted wall rock samples multiplied by some factor such that:

Column A - The alumina of the wall rock is equal to that of the cinnabar.

Column B - The titania of the wall rock is equal to that of the cinnabar.

Column C - The total impurity of the wall rock sample is equal to that of the cinnabar.

Table 10

Re-calculated Wall Rock Values*
(In percent)

Mines	Co_2O_3			PbO			Ag_2O		
	A	B	C	A	B	C	A	B	C
Cuddeback	<.0079	-	.009	<.017	-	<.0198	<.00023	-	<.000257
Klau	<.000462	-	.000381	<.00115	-	<.000951	<.0000185	-	<.0000152
Oceanic	<.0056	<.0088	<.00424	<.014	<.0022	<.0106	<.000196	<.00031	<.000148
New Idria	<.00036	<.00042	<.000658	<.00072	<.00085	<.00132	<.000009	<.00001	<.0000164
Aurora	.00394	.0018	.000876	<.00157	<.00072	<.000347	<.00236	<.000011	<.0000052
Bradford	.00082	.0036	.000321	<.00038	<.003	<.000267	<.0000164	<.00072	<.0000064
Great Western	.00158	-	.00141	<.00144	-	<.00128	<.0000216	-	<.0000192
Aetna	.0024	-	.00765	<.0044	-	<.0141	<.000062	-	<.000198
Cloverdale	<.0017	<.00088	<.000327	<.00496	<.0025	<.000935	<.0000496	<.000025	<.0000093
Mount Diablo	<.00071	-	.000235	<.0015	-	<.000501	<.000019	-	<.00000626
Sulphur Bank(Basalt)	<.0021	<.0016	<.0422	<.0043	<.0032	<.00844	.000096	.000073	.0019
Sulphur Bank(Gravel)	<.0027	<.0016	<.00118	<.0063	<.0037	<.00276	<.00009	<.000053	<.0000394
Bonanza	<.0032	<.0035	<.00216	<.0079	<.0087	<.00544	<.000079	<.00009	<.000054
Black Butte	<.00177	<.00068	<.00126	<.00322	<.0012	<.00228	.0000694	.0003	.0000456
Horse Heaven	<.00014	-	<.000573	<.00019	-	<.00082	<.000001	-	<.0000408
Maury Mountain	<.00169	<.0056	<.00107	<.0039	<.013	<.00248	<.000076	<.000026	<.0000495
Cardinal	<.0000217	<.00038	<.00017	<.0000434	<.00076	<.000335	<.00000625	<.00001	<.00000508
Mazatzal	<.00119	<.0012	<.00829	<.00238	<.0024	<.0178	<.0000357	<.000036	<.0000268
Terlingua	<.0002	<.00037	<.000362	<.0006	<.00112	<.00109	<.000008	<.000015	<.0000245
Arkansas	<.000486	<.00029	<.000219	<.00118	<.0007	<.00053	.0000139	.000008	.00000623

*All elements of the 3% diluted wall rock samples multiplied by some factor such that:
Column A - The alumina of the wall rock is equal to that of the cinnabar.
Column B - The titania of the wall rock is equal to that of the cinnabar.
Column C - The total impurity of the wall rock sample is equal to that of the cinnabar.

Table 11

Differential Concentrations of Elements (Values C and D)*
(In percent)

Mines	SiO_2			Al_2O_3			Fe_2O_3		
	A	B	C	A	B	C	A	B	C
Cuddeback	1.11	-	.40	-	-	(.18)	.15	-	.14
Klau	(.347)	-	(.27)	-	-	.023	.061	-	(.44)
Oceanic	(1.7)	(4.45)	(.61)	-	(1.32)	.54	.18	.04	.24
New Idria	.466	.112	(.090)	-	(.024)	(.11)	.018	.025	.005
Aurora	(.245)	(.044)	.049	-	.054	.071	(.13)	(.036)	.003
Bradford	(.006)	(1.05)	.18	-	(.28)	.051	.030	(.17)	.066
Great Western	(.12)	-	.73	-	-	.011	(.061)	-	(.042)
Aetna	4.04	-	(.04)	-	-	(.64)	.20	-	0
Cloverdale	(5.75)	(2.44)	(.46)	-	.13	.19	(.059)	.032	.090
Mount Diablo	(1.79)	-	(.41)	-	-	.083	.12	-	.27
Sulphur Bank(Basalt)	1.8	2.1	.66	-	.29	(1.13)	.54	.594	.48
Sulphur Bank(Gravel)	(7.00)	(2.56)	(.94)	-	.48	.66	(.06)	.10	.15
Bonanza	4.99	(5.85)	(2.34)	-	(.22)	.68	(2.57)	(.013)	.12
Black Butte	(2.09)	.17	(1.02)	-	.44	.21	(.11)	.18	.14
Horse Heaven	1.77	-	.38	-	-	(.30)	.019	-	(.071)
Maury Mountain	(1.63)	(7.52)	(.70)	-	(2.05)	.32	(.014)	(.403)	.048
Cardinal	.038	(.247)	(.080)	-	(.1726)	(.071)	.0097	.020	.028
Mazatzal	(1.21)	(1.30)	(.71)	-	.005	.191	(.052)	(.052)	(.031)
Terlingua	(.043)	(.294)	(.27)	-	(.197)	(.12)	.14	.119	.12
Arkansas	(1.23)	(.47)	(.20)	-	.042	.067	.040	.048	.051

*Where A equals the amount of an element in the cinnabar and B equals the amount of an element in the corrected wall rock, then (where A is larger than B) A-B (equals C) equals the differential concentration of an element in the cinnabar.

Where B is the larger, then B-A (equals D) equals the differential concentration of an element in the wall rock. (Values D are parenthesized in the above table.)

Column A - differential concentrations obtained where wall rock recalculated by the alumina method.

Column B - differential concentrations obtained where wall rock re-calculated by the titania method.

Column C - differential concentrations obtained where wall rock re-calculated by the total impurity method.

Table 11

Differential Concentrations of Elements (Values C and D)*
(In percent)

Mines	CaO			MgO			Cr_2O_3		
	A	B	C	A	B	C	A	B	C
Cuddeback	(.001)	-	(.007)	.011	-	.005	-	-	-
Klau	.0057	-	.007	(.011)	-	(.005)	-	-	-
Oceanic	(.13)	(.29)	(.062)	(.074)	(.235)	(.007)	>.056	>.0196	>.056
New Idria	.010	.009	.005	.010	.008	.003	0	(.0007)	(.003)
Aurora	(.093)	(.032)	(.0048)	(1.25)	(.531)	(.21)	(.075)	(.022)	.001
Bradford	(.91)	(5.13)	(.43)	(.33)	(2.48)	.054	(.060)	(.416)	.004
Great Western	(.007)	-	.002	(.024)	-	(.013)	(.10)	-	(.086)
Aetna	(.031)	-	(.13)	(.062)	-	(.25)	1.23	-	1.00
Cloverdale	.071	.024	.029	(.075)	(.020)	.014	-	-	-
Mount Diablo	(.002)	-	.017	(.022)	-	.023	(.19)	-	(.048)
Sulphur Bank(Basalt)	.37	.43	.12	(.099)	(.070)	(.22)	.043	.047	.029
Sulphur Bank(Gravel)	(.037)	(.001)	.012	(.14)	(.022)	.022	(.006)	.010	.015
Bonanza	(3.21)	(.009)	.005	(.029)	(.041)	.008	.070	.065	.084
Black Butte	.015	.023	.02	(.0018)	.019	.008	>.085	>.0081	>.086
Horse Heaven	.003	-	(.0057)	.004	-	(.014)	-	-	-
Maury Mountain	.003	(.049)	.011	.014	(.077)	.029	(.009)	(.155)	.013
Cardinal	.020	.010	.016	.014	(.003)	.007	.010	.0075	.010
Mazatzal	.0004	.0005	.218	.002	.002	.011	.029	.029	.04
Terlingua	.26	.256	.26	.057	.045	.045	.0077	.0051	.005
Arkansas	.001	.0148	.015	.016	.009	.012	-	-	-

*Where A equals the amount of an element in the cinnabar and B equals the amount of an element in the corrected wall rock, then (where A is larger than B) A-B (equals C) equals the differential concentration of an element in the cinnabar.

Where B is the the larger, then B-A (equals D) equals the differential concentration of an element in the wall rock. (Values D are parenthesized in the above table.)

Column A - differential concentrations obtained where wall rock re-calculated by the alumina method.
Column B - differential concentrations obtained where wall rock re-calculated by the titania method.
Column C - differential concentrations obtained where wall rock re-calculated by the total impurity method.

Table 11

Differential Concentrations of Elements (Values C and D)*
(In percent)

Mines	NiO			TiO$_2$			CuO		
	A	B	C	A	B	C	A	B	C
Cuddeback	-	-	-	-	-	-	.030	-	.028
Klau	.0004	-	.0004	>(.0056)	-	>(.0038)	.035	-	.036
Oceanic	.0023	.0002	.0032	.044	-	.064	.007	(.010)	.014
New Idria	.0001	.00002	(.0004)	.001	-	(.005)	.013	.012	.011
Aurora	.004	.001	.015	(.005)	-	.0025	.015	.017	.019
Bradford	.014	(.003)	.017	.014	-	.014	.013	.007	.014
Great Western	(.0083)	-	(.007)	>(.0028)	-	>(.071)	.037	-	.0038
Aetna	.036	-	(.0093)	> .022	-	-	.082	-	.051
Cloverdale	.0006	.0017	.0024	>(.009)	-	.0063	.024	.034	.040
Mount Diablo	(.00005)	-	.0006	>(.013)	-	>(.0008)	.012	-	.015
Sulphur Bank(Basalt)	-	-	-	(.014)	-	(.069)	.057	.0584	.050
Sulphur Bank(Gravel)	(.0025)	(.0007)	0	(.037)	-	.014	.045	.057	.051
Bonanza	(.0005)	(.0007)	.0001	.012	-	.059	.079	.076	.089
Black Butte	.0071	.0088	.0079	(.078)	-	.036	.059	.068	.062
Horse Heaven	.0004	-	.00009	-	-	>(.0048)	.053	-	.049
Maury Mountain	.004	(.0005)	.005	.11	-	.12	.019	(.003)	.023
Cardinal	.0004	.00002	.00023	.006	-	.0033	.006	.0042	.0052
Mazatzal	(.0004)	(.0005)	(.00004)	0	-	.021	(.0005)	(.0004)	.005
Terlingua	>(.00012)	>(.0004)	>(.0004)	.009	-	.0011	.039	(.014)	.014
Arkansas	(.0004)	.00004	.0001	.006	-	.002	.022	.024	.025

*Where A equals the amount of an element in the cinnabar and B equals the amount of an element in the corrected wall rock, then (where A is larger than B) A-B (equals C) equal the differential concentration of an element in the cinnabar.

Where B is the larger, then B-A (equals D) equals the differential concentration of an element in the wall rock. (Values D are parenthesized in the above table.)

Column A - differential concentrations obtained where wall rock re-calculated by the alumina method.
Column B - differential concentrations obtained where wall rock re-calculated by the titania method.
Column C - differential concentrations obtained where wall rock re-calculated by the total impurity method.

Table 11

Differential Concentrations of Elements (Values C and D)*
(In percent)

Mines	GeO			ZnO			MnO		
	A	B	C	A	B	C	A	B	C
Cuddeback	-	-	-	-	-	-	-	-	> .028
Klau	>.010	-	>.009	.12	-	.120	>(.0020)	-	>(.0015)
Oceanic	-	-	-	>(.046)	>(.080)	>(.022)	(.005)	(.011)	.005
New Idria	-	-	-	.25	.247	.25	>(.0004)	>(.0006)	>(.0011)
Aurora	>.0011	>.0018	>.0021	>(.008)	-	-	(.037)	(.014)	(.0043)
Bradford	>.0008	-	>.00091	.0036	(.010)	.0061	(.004)	(.056)	.0053
Great Western	>.036	-	>.036	-	-	>(.0016)	>(.0055)	-	>(.0047)
Aetna	>.0009	-	-	.033	-	(.040)	.050	-	.027
Cloverdale	-	-	-	>(.023)	>(.008)	-	(.071)	.015	.069
Mount Diablo	>.005	-	>.0056	(.004)	-	-	-	-	-
Sulphur Bank(Basalt)	>.003	>.0036	-	.007	.010	(.0054)	.31	.31	.29
Sulphur Bank(Gravel)	-	-	-	(.026)	(.015)	(.0077)	(.037)	(.010)	0
Bonanza	-	-	-	1.48	1.48	1.53	(.006)	(.008)	(.0024)
Black Butte	-	-	-	.50	.518	.51	.0021	.0060	.0044
Horse Heaven	.018	-	.017	.0098	-	.0017	>(.0001)	-	>(.003)
Maury Mountain	-	-	-	.16	.116	.17	.001	(.010)	.003
Cardinal	-	-	-	.004	.0006	.0025	> .006	>(.0010)	> 0
Mazatzal	-	-	-	(.004)	(.005)	(.002)	(.007)	(.009)	(.006)
Terlingua	-	-	-	-	.0045	.0046	-	.0085	.009
Arkansas	-	-	-	.003	.005	.006	.0021	.0026	.0028

*Where A equals the amount of an element in the cinnabar and B equals the amount of an element in the corrected wall rock, then (where A is larger than B) A-B (equals C) equal the differential concentration of an element in the cinnabar.

Where B is larger, then B-A (equals D) equals the differential concentration of an element in the wall rock. (Values D are parenthesized in the above table.)

Column A - differential concentrations obtained where wall rock re-calculated by the alumina method.

Column B - differential concentrations obtained where wall rock re-calculated by the titania method.

Column C - differential concentrations obtaned where wall rock rock re-calculated by the total impurity method.

Table 11

Differential Concentrations of Elements (Values C and D)*
(In percent)

Mines	Na_2O A	Na_2O B	Na_2O C	BaO A	BaO B	BaO C	Co_2O_3 A	Co_2O_3 B	Co_2O_3 C
Cuddeback	-	-	-	-	-	-	-	-	-
Klau	-	-	-	-	-	-	-	-	-
Oceanic	(.36)	(.72)	(.13)	(.0017)	(.006)	(.0015)	-	-	-
New Idria	>(.009)	>(.026)	>(.050)	.00006	(.00004)	(.0004)	-	-	-
Aurora	>(.029)	-	-	.0002	.0007	.0010	(.0016)	.0005	.0015
Bradford	-	-	-	.001	.014	.0033	.002	.0006	.0027
Great Western	-	-	-	-	-	-	>(.0006)	-	>(.0004)
Aetna	.13	-	(.16)	-	-	-	.008	-	.0023
Cloverdale	>(.16)	>(.052)	-	.0017	.0024	.0029	>.0003	>.0011	>.0017
Mount Diablo	-	-	-	(.0008)	-	.00054	-	-	-
Sulphur Bank(Basalt)	(.03)	.018	(.23)	.0008	.0016	(.0024)	-	-	-
Sulphur Bank(Gravel)	-	-	-	(.0002)	.0016	.0023	-	-	-
Bonanza	>(.34)	>(.369)	>(.20)	(.0016)	(.0019)	(.0006)	-	-	-
Black Butte	-	-	-	-	-	-	>.0046	>.0057	>.0051
Horse Heaven	> .009	-	>(.013)	>.0001	-	(.00076)	-	-	-
Maury Mountain	-	-	-	> 0	-	>.0007	>.001	-	>.0015
Cardinal	-	-	-	.050	.052	.56	-	-	-
Mazatzal	-	-	-	(.0009)	(.0009)	(.00058)	-	-	-
Terlingua	-	>(.056)	>(.056)	-	.0021	.0021	-	-	-
Arkansas	-	-	-	-	-	-	-	-	-

*Where A equals the amount of an element in the cinnabar and B equals the amount of an element in the corrected wall rock, then (where A is larger than B) A-B (equals C) equals the differential concentration of an element in the cinnabar.

Where B is the larger, then B-A (equals D) equals the differential concentration of an element in the wall rock. (Values D are parenthesized in the above table.)

Column A - differential concentrations obtained where wall rock re-calculated by the alumina method.
Column B - differential concentrations obtained where wall rock re-calculated by the titania method.
Column C - differential concentrations obtained where wall rock re-calculated by the total impurity method.

Table 11

Differential Concentrations of Elements (Values C and D)*
(In percent)

Mines	PbO			Ag_2O			Total Impurities in Cinnabar		
	A	B	C	A	B	C	A	B	C
Cuddeback	-	-	-	>.0019	-	>.0018	1.3	-	.60
Klau	>.0010	-	>.0011	>.00011	-	>.00011	.21	-	.20
Oceanic	-	-	-	-	-	-	.36	.06	.92
New Idria	-	-	-	>.0002	>.0001	>.00008	.77	.41	.27
Aurora	-	-	-	-	-	-	.02	.09	.17
Bradford	>.0007	-	>.00047	>.00014	-	>.00015	.08	.01	.42
Great Western	-	-	-	>.00043	-	>.00043	.07	-	.75
Aetna	-	-	-	-	-	-	5.83	-	1.08
Cloverdale	-	-	-	>.00008	>.00008	>.0001	.04	.24	.45
Mount Diablo	>.0009	-	>.0019	>.00002	-	>.000034	.12	-	.42
Sulphur Bank(Basalt)	-	-	-	.00005	>.00008	(.00004)	3.13	3.87	1.63
Sulphur Bank(Gravel)	-	>.0003	>.0012	>.00017	>.00021	>.00022	.05	.65	.94
Bonanza	-	-	>.0015	>.0006	>.00061	>.0007	1.64	1.62	2.58
Black Butte	>.0072	>.0092	>.008	.0002	>.00027	.00025	.79	1.46	1.06
Horse Heaven	>.0025	-	>.0019	>.00004	-	>.000009	1.89	-	.45
Maury Mountain	-	-	-	-	-	-	.31	.12	.75
Cardinal	-	-	-	>.00016	>.00015	>.00015	.16	.10	.13
Mazatzal	-	-	-	>.00004	>.00003	>.000043	.03	.037	.49
Terlingua	-	-	-	>.00044	>.00005	>.00006	.51	.46	.46
Arkansas	-	-	-	.00001	.00002	.000024	.09	.15	.18

*Where A equals the amount of an element in the cinnabar and B equals the amount of an element in the corrected wall rock, then (where A is larger than B) A-B (equals C) equals the differential concentration of an element in the cinnabar.

Where B is the larger, then B-A (equals D) equals the differential concentration of an element in the wall rock. (Values D are parenthesized in the above table.)

Column A - differential concentrations obtained where wall rock re-calculated by the alumina method.
Column B - differential concentrations obtained where wall rock-re-calculated by the titania method.
Column C - differential concentrations obtained where wall rock re-calculated by the total impurity method.

Table 12

Ratios of Relative Differential Concentrations in Cinnabar and Wall Rock (Values E and F)*

Mines	SiO_2			Al_2O_3			Fe_2O_3		
	A	B	C	A	B	C	A	B	C
Cuddeback	.18	-	.06	-	-	(.73)	.75	-	.70
Klau	(.83)	-	(.79)	-	-	.22	.47	-	(.78)
Oceanic	(.36)	(.60)	(.17)	-	(.37)	.24	.43	.09	.57
New Idria	.99	.23	(.16)	-	(.15)	(.45)	.54	.76	.15
Aurora	(.66)	(.25)	.36	-	.55	.72	(.76)	(.46)	.70
Bradford	(.02)	(.78)	.60	-	(.77)	.61	.33	(.64)	.73
Great Western	(.08)	-	.53	-	-	.11	(.56)	-	(.28)
Aetna	.69	-	(.01)	-	-	(1.00)	.69	-	0
Cloverdale	(.92)	(.76)	(.39)	-	.57	.83	(.52)	.26	.72
Mount Diablo	(.86)	-	(.59)	-	-	.67	.34	-	.77
Sulphur Bank(Basalt)	.8	.70	.22	-	.25	(.49)	.85	.91	.74
Sulphur Bank(Gravel)	(.65)	(.40)	(.20)	-	.41	.56	(.17)	.32	.48
Bonanza	(.60)	(.64)	(.41)	-	(.09)	.47	(.89)	(.05)	.38
Black Butte	(.57)	.11	(.39)	-	.62	.30	.55	.78	.61
Horse Heaven	.81	-	.17	-	-	(.75)	.40	-	(.60)
Maury Mountain	(.84)	(.90)	(.44)	-	(.70)	.36	(.06)	(.72)	.31
Cardinal	.69	(.82)	(.59)	-	(.94)	(.87)	.92	.57	.80
Mazatzal	(.51)	(.55)	(.40)	-	.07	.25	(.61)	(.62)	(.49)
Terlingua	(.15)	(.54)	(.51)	-	(.46)	(.29)	.86	.74	.75
Arkansas	(.66)	(.42)	(.24)	-	.41	.65	.67	.80	.85

*Where A equals the percentage content of an element in the cinnabar and B equals the percentage content of an element in the corrected wall rock, then A-B equals C and B-A equals D. C/A (equals E) equals the ratio of the relative differential concentration of an element in the cinnabar and D/B (equals F) equals the ratio of the relative differential concentration of an element in the wall rock.

Column A - relative differential concentrations obtained where wall rock re-calculated by alumina method.

Column B - relative differential concentrations obtained where wall rock re-calculated by titania method.

Column C - relative differential concentrations obtained where wall rock re-calculated by total impurity method.

Table 12

Ratios of Relative Differential Concentrations in Cinnabar and Wall Rock (Values E and F)*

Mines	CaO A	CaO B	CaO C	MgO A	MgO B	MgO C	Cr_2O_3 A	Cr_2O_3 B	Cr_2O_3 C
Cuddeback	(.026)	-	(.19)	.20	-	.89	-	-	-
Klau	.48	-	.58	(.33)	-	(.96)	-	-	-
Oceanic	(.28)	(.77)	(.41)	(.85)	(.53)	(.03)	>.61	>.10	>.62
New Idria	.59	.53	.29	.53	.42	.16	0	(.19)	(.53)
Aurora	.82	(.62)	(.19)	(.93)	(.86)	(.71)	(.78)	(.50)	.04
Bradford	(.78)	(.99)	(.30)	(.52)	(.89)	.18	(.57)	(.90)	.09
Great Western	(.25)	-	.10	(.23)	-	(.14)	(.58)	-	(.56)
Aetna	(.67)	-	(.87)	(.71)	-	(.91)	.93	.81	.75
Cloverdale	.58	.75	.91	(.69)	(.37)	.41	-	-	-
Mount Diablo	(.69)	-	.63	(.21)	-	.55	(.96)	-	(.73)
Sulphur Bank(Basalt)	.59	.68	.19	(.81)	(.76)	(.91)	.74	.81	.50
Sulphur Bank(Gravel)	(.43)	(.02)	.25	(.48)	(.13)	.15	(.16)	.45	.47
Bonanza	(.96)	(.25)	.19	(.25)	(.01)	.93	(.82)	.56	.73
Black Butte	.58	.88	.77	(.05)	.59	.25	> .93	>.90	>.95
Horse Heaven	.5	-	(.43)	.44	-	(.62)	-	-	-
Maury Mountain	.12	(.66)	.44	.26	(.59)	.55	(.14)	(.72)	.24
Cardinal	.95	.48	.76	.93	(.17)	.47	.94	.70	.94
Mazatzal	.02	.02	.98	.5	.05	.27	.39	.39	.54
Terlingua	.94	.93	.94	.8	.64	.63	.72	.48	.47
Arkansas	.63	.93	.94	.89	.50	.67	-	-	-

*Where A equals the percentage content of an element in the cinnabar and B equals the percentage content of an element in the corrected wall rock, then A-B equals C and B-A equals D. C/A (equals E) equals the ratio of the relative differential concentration of an element in the cinnabar and D/B (equals F) equals the ratio of the relative differential concentration of an element in the wall rock.

Column A - relative differential concentrations obtained where wall rock re-calculated by alumina method.
Column B - relative differential concentrations obtained where wall rock re-calculated by titania method.
Column C - relative differential concentrations obtained where wall rock re-calculated by total impurity method.

Table 12

Ratios of Relative Differential Concentrations in Cinnabar and Wall Rock (Values E and F)*

Mines	NiO			TiO_2			CuO		
	A	B	C	A	B	C	A	B	C
Cuddeback	-	-	-	-	-	-	.72	-	.67
Klau	.22	-	.22	>(.59)	-	>(.95)	.92	-	.95
Oceanic	.39	.03	.53	.36	-	.38	.19	(.21)	-
New Idria	.33	.67	(.93)	.1	-	(.32)	.93	.86	.79
Aurora	.22	.61	.83	(.49)	-	.53	.75	.85	.95
Bradford	.74	(.14)	.89	.78	-	.78	.87	.47	.93
Great Western	(.64)	-	(.58)	>(.32)	-	>(.92)	.90	-	.93
Aetna	.65	-	(.14)	> .65	-	-	.9	-	.56
Cloverdale	.21	.61	.86	(.48)	-	.63	.54	.85	.91
Mount Diablo	(.52)	-	.67	>(.74)	-	>(.14)	.71	-	.88
Sulphur Bank(Basalt)	-	-	-	(.32)	-	(.62)	.89	.91	.78
Sulphur Bank(Gravel)	(.56)	(.26)	.0	(.41)	-	.26	.62	.78	.84
Bonenza	(.25)	(.32)	.07	(.08)	-	.16	.73	.70	.82
Black Butte	.73	.91	.81	(.71)	-	(.46)	.81	.93	.85
Horse Heaven	.8	-	.04	-	-	>(.96)	.98	-	.91
Maury Mountain	.67	(.08)	.83	.75	-	.82	.66	(.09)	.79
Cardinal	1	.05	.58	1	-	.55	1	.70	.87
Mazatzal	(.22)	(.28)	(.03)	0	-	.23	(.02)	(.02)	.24
Terlingua	> .38	>(.67)	>(.69)	.64	-	.07	.22	.78	.56
Arkansas	(.36)	.57	.14	.86	-	.29	.79	.85	.89

*Where A equals the percentage content of an element in the cinnabar and B equals the percentage content of an element in the corrected wall rock, then A-B equals C and B-A equals D. C/A (equals E) equals the ratio of the relative differential concentration of an element in the cinnabar and D/B (equals F) equals the ratio of the relative differential concentration of an element in the wall rock.

Column A - relative differential concentrations obtained where wall rock re-calculated by alumina method.
Column B - relative differential concentrations obtained where wall rock re-calculated by titania method.
Column C - relative differential concentrations obtained where wall rock re-calculated by total impurity method.

Table 12

Ratios of Relative Differential Concentrations in Cinnabar and Wall Rock (Values E and F)*

Mines	GeO A	GeO B	GeO C	ZnO A	ZnO B	ZnO C	MnO A	MnO B	MnO C
Cuddeback	-	-	-	-	-	-	-	-	> .82
Klau	>1.00	-	> .90	.97	-	.97	>(.69)	-	>(.17)
Oceanic	-	-	>(.50)	>(.78)	>(.87)	>(.30)	(.18)	(.32)	.30
New Idria	-	-	-	1.00	.99	1.00	>(.44)	>(.55)	>(.67)
Aurora	> .46	>.75	> .88	> .50	-	-	(.88)	(.72)	(.46)
Bradford	> .06	-	> .69	.47	(.56)	.79	.32	(.82)	.43
Great Western	>.97	-	> .97	-	-	>(.17)	>(.81)	-	>(.78)
Aetna	>.20	-	-	.51	-	(.62)	.83	-	.45
Cloverdale	-	-	-	> (.74)	>(.51)	-	>(.41)	.15	.68
Mount Diablo	>.83	-	> .95	(.99)	-	-	-	-	-
Sulphur Bank(Basalt)	>.5	>.60	-	.35	.50	(.27)	.97	.97	.91
Sulphur Bank (Gravel)	-	-	-	(.53)	(.52)	(.35)	(.57)	(.26)	0
Bonanza	-	-	-	.95	.95	.98	(.5)	(.59)	(.24)
Black Butte	-	-	-	.94	.98	.96	.25	.70	.52
Horse Heaven	1.00	-	.95	.80	-	.14	>(.12)	-	>(.43)
Maury Mountain	-	-	-	.89	.64	.95	.17	(.61)	.50
Cardinal	-	-	-	1.00	.15	.62	> .86	>(.60)	> .70
Mazatzal	-	-	-	(.4)	(.46)	(.24)	(.62)	(.68)	(.60)
Terlingua	-	-	-	-	.60	.61	-	.80	.85
Arkansas	-	-	-	.38	.63	.75	.62	.76	.82

*Where A equals the percentage content of an element in the cinnabar and B equals the percentage content of an element in the corrected wall rock, then A-B equals C and B-A equals D. C/A (equals E) equals the ratio of the relative differential concentration of an element in the cinnabar and D/B (equals F) equals the ratio of the relative differential concentration of an element in the wall rock.

Column A - relative differential concentrations obtained where wall rock re-calculated by alumina method.
Column B - relative differential concentrations obtained where wall rock re-calculated by titania method.
Column C - relative differential concentrations obtained where wall rock re-calculated by total impurity method.

Table 12

Ratios of Relative Differential Concentrations in Cinnabar and Wall Rock (Values E and F)*

Mines	Na_2O			BaO			Co_2O_3		
	A	B	C	A	B	C	A	B	C
Cuddeback	-	-	-	-	-	-	-	-	-
Klau	-	-	-	-	-	-	-	-	-
Oceanic	>(.57)	(.72)	(.27)	(.25)	(.57)	(.30)	-	-	-
New Idria	>(.33)	>(.17)	>(.73)	.1	(.63)	(.40)	-	-	-
Aurora	>(.35)	-	-	.17	.58	.83	(.41)	.22	.65
Bradford	-	-	-	.2	(.74)	.66	.67	(.17)	.80
Great Western	-	-	-	-	-	-	>(.38)	-	>(.29)
Aetna	.5	-	(.38)	-	-	-	.8	-	.23
Cloverdale	>(.77)	>(.49)	-	.58	.75	.91	> .15	> .55	> .85
Mount Diablo	-	-	-	(.18)	-	.45	-	-	-
Sulphur Bank(Basalt)	(.17)	.10	(.56)	.20	.39	(.58)	-	-	-
Sulphur Bank(Gravel)	-	-	-	(.04)	.36	.54	-	-	-
Bonanza	>(.51)	>(.85)	>(.74)	(.5)	(.54)	(.28)	-	-	-
Black Butte	-	-	-	-	-	-	> .72	> .89	> .80
Horse Heaven	> .32	-	>(.16)	> .33	-	>(.72)	-	-	-
Maury Mountain	-	-	-	> 0	-	> .70	> .38	-	> .58
Cardinal	-	-	-	1.00	.87	.93	-	-	-
Mazatzal	-	-	-	(.69)	(.69)	(.59)	-	-	-
Terlingua	-	>(.75)	>(.74)	-	.58	.58	-	-	-
Arkansas	-	-	-	-	-	-	-	-	-

*Where A equals the percentage content of an element in the cinnabar and B equals the percentage content of an element in the corrected wall rock, then A-B equals C and B-A equals D. C/A (equals E) equals the ratio of the relative differential concentration of an element in the cinnabar and D/B (equals F) equals the ratio of the relative differential concentration of an element in the wall rock.

Column A - relative differential concentrations obtained where wall rock re-calculated by alumina method.
Column B - relative differential concentrations obtained where wall rock re-calculated by titania method.
Column C - relative differential concentrations obtained where wall rock re-calculated by total impurity method.

Table 12

Ratios of Relative Differential Concentrations in Cinnabar and Wall Rock (Values E and F)*

Mines	PbO			Ag_2O		
	A	B	C	A	B	C
Cuddeback	-	-	-	>.91	-	>.86
Klau	>.50	-	>.52	>.84	-	>.85
Oceanic	-	-	-	-	-	-
New Idria	-	-	-	1.00	>.10	> .40
Aurora	-	-	-	-	-	-
Bradford	>.54	-	> .36	>.88	-	>.94
Great Western	-	-	-	>.96	-	> .95
Aetna	-	-	-	-	-	-
Cloverdale	-	-	-	>.8	-	1.00
Mount Diablo	>.38	-	>.80	>.5	-	> .85
Sulphur Bank(Basalt)	-	-	-	.33	.55	.01
Sulphur Bank (Gravel)	-	>.75	>.30	>.19	>.81	> .85
Bonanza	-	-	> .22	>.86	>.87	1.00
Black Butte	>.69	>.88	> .77	.67	.90	.83
Horse Heaven	>.93	-	> .70	>.8	-	> .18
Maury Mountain	-	-	-	-	-	-
Cardinal	-	-	-	1.00	>.94	> .94
Mazatzal	-	-	-	>.57	>.43	> .61
Terlingua	-	-	-	>.11	>.79	> .86
Arkansas	-	-	-	.33	.67	.80

*Where A equals the percentage content of an element in the cinnabar and B equals the percentage content of an element in the corrected wall rock, then A-B equals C and B-A equals D. C/A (equals E) equals the ratio of the relative differential concentration of an element in the cinnabar and D/B (equals F) equals the ratio of the relative differential concentration of an element in the wall rock.

Column A - relative differential concentrations obtained where wall rock re-calculated by alumina method.
Column B - relative differential concentrations obtained where wall rock re-calculated by titania method.
Column C - relative differential concentrations obtained where wall rock re-calculated by total impurity method.

parenthesized whereas relative concentrations in the cinnabar (E) are not parenthesized.)

Plate 5 shows the ratios of Table 12 with mines plotted against ratios. Each graph then represents the total differential concentration of one element in all of the deposits as shown by each of the three methods of wall rock re-calculation. All values plotted above the zero line represent differential concentrations in the cinnabar whereas all values plotted below the zero line represent relative differential concentrations in the wall rock. It will be noted that lines have been drawn at the ratio 0.3. These lines represent the ratio of maximum possible analytical error. It has been determined, empirically, that, when the elements are plotted as ratios, the maximum possible error is 15%. If now, any two values are actually equal, but are in error by 15% in opposite directions (thus a total error of 30%) the ratio of the elements is then 0.26. For the sake of convenience and to allow the widest necessary margin of error, the lines of maximum possible analytical error have been drawn at the ratio 0.3. Any ratios greater than the ratio 0.3 represented by the two outer lines are, therefore, significant concentrations and cannot possibly be the result of analytical errors. Plate 6 shows the average ratios for each element as determined by each of the three methods of re-calculation. Plate 7 shows the mines plotted against the actual differential percentage concentrations (values C and D) as determined by each of the three methods of re-calculation. On the same graph is shown the actual total percentage content of each element in the wall rock after the wall rock has been calculated to 100%. The scale for the total wall rock content of an element is ten times the scale for the actual differential concentrations. Plate 8 shows elements plotted against ratios for each of the five deposits in serpentine as calculated by the alumina method. Plate 9 shows elements plotted against ratios for each of the five deposits in serpentine as calculated by the total impurity method. Only two of the samples have sufficient titania to allow re-calculation by the titania method; hence, no graph is presented for the deposits in serpentine as calculated by the titania method.

Certain general rules have been followed in plotting values on all of the accompanying graphs. To facilitate comprehension of the graphs, these rules are listed below:

(1) In plotting total wall rock content on Plate 7, only those elements in the wall rock that are a definite value are plotted. Any elements preceded by a "less than" sign are not plotted since it means little to plot a "less than" value after it has been raised some thirty times.

(2) In determining the actual percentage differential concentrations (values C and D) of Table 11 as plotted on Plate 7, if only one of the two values of the cinnabar and corresponding wall rock (thus either value A or B) is preceded by a "less than" sign, the value with the "less than" sign will always be the subtrahend and the result will be preceded by a "greater than" sign. This result is plotted as the actual value indicated; thus a minimum value is plotted. If both values A and B are preceded by a "less than" sign, the values C and D are neither

calculated nor plotted since the result would be meaningless.

(3) In plotting the relative differential concentrations (ratios E and F) shown in Table 12 and plotted on Plates 5, 6, 8, and 9, the value C or D is always the dividend. Under rule 2 above, if C or D is preceded by a "greater than" sign, the corresponding divisor A or B used to determine the ratio E or F will not be preceded by any sign and the resulting ratio will bear the "greater than" sign of the dividend. This ratio is plotted as the actual value indicated; thus, a minimum value is plotted.

Table 13

Key to Graphs

1. Key to Plates 5 and 6.

Values derived when wall rock content has been re-calculated by the alumina method are plotted as a dash-dot-dash line (-.-.-). This line is always the intermediate of the three plotted as a group. Values derived when wall rock content has been re-calculated by the total impurity method are plotted as a solid line (_______). This line is always the uppermost of the three plotted as a group. Values derived when the wall rock content has been re-calculated by the titania method are plotted as a dashed line (-----). This line is always the lower of the three plotted as a group.

2. Key to Plate 7.

The three lines of the lower graph are plotted as indicated above at 1/10th the scale used for the total wall rock content of the upper graph.

The total wall rock content of the upper graph is plotted as a dash-dot-dot-dash line (-..-..-).

3. Key to Plates 8 and 9.

Aetna ....

Aurora -----------

Bradford -...-...-

Great Western __________

Mount Diablo -.-.-.-.

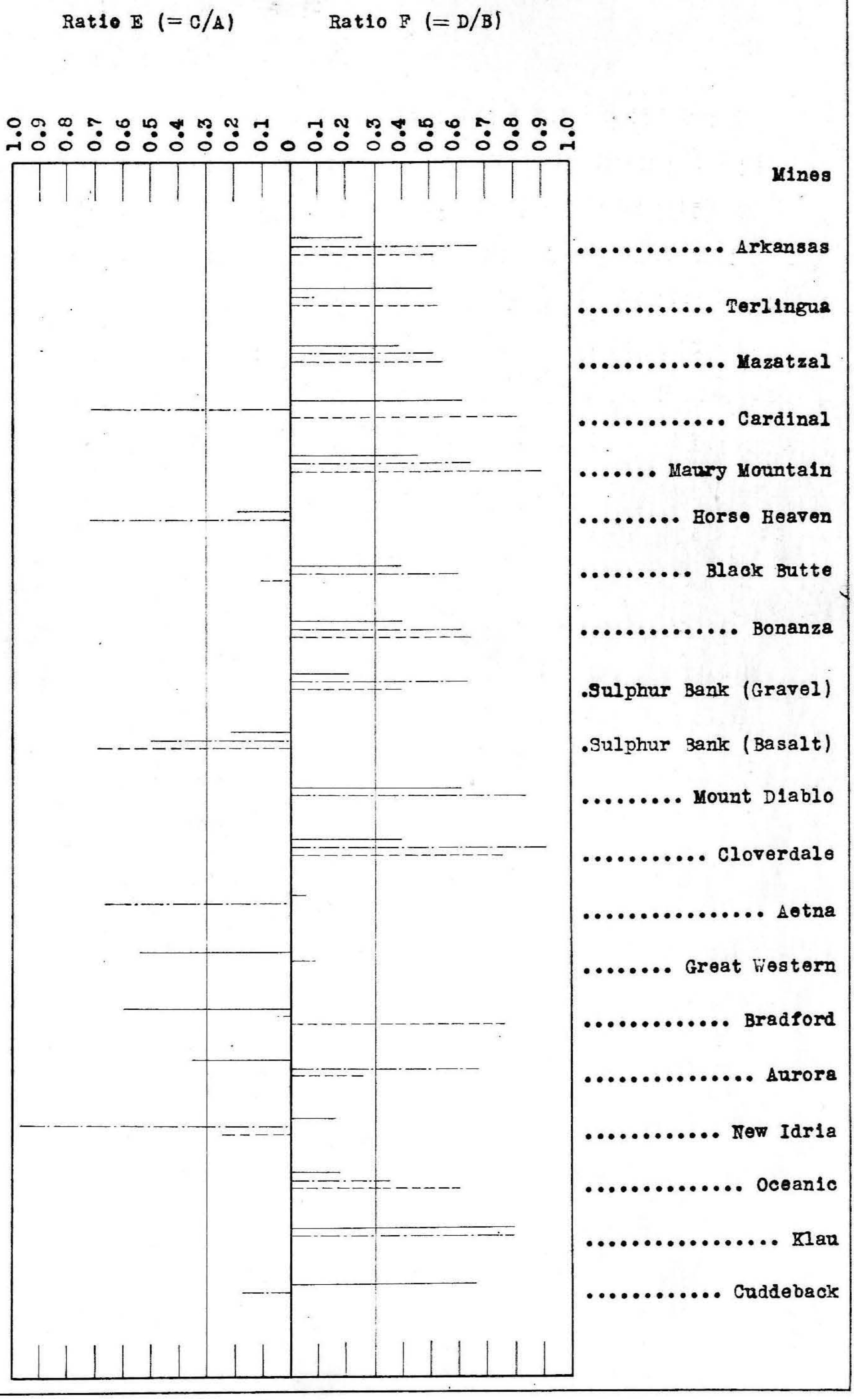


Plate 5 - A 3102

Relative Concentrations of Elements in Cinnabar and Wall Rock

Plate 5 - 3 Al_2O_3

Relative Concentrations of Elements in Cinnabar and Wall Rock

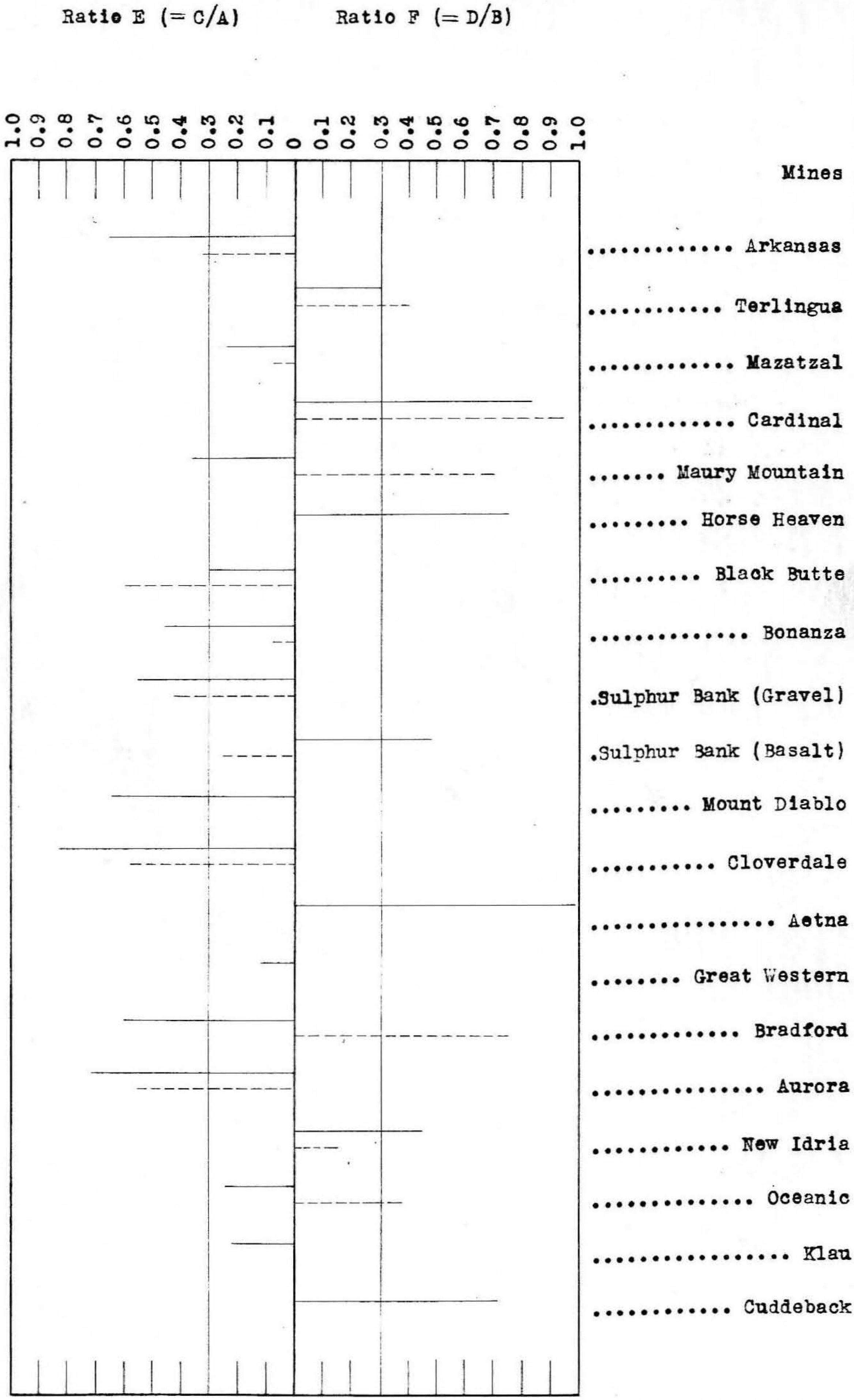


Plate 5 - C Fe_2O_3

Relative Concentrations of Elements in Cinnabar and Wall Rock

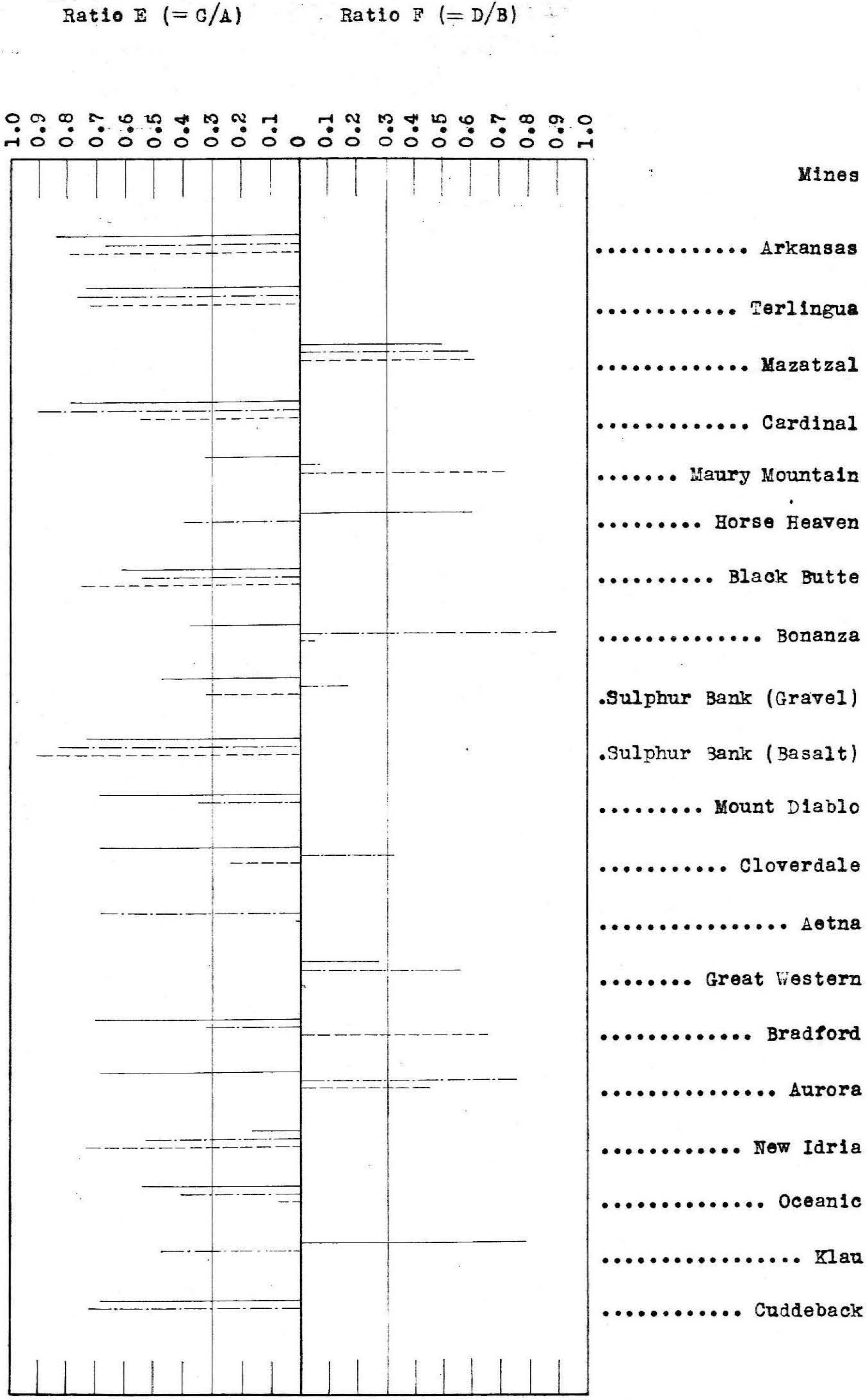
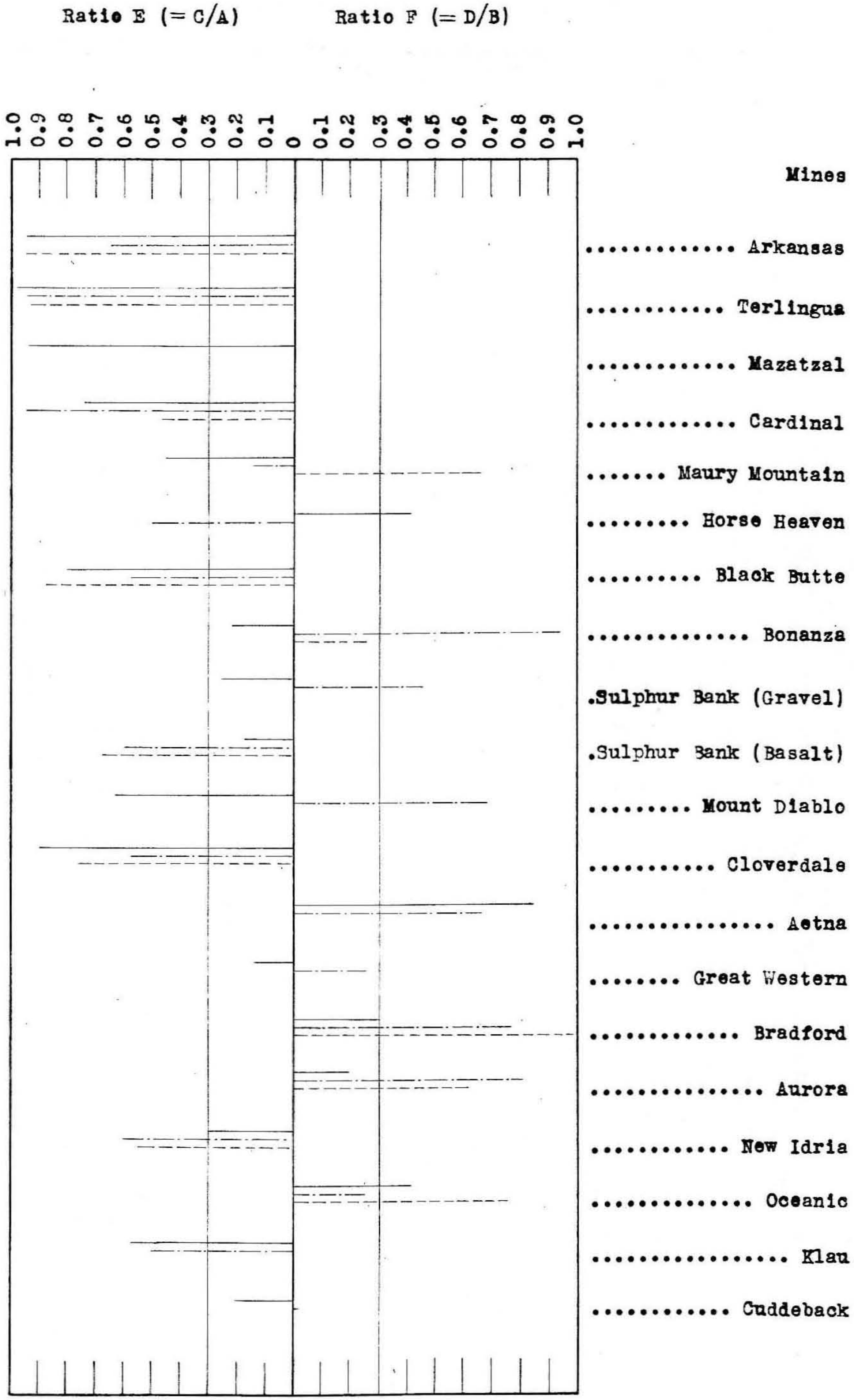


Plate 5 - D CaO

Relative Concentrations of Elements in Cinnabar and Wall Rock



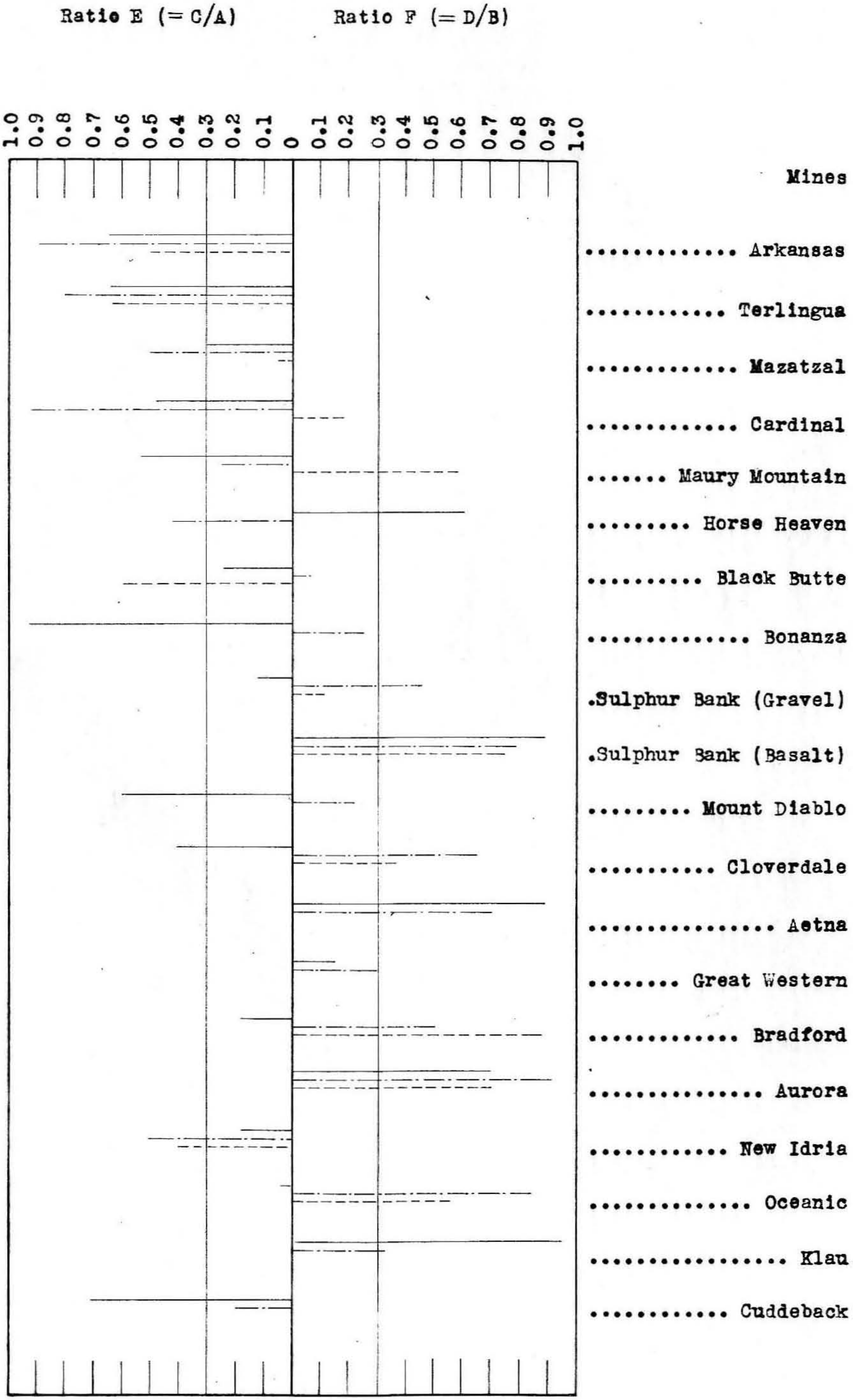


Plate 5 - B MgO

Relative Concentrations of Elements in Cinnabar and Wall Rock

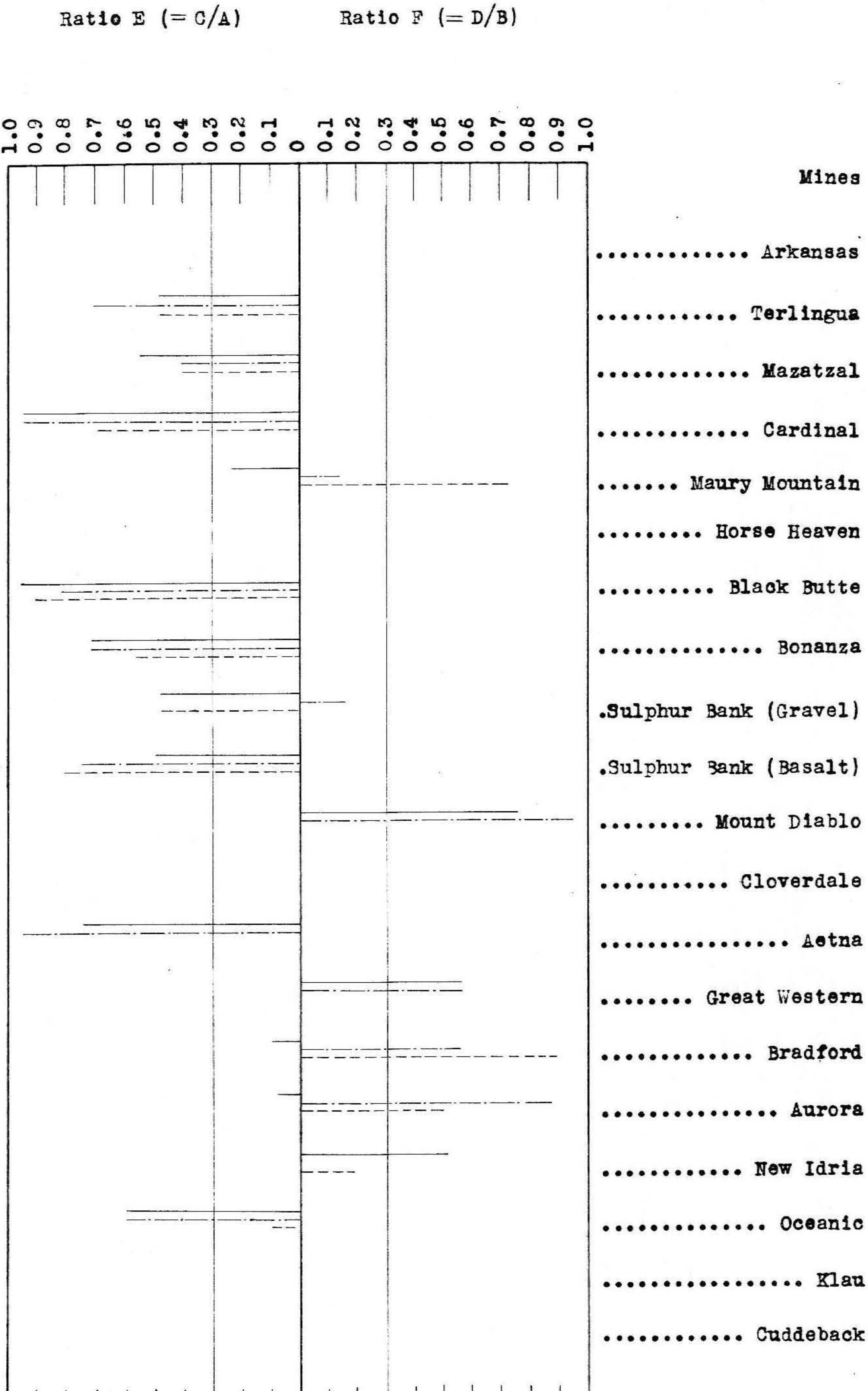
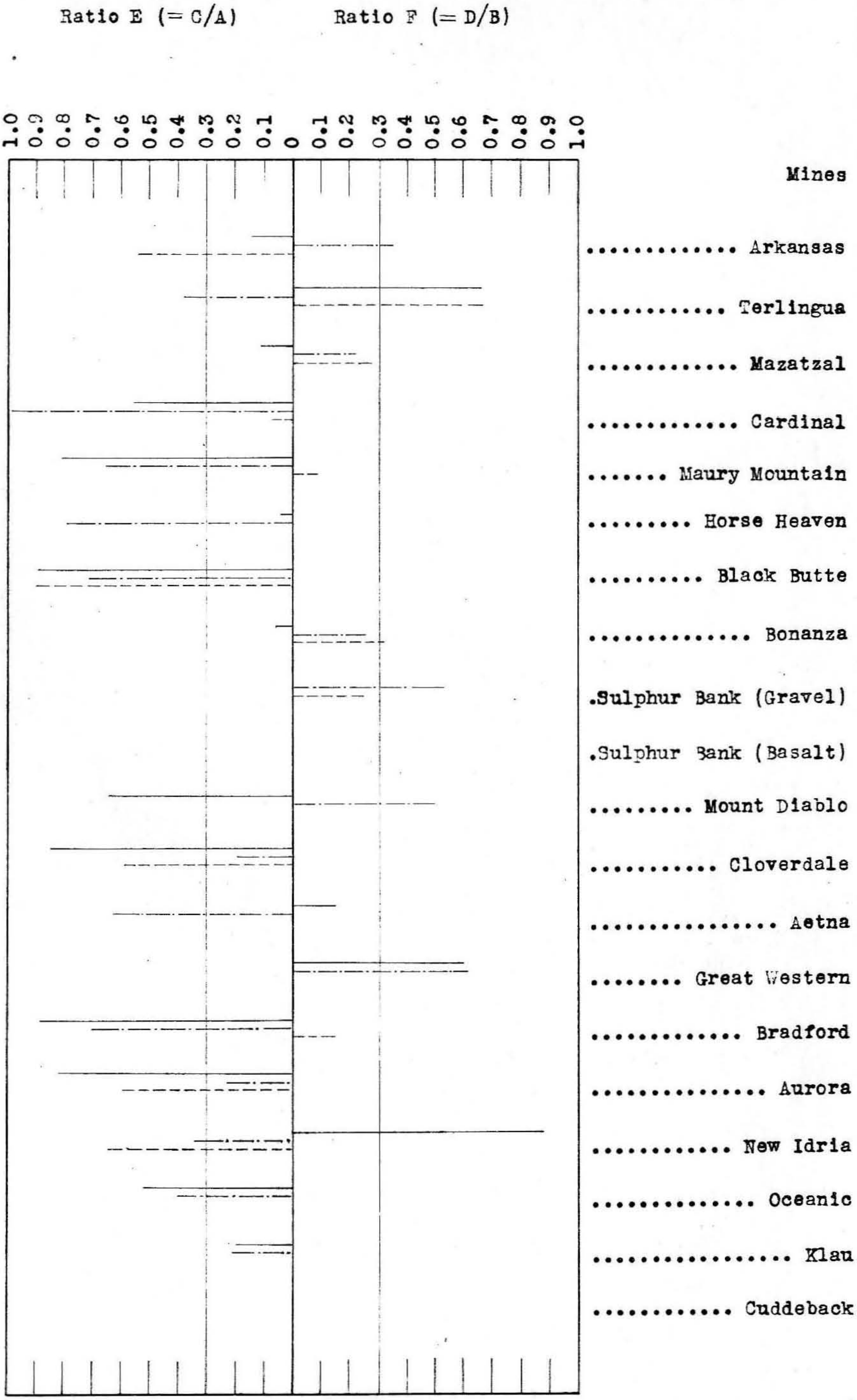


Plate 5 - F Cr_2O_3

Relative Concentrations of Elements in Cinnabar and Wall Rock

Plate 5 - G NiO

Relative Concentrations of Elements in Cinnabar and Wall Rock



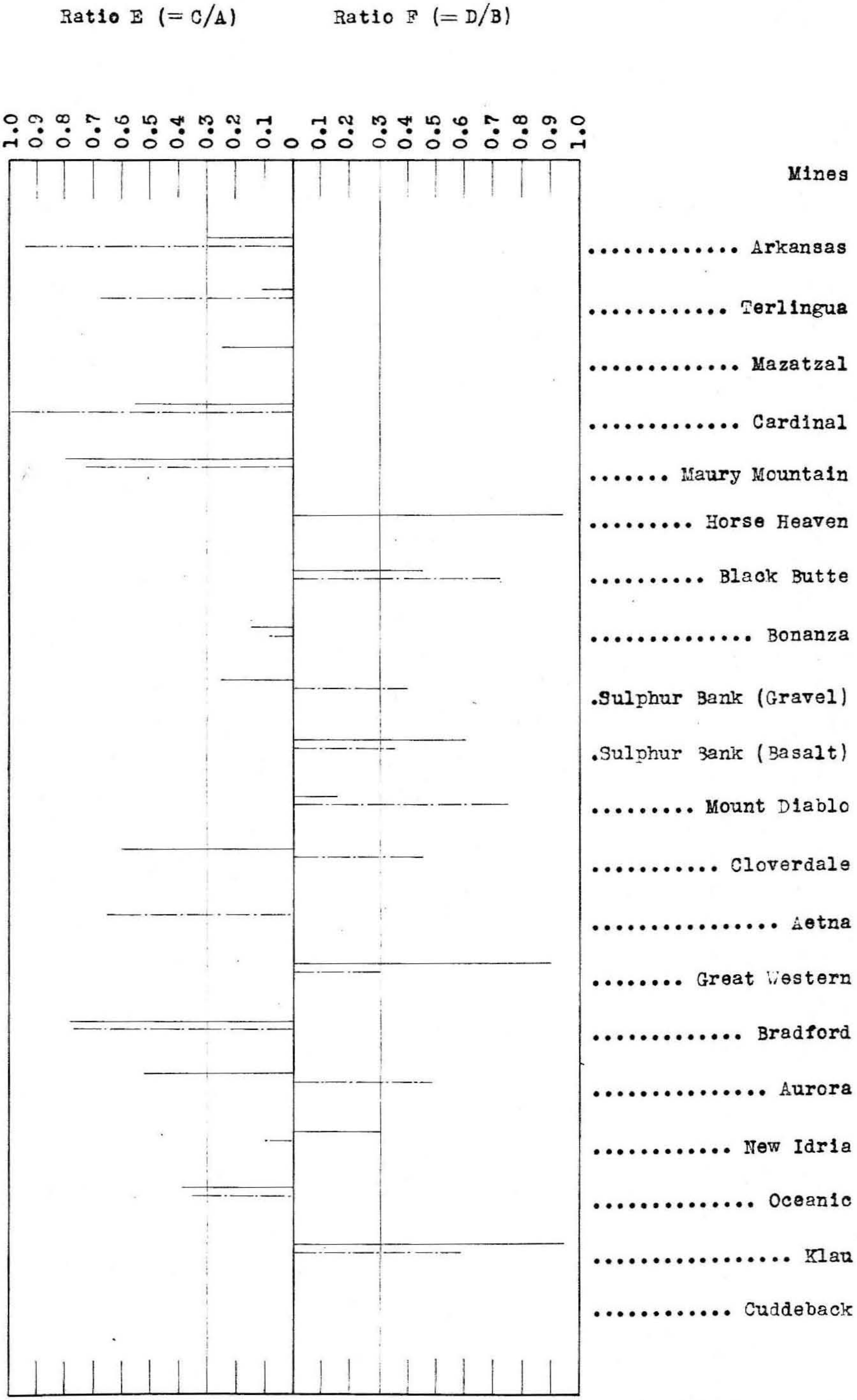


Plate 5 - H SiO$_2$

Relative Concentrations of Elements in Cinnabar and Wall Rock

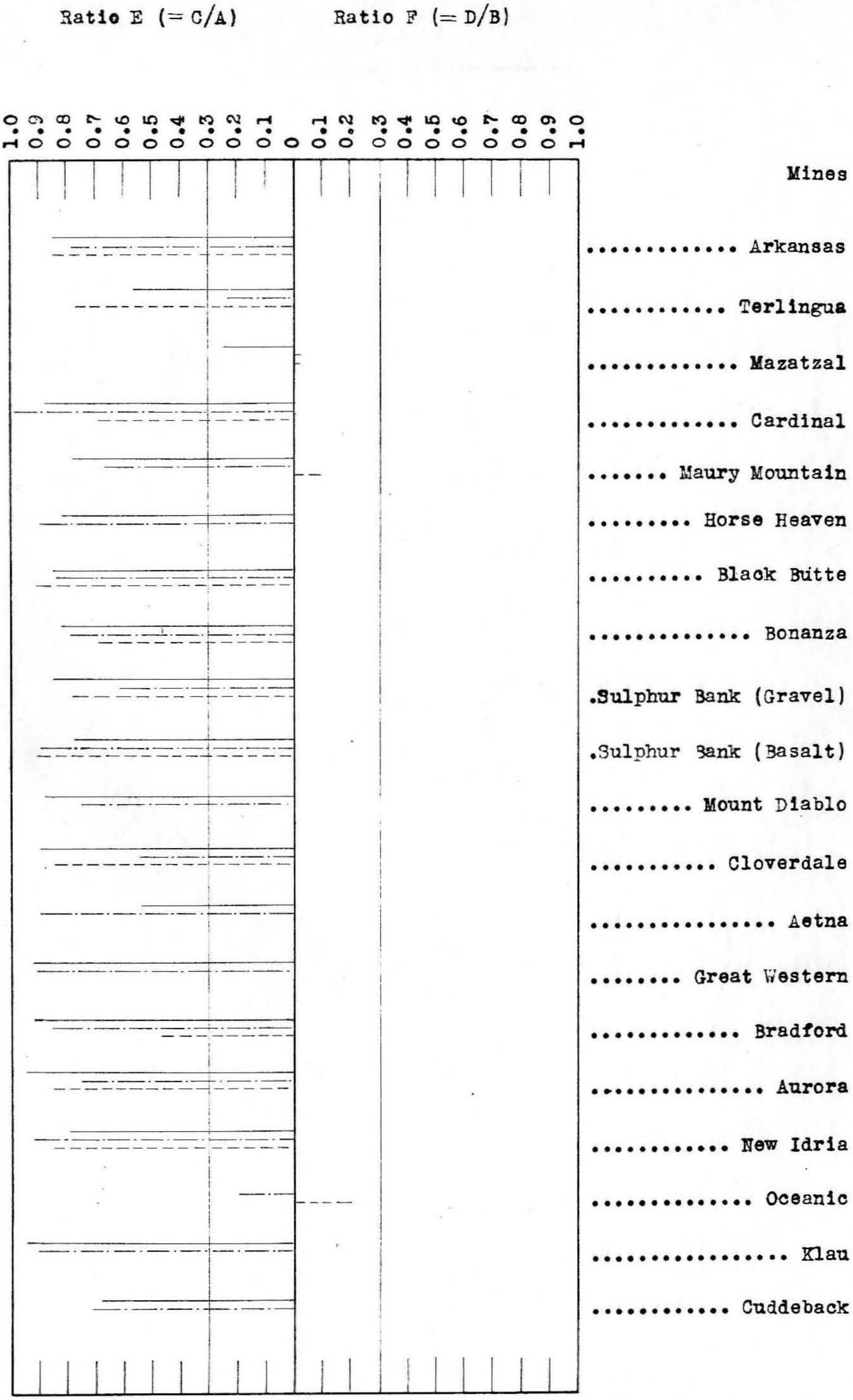
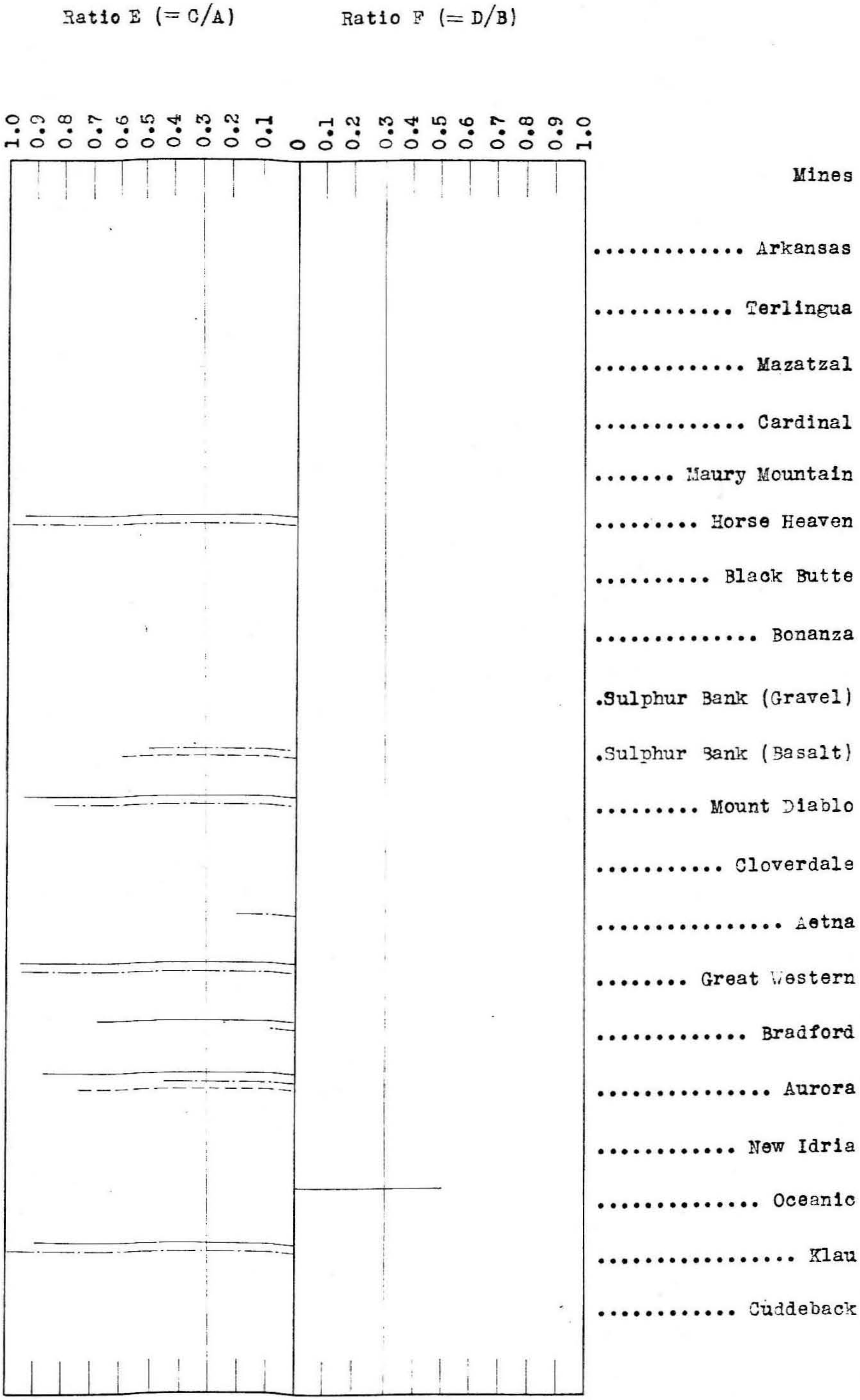


Plate 5 - I CuO

Relative Concentrations of Elements in Cinnabar and Wall Rock

Plate 5- J Geo

Relative Concentrations of Elements in Cinnabar and Wall Rock



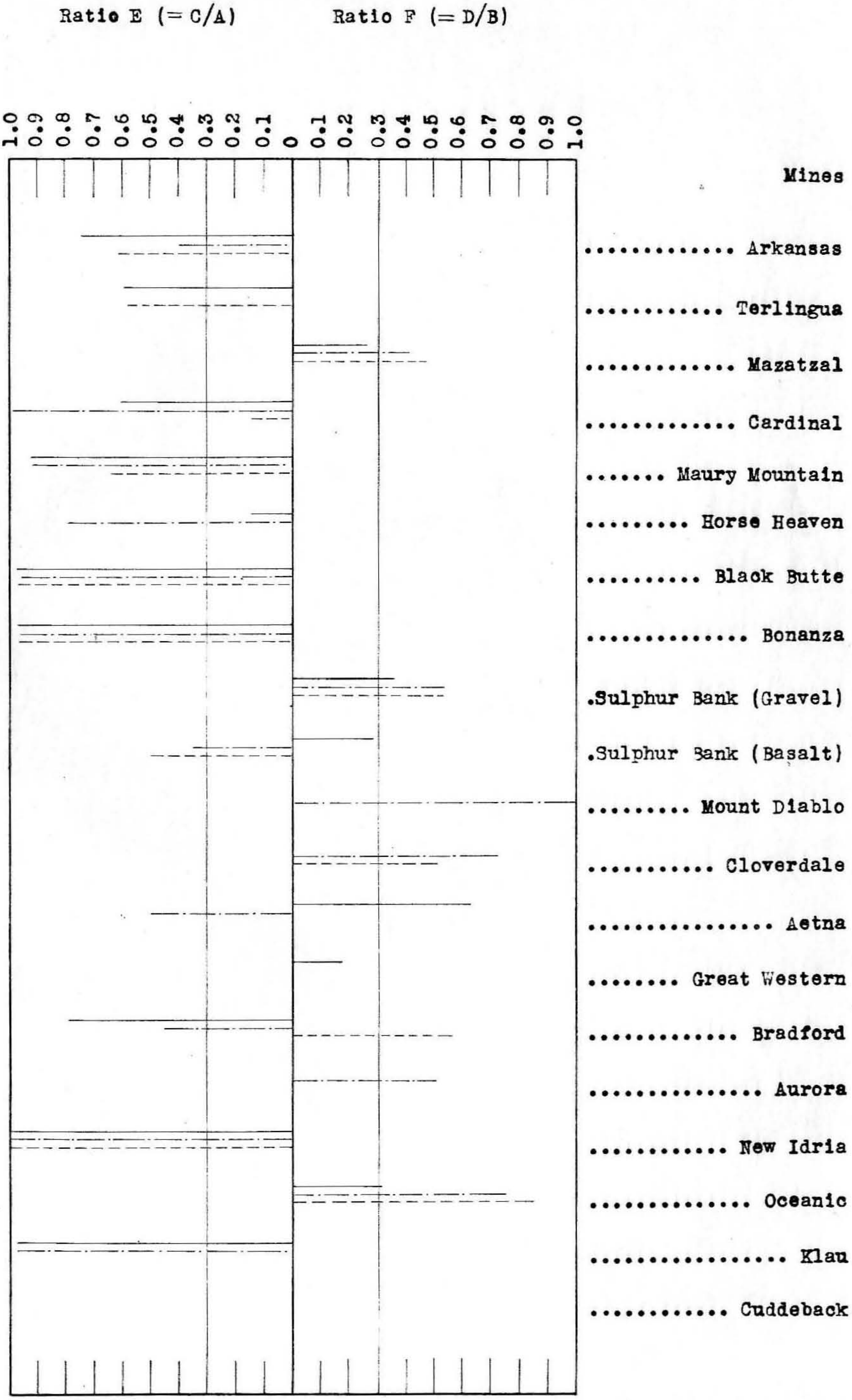


Plate 5 - K ZnO

Relative Concentrations of Elements in Cinnabar and Wall Rock

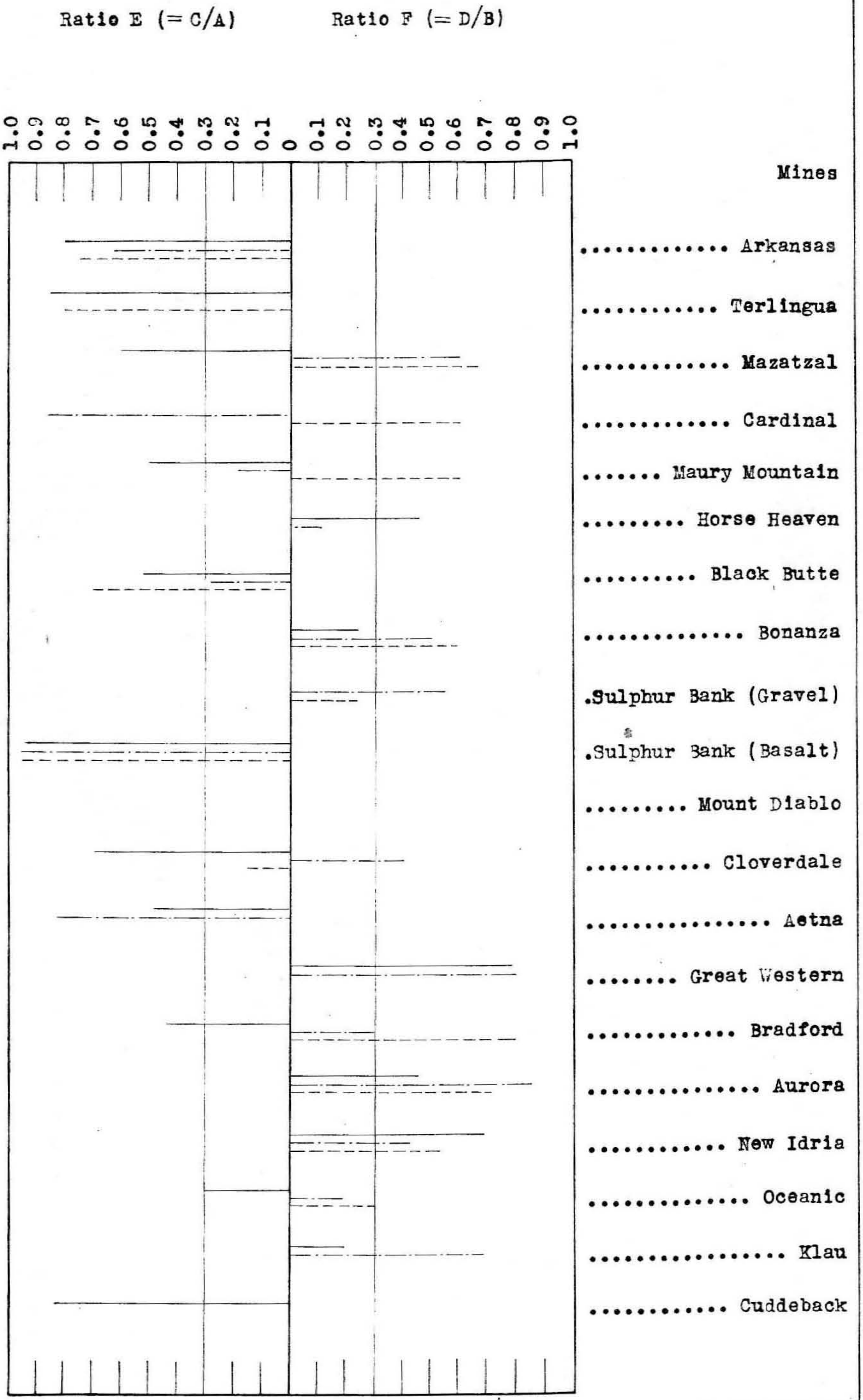
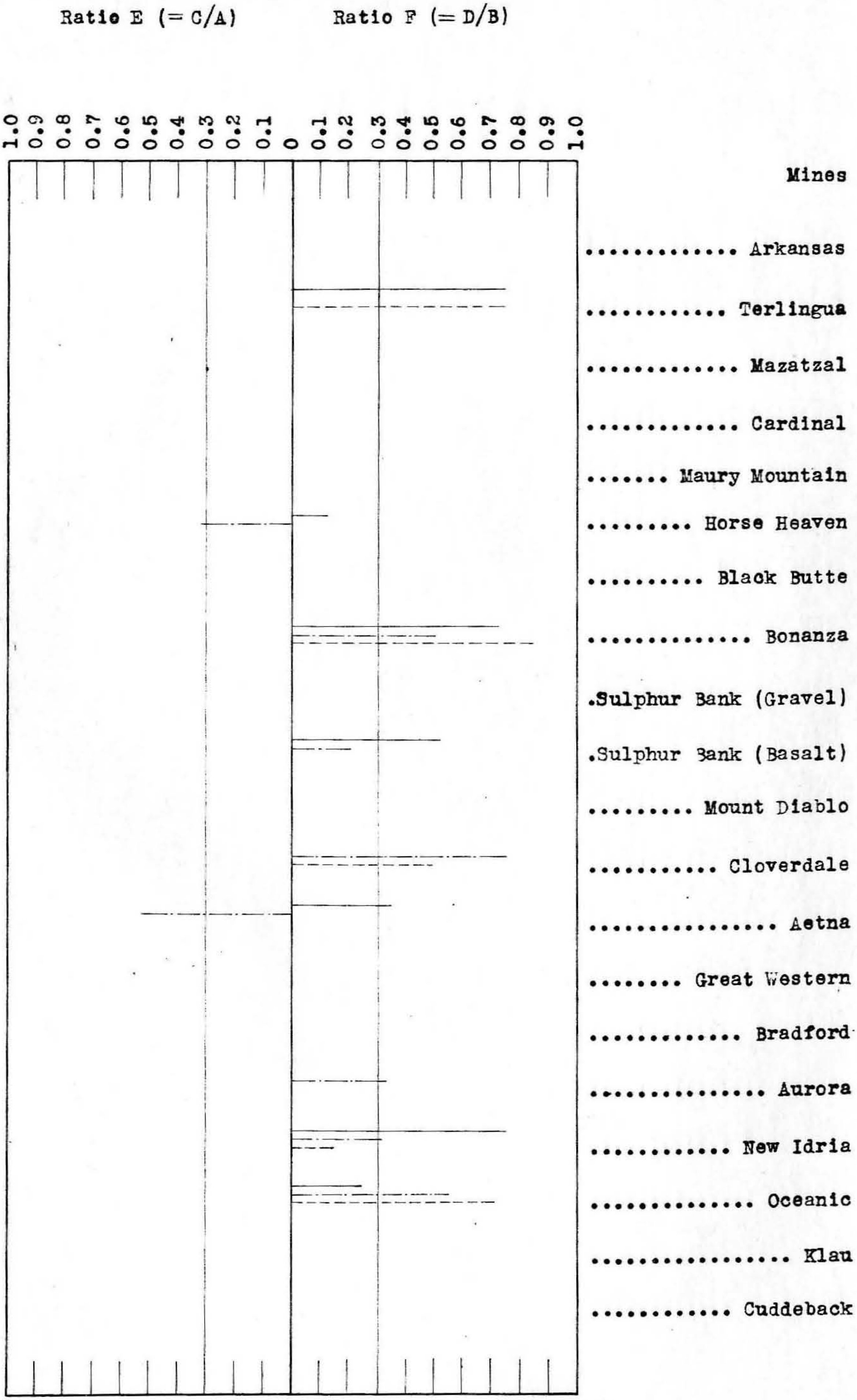


Plate 5 - L MnO

Relative Concentrations of Elements in Cinnabar and Wall Rock

Plate 5 - M Na$_2$O

Relative Concentrations of Elements in Cinnabar and Wall Rock



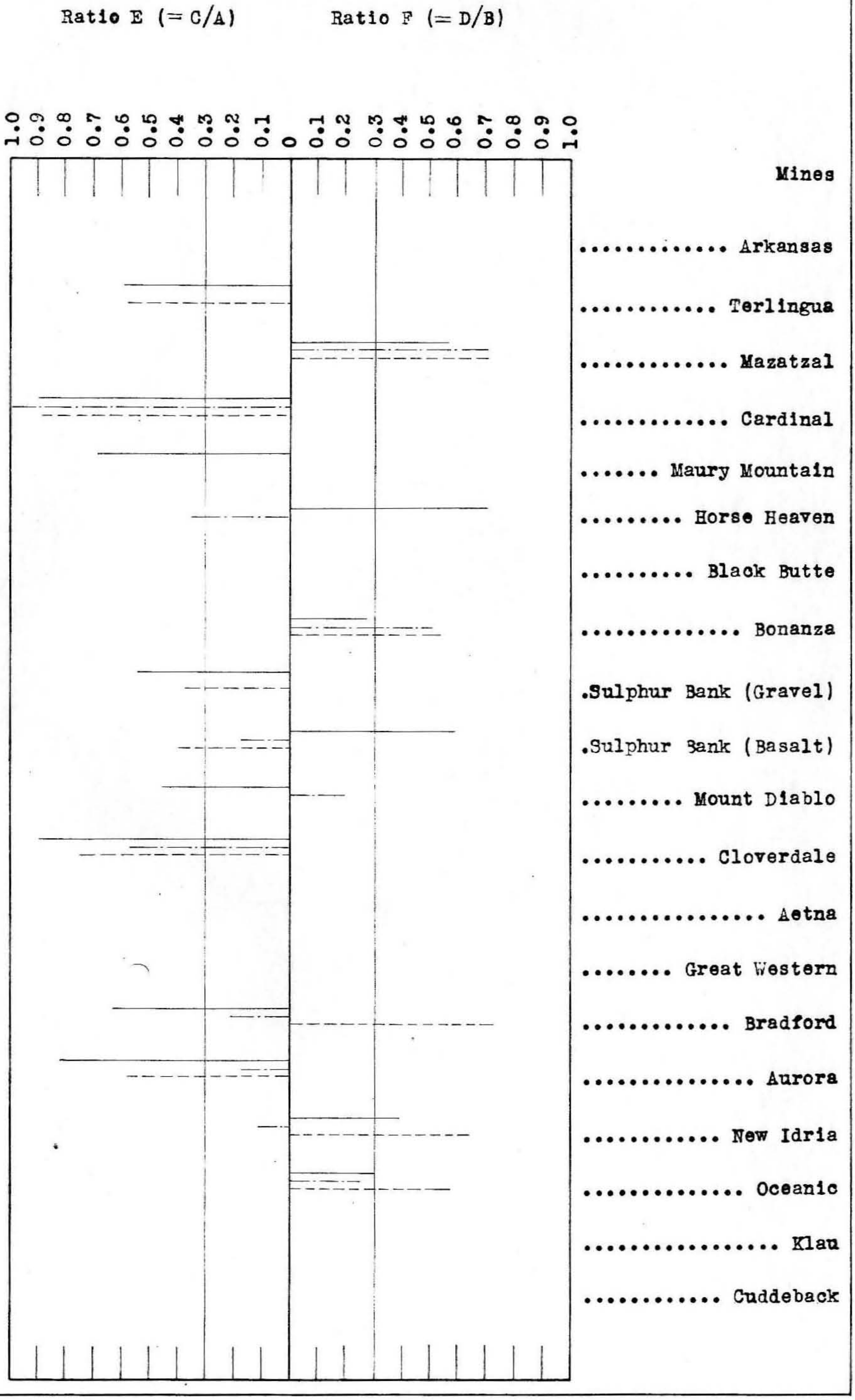
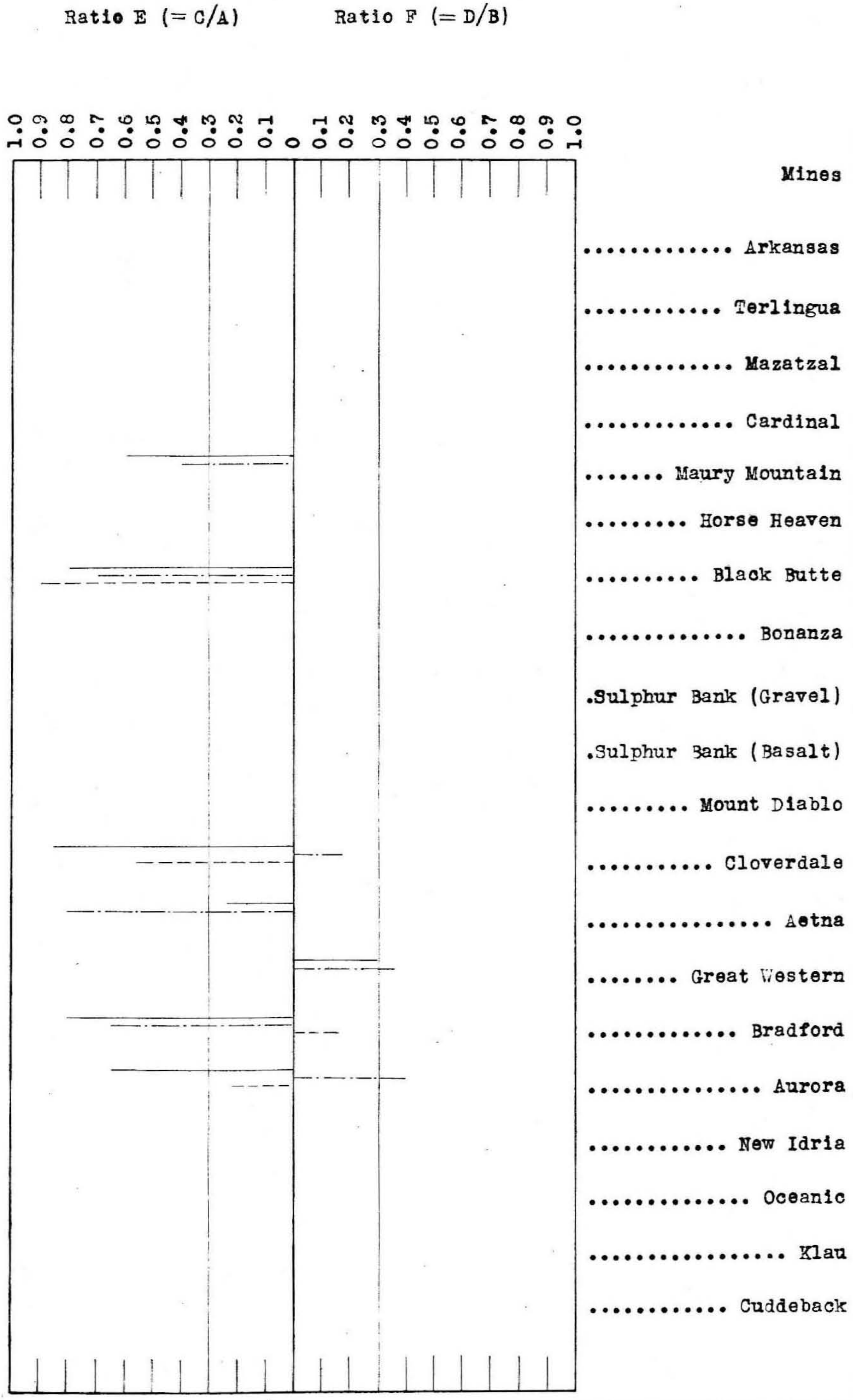


Plate 5 - N 380

Relative Concentrations of Elements in Cinnabar and Wall Rock

Plate 5 - 0 Co_2O_3

Relative Concentrations of Elements in Cinnabar and Wall Rock



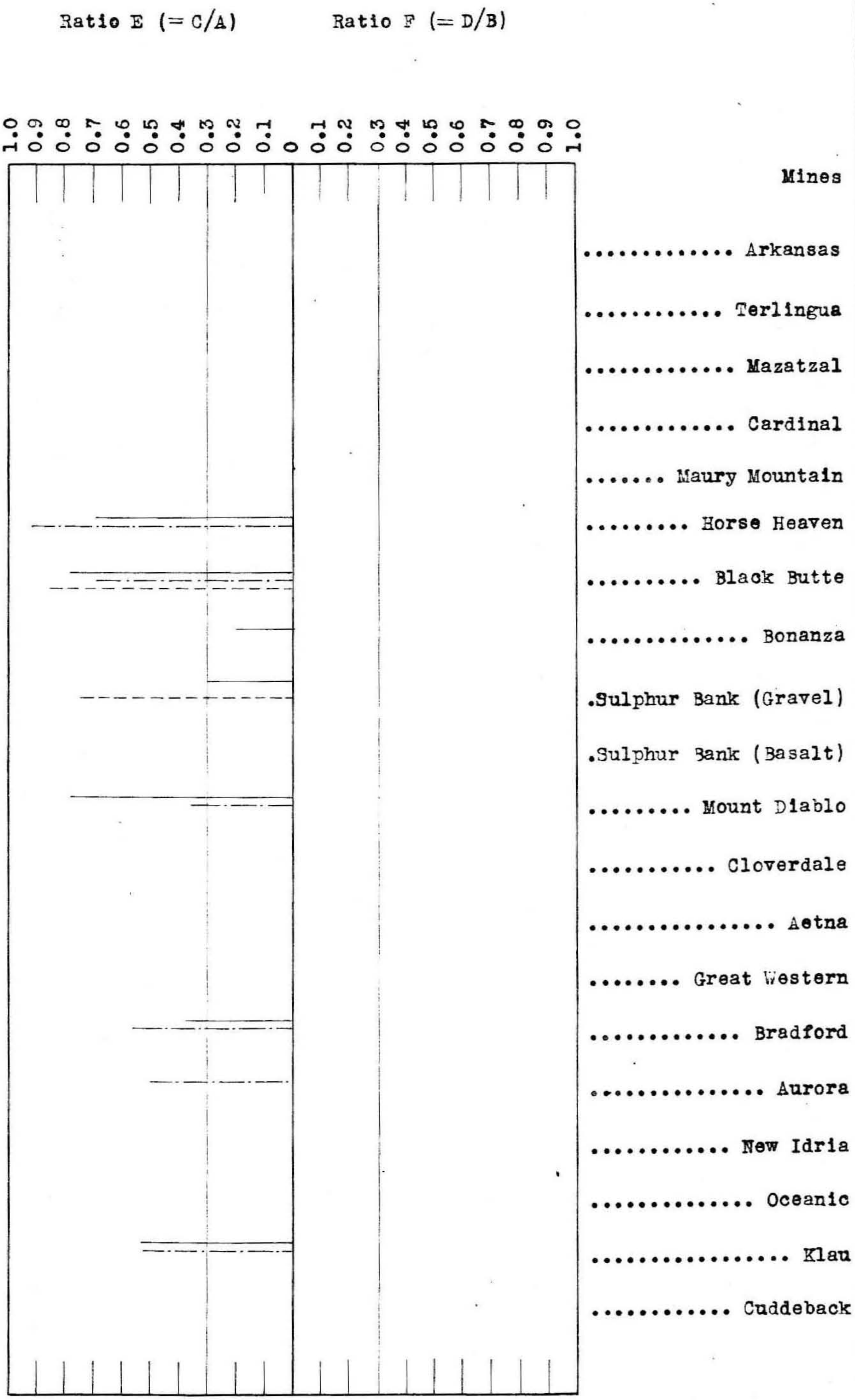


Plate 5 - P PbO

Relative Concentrations of Elements in Cinnabar and Wall Rock

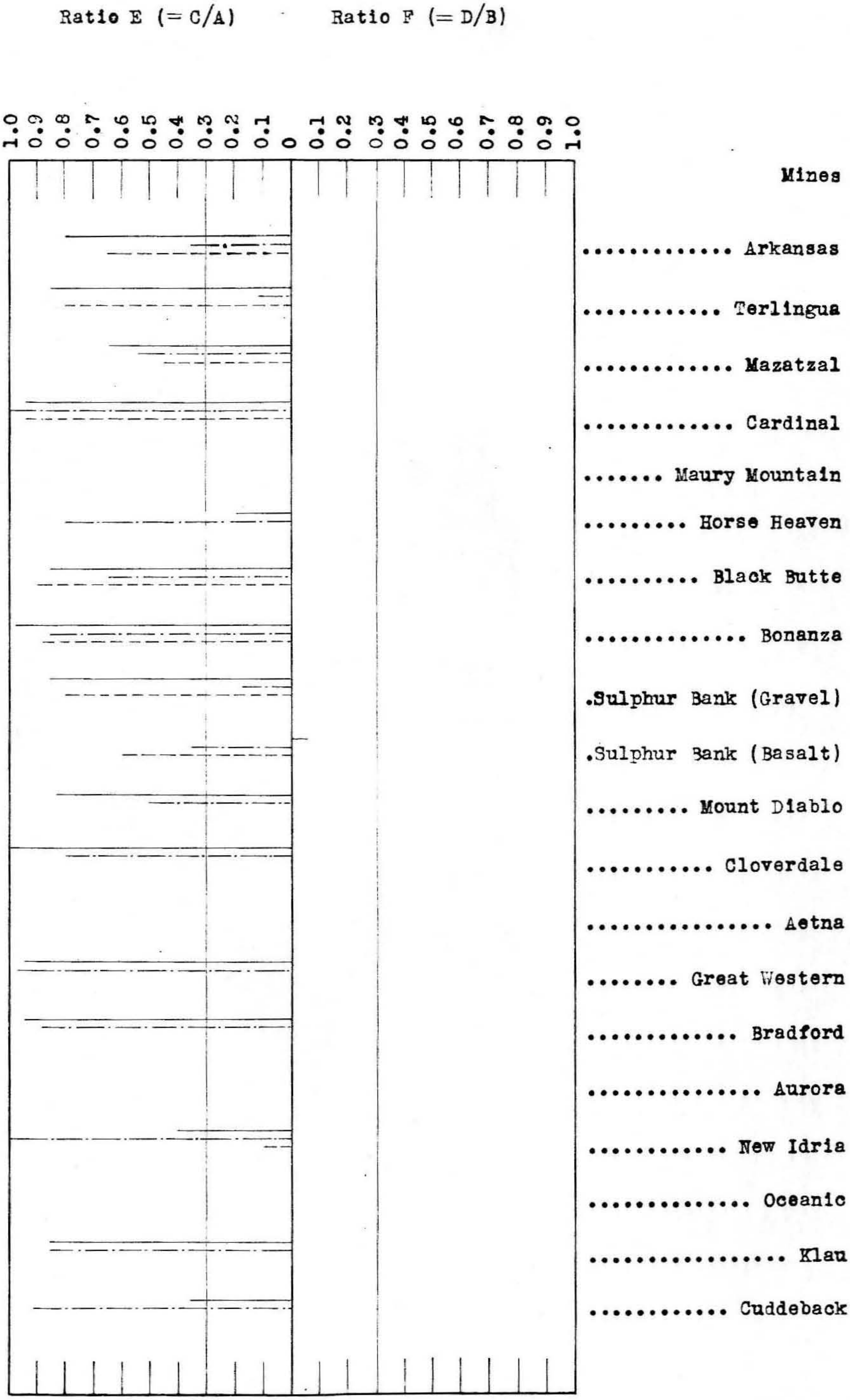
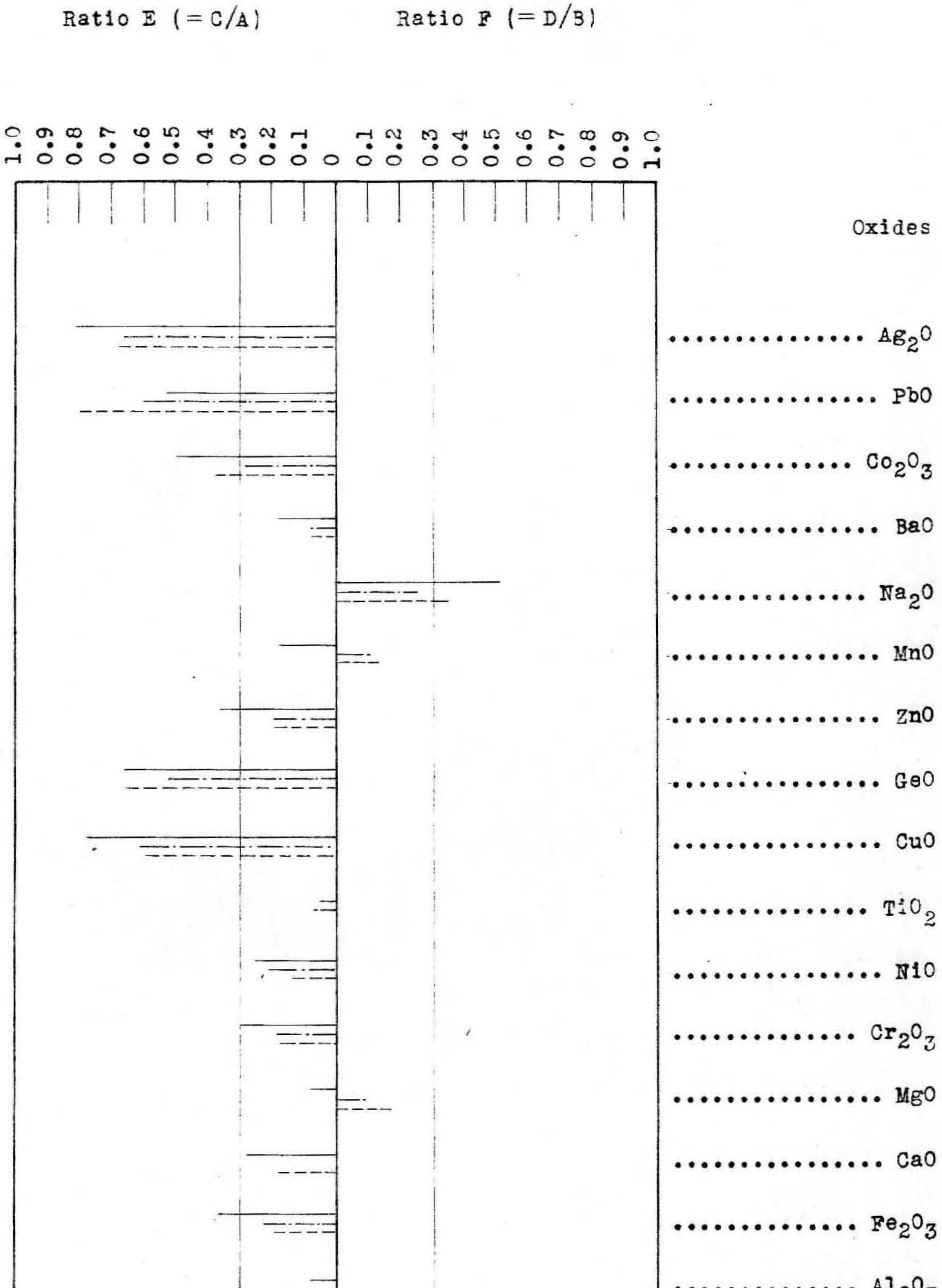


Plate 5 - C Ag

Relative Concentrations of Elements in Cinnabar and Wall Rock

Plate 6

Average Relative Concentrations of Elements in Cinnabar and Wall Rock



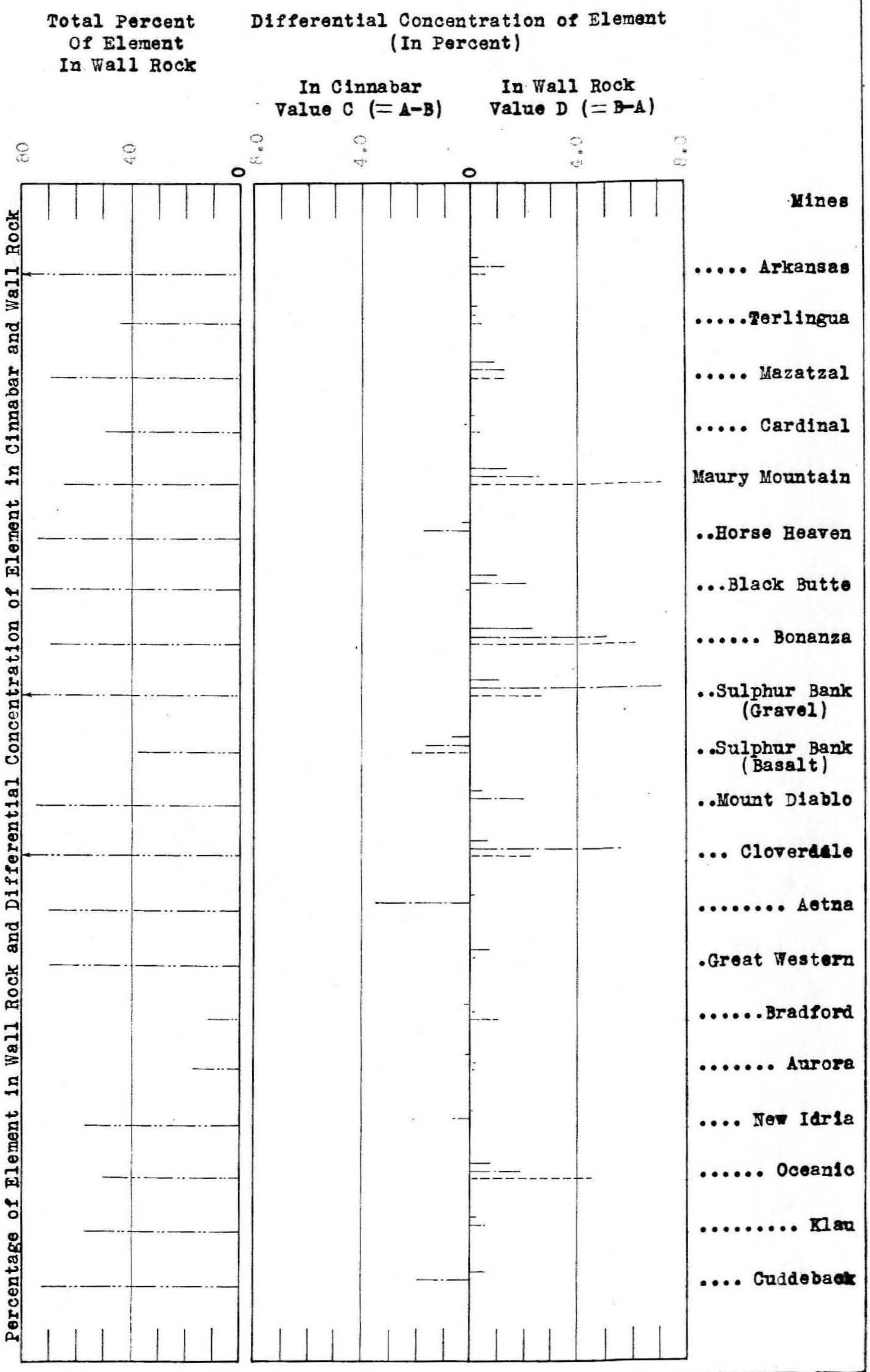


Plate 7 - A SiO_2

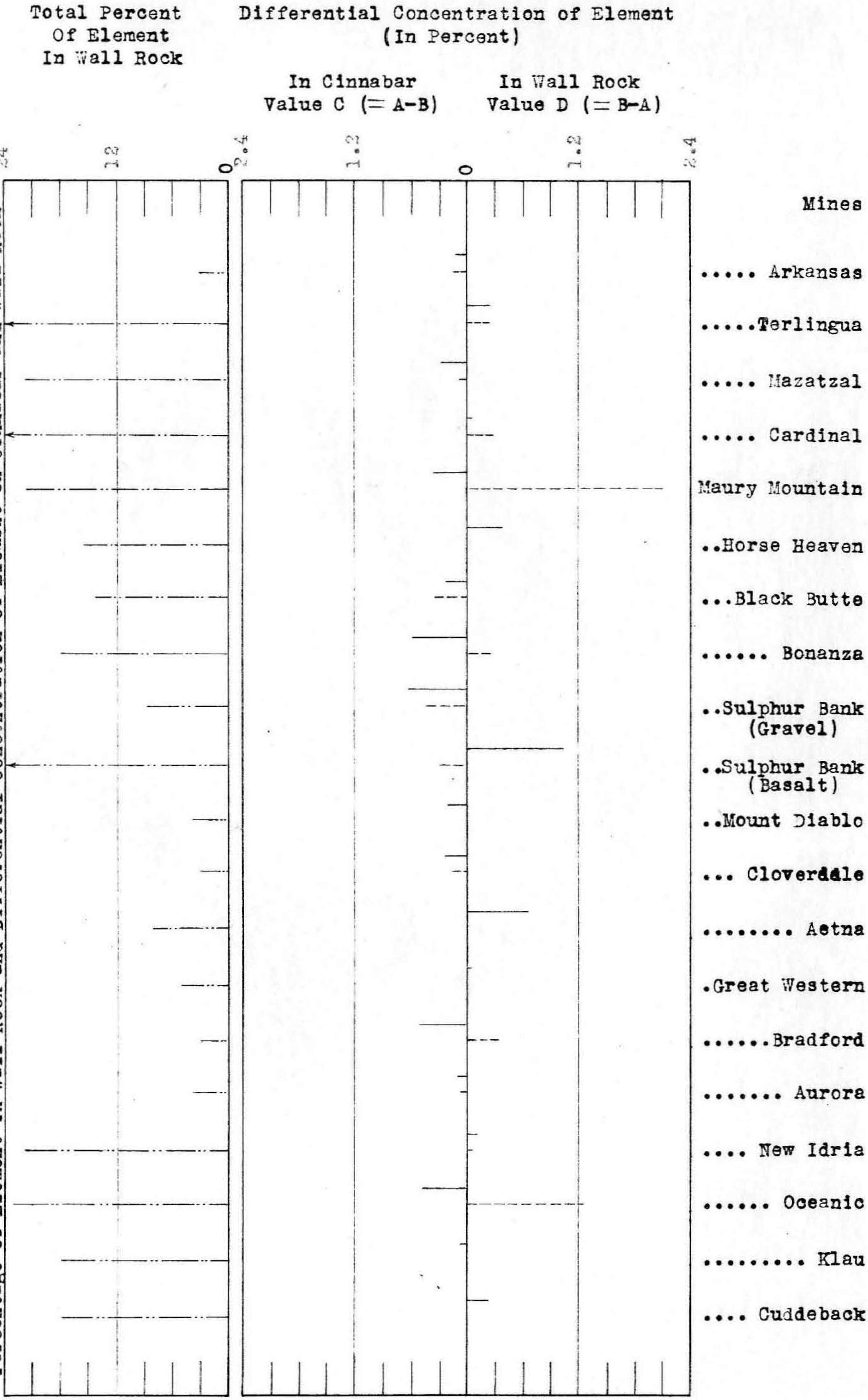


Plate 7 - B Al_2O_3

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

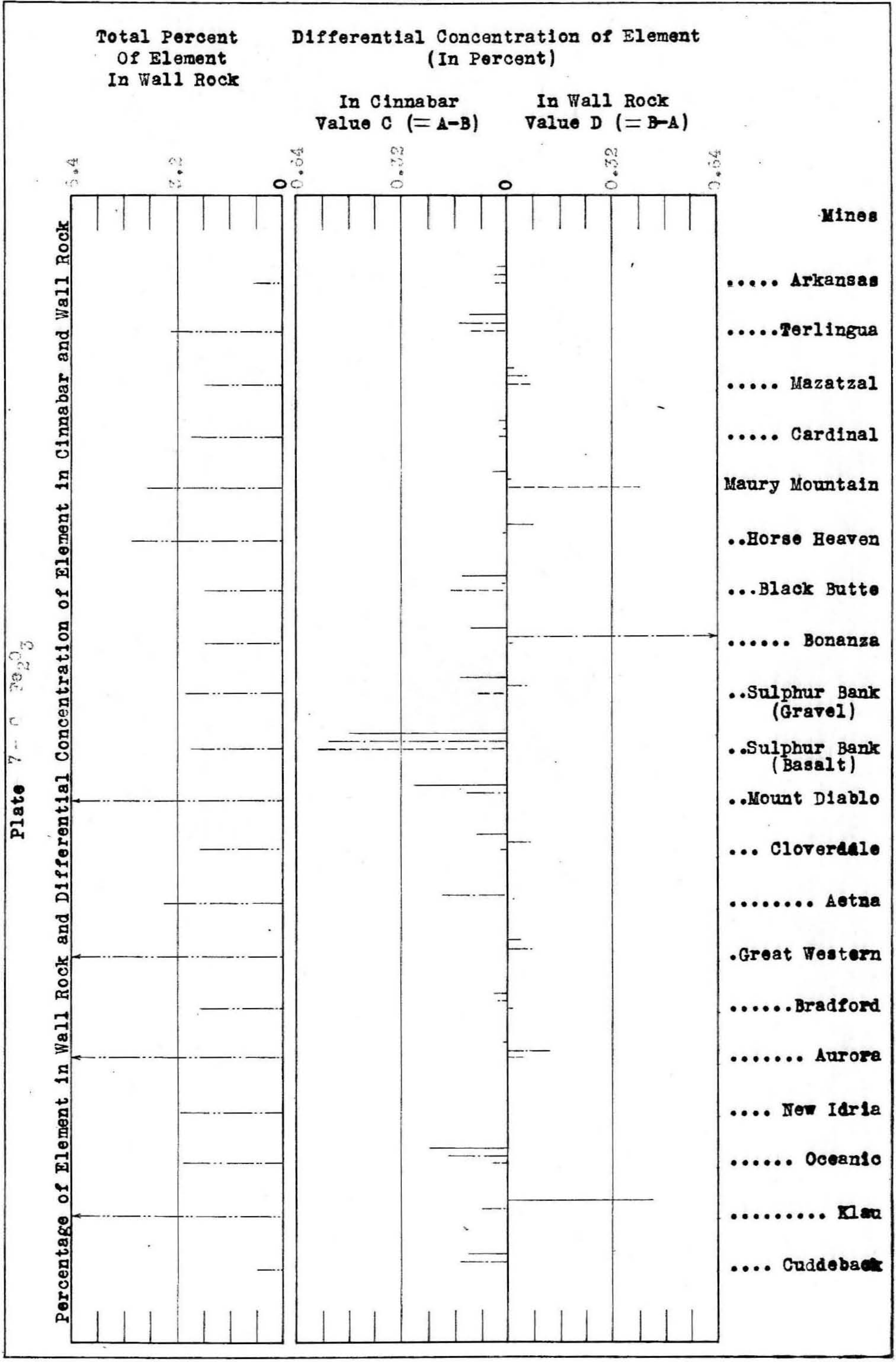
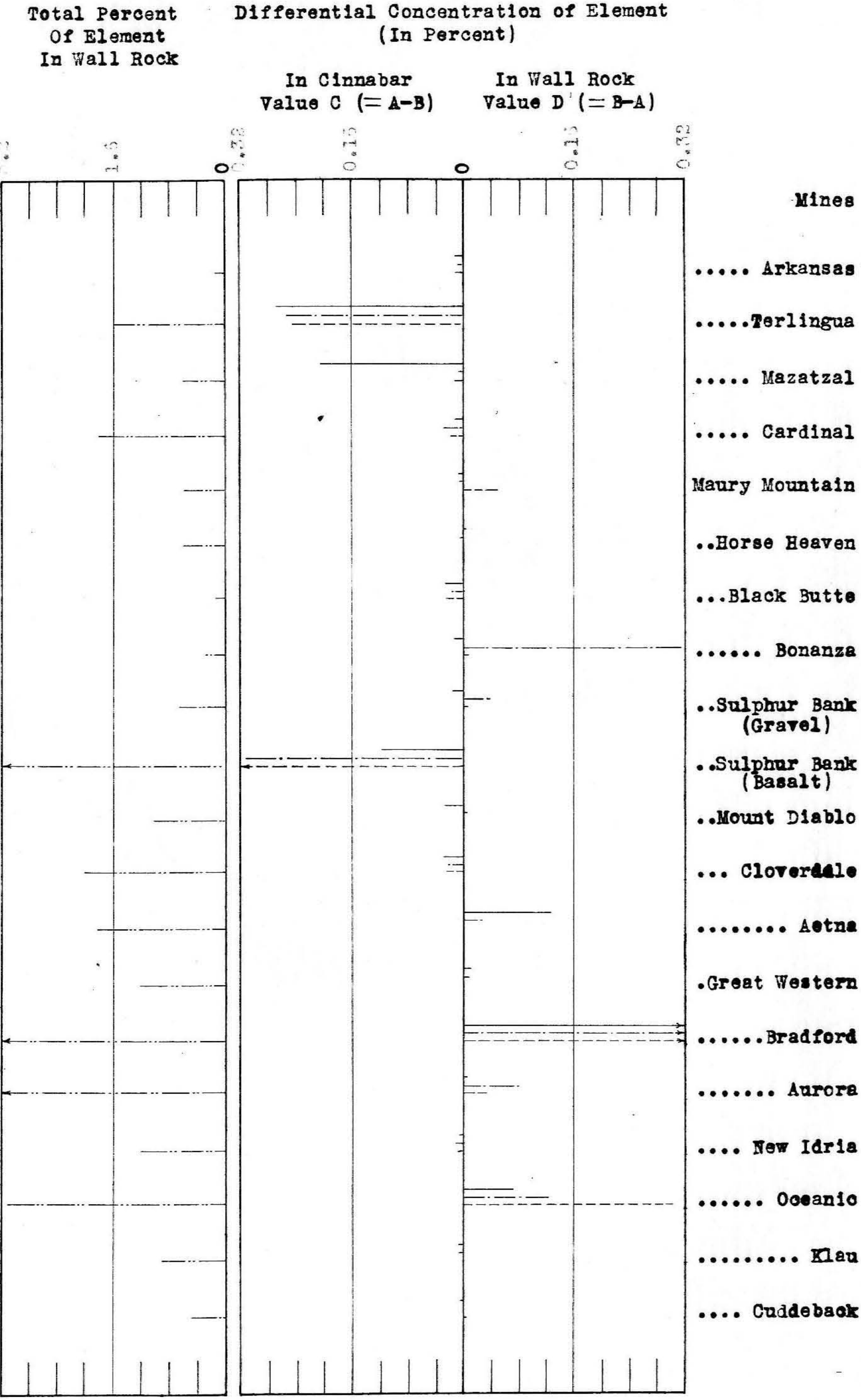


Plate 7 - C Fe_2O_3

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

Plate 7-3 CaO

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock



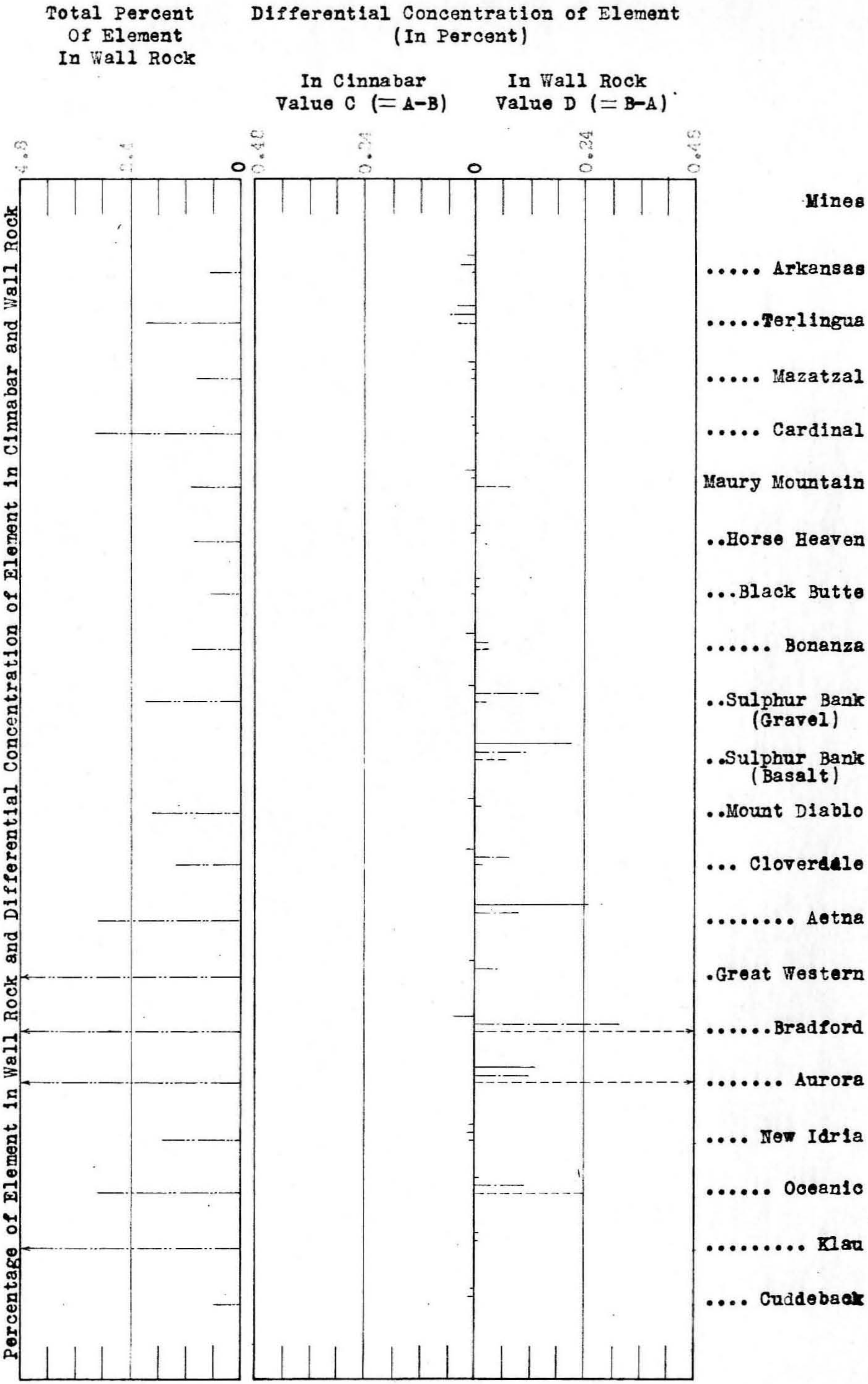


Plate 7 - E MgO

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

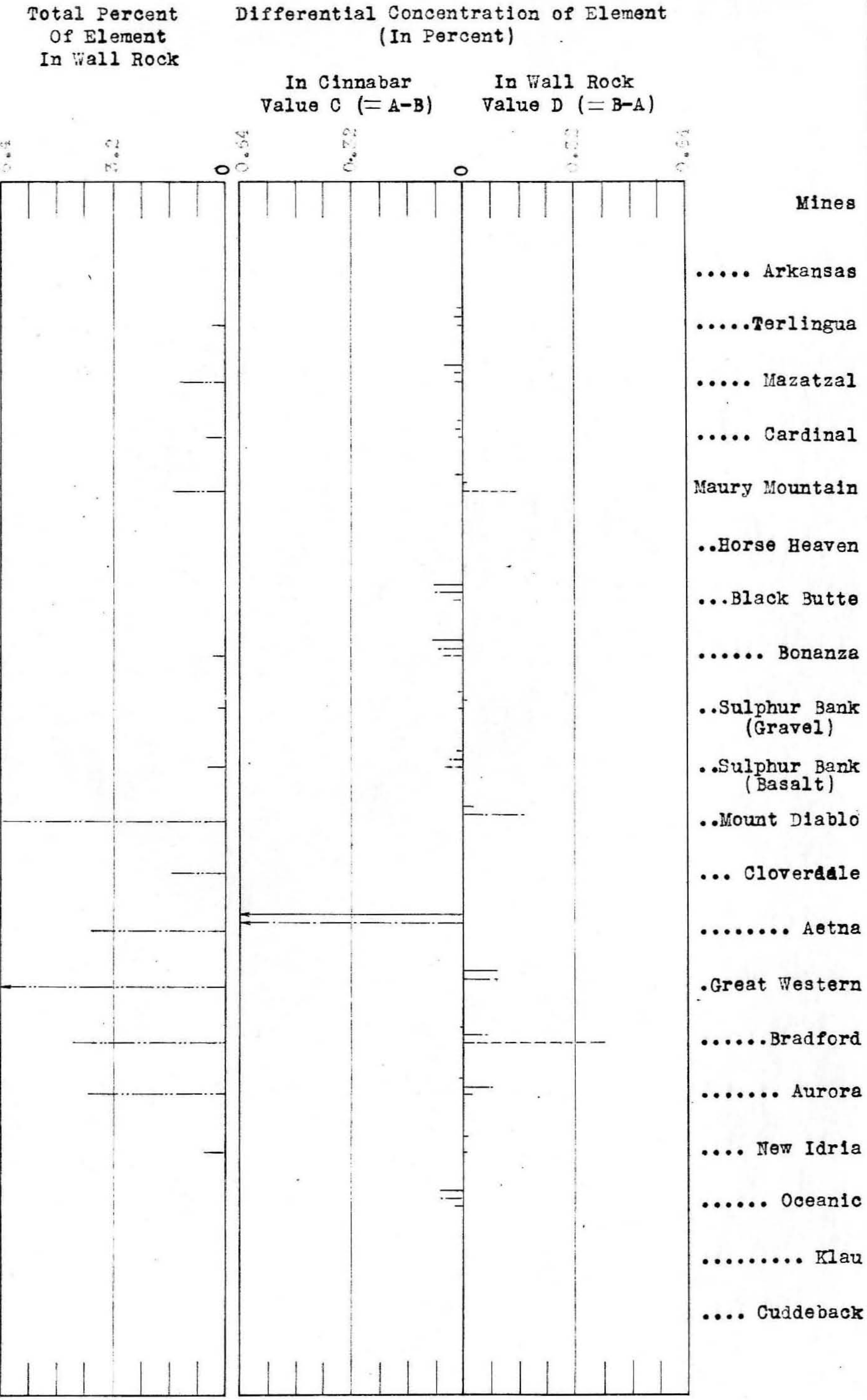


Plate 7 - 8 Cr_2O_3

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

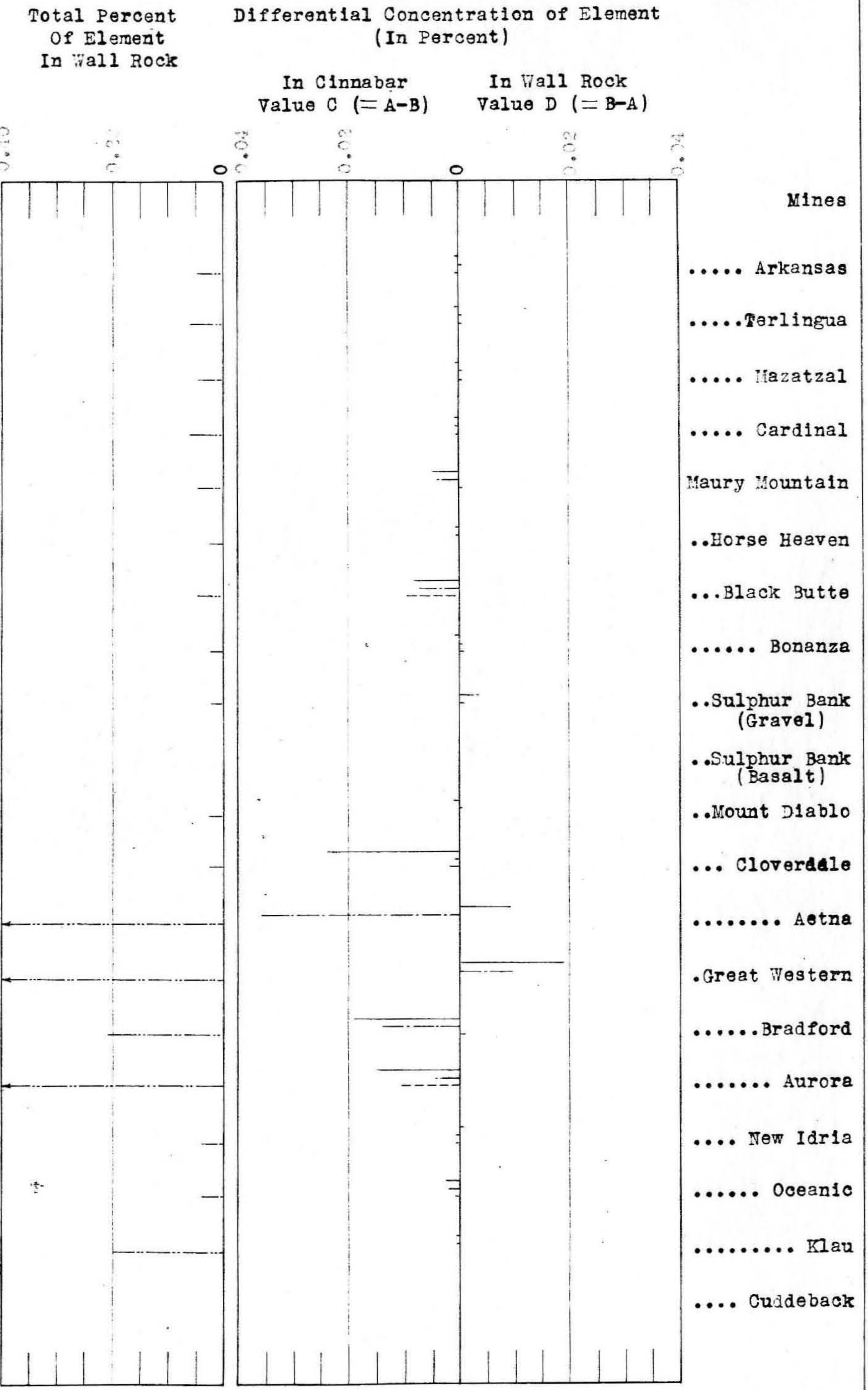


Plate 7 - G NiO

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

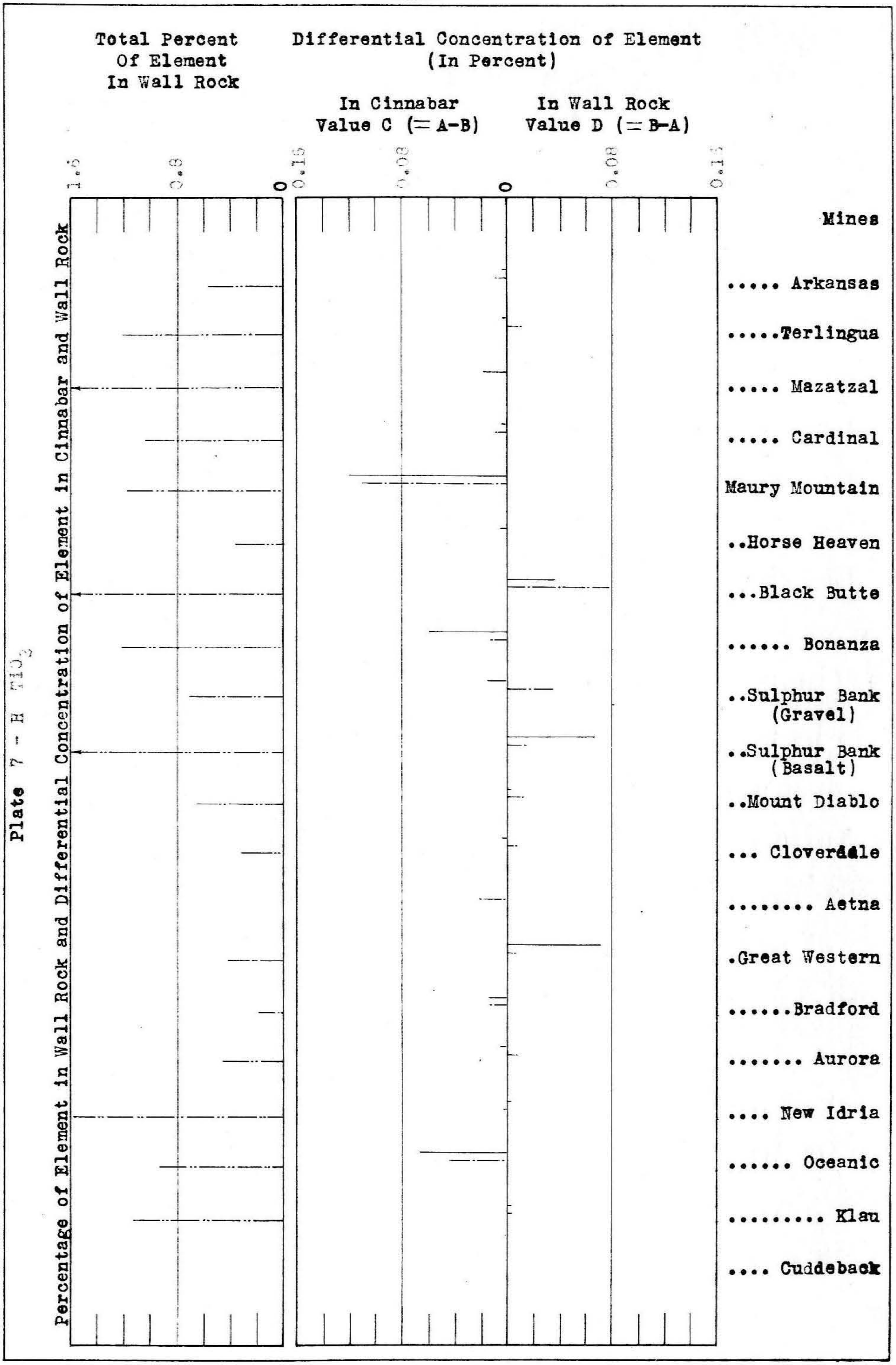


Plate 7 - H TiO_2

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

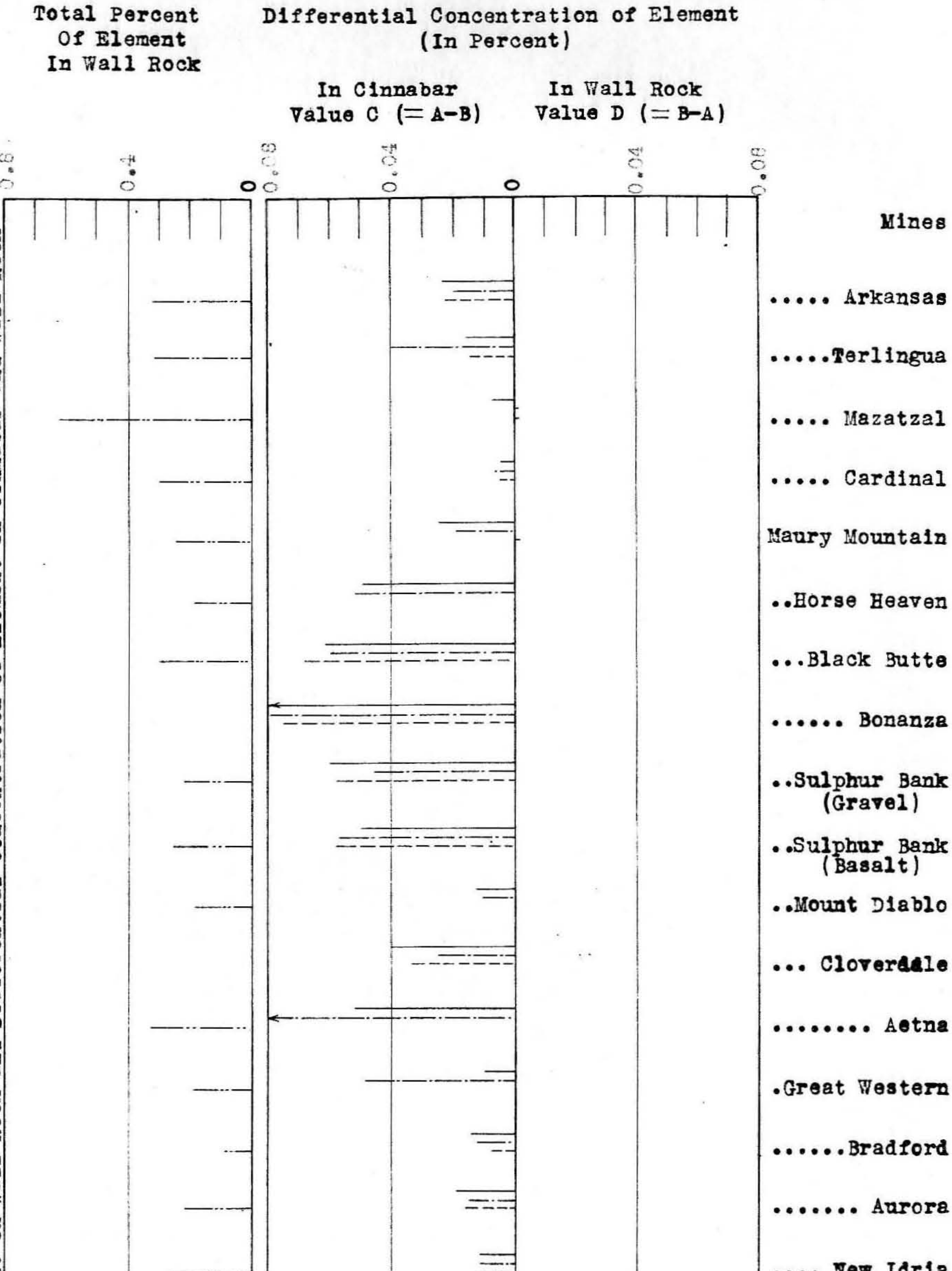


Plate 7 - 1 [illegible]

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

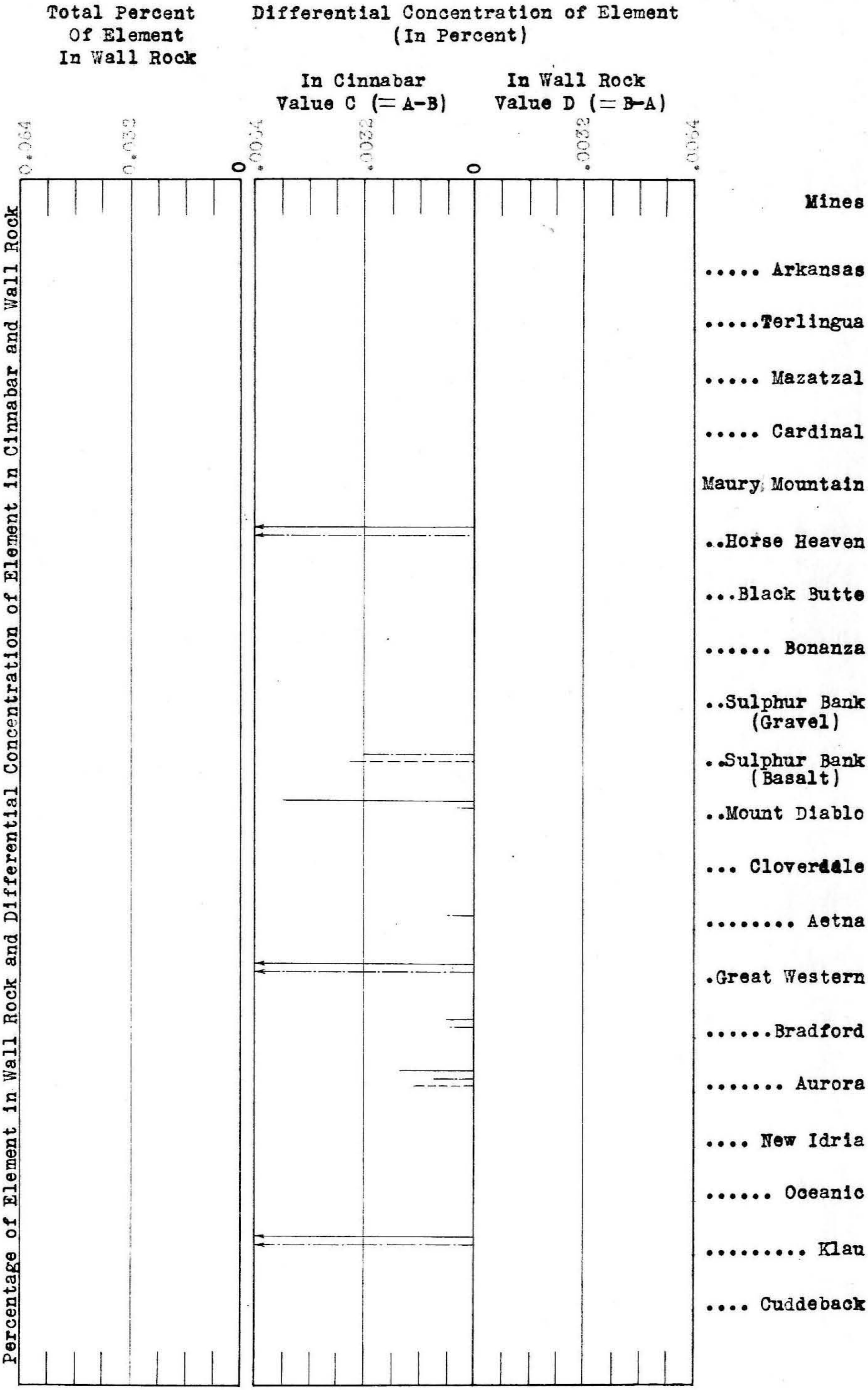


Plate 7 - J GeO

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

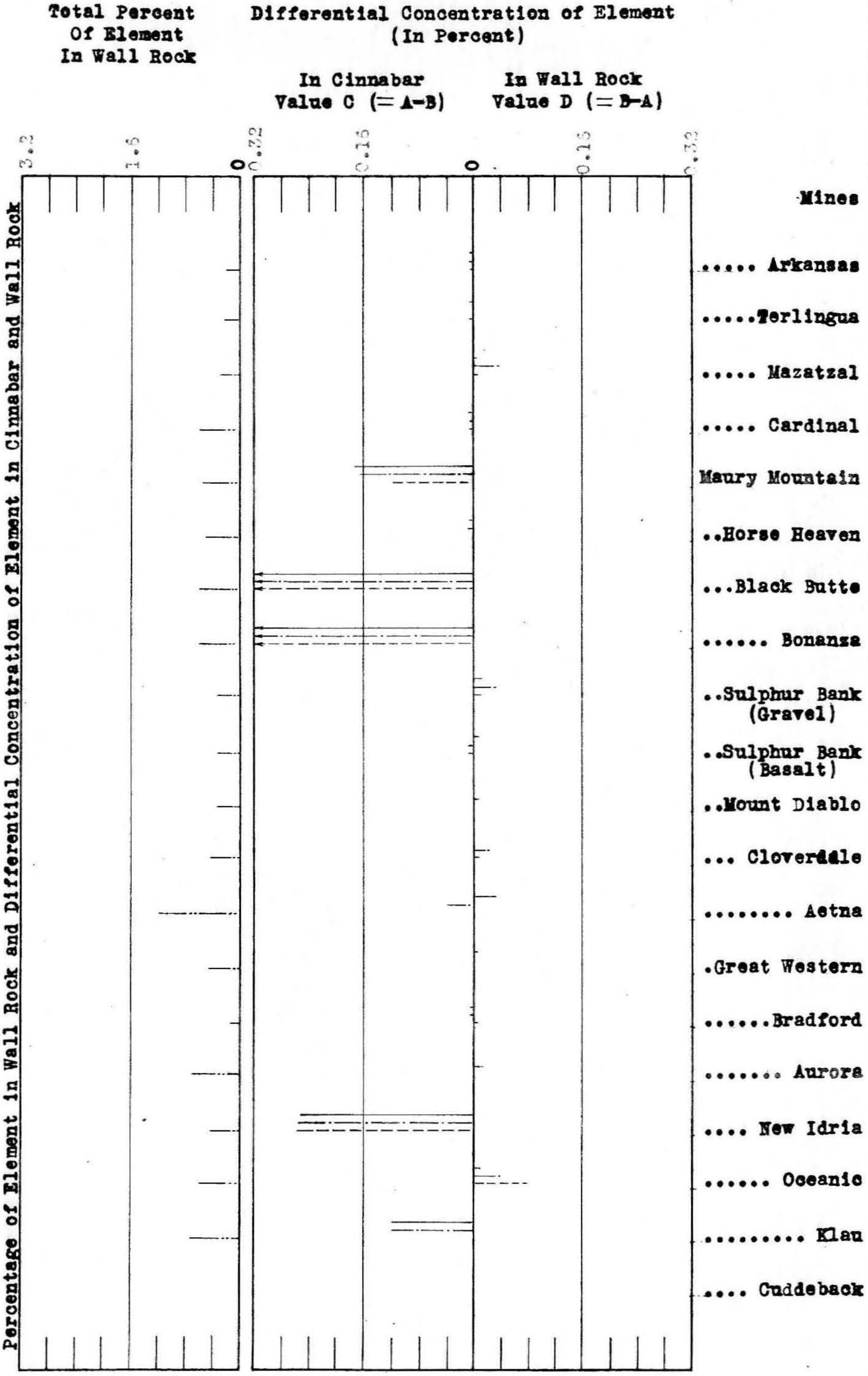


Plate 7 - K ZnO

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

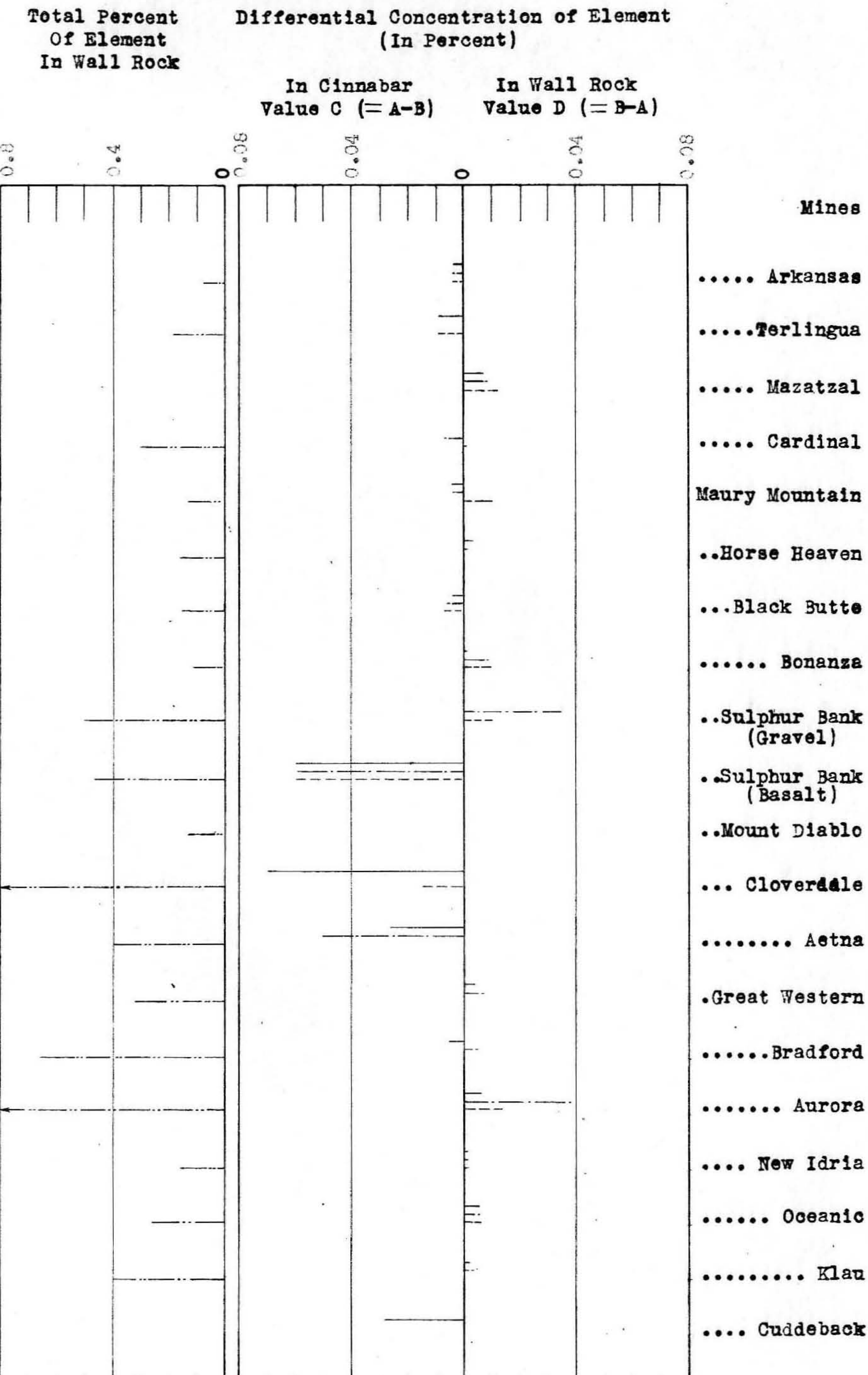


Plate 7 - E MnO

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

Plate 7 - M Na$_2$O

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

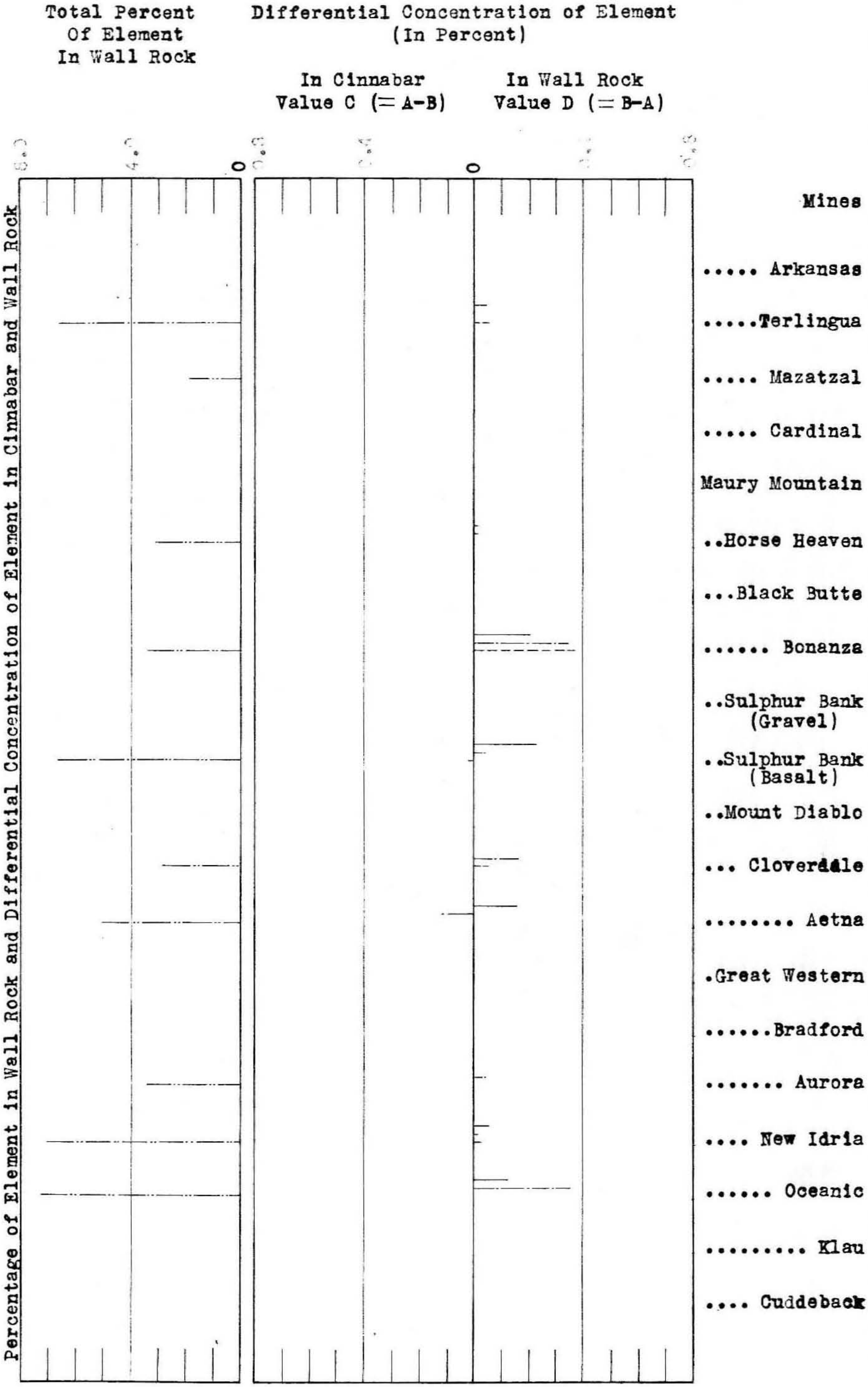
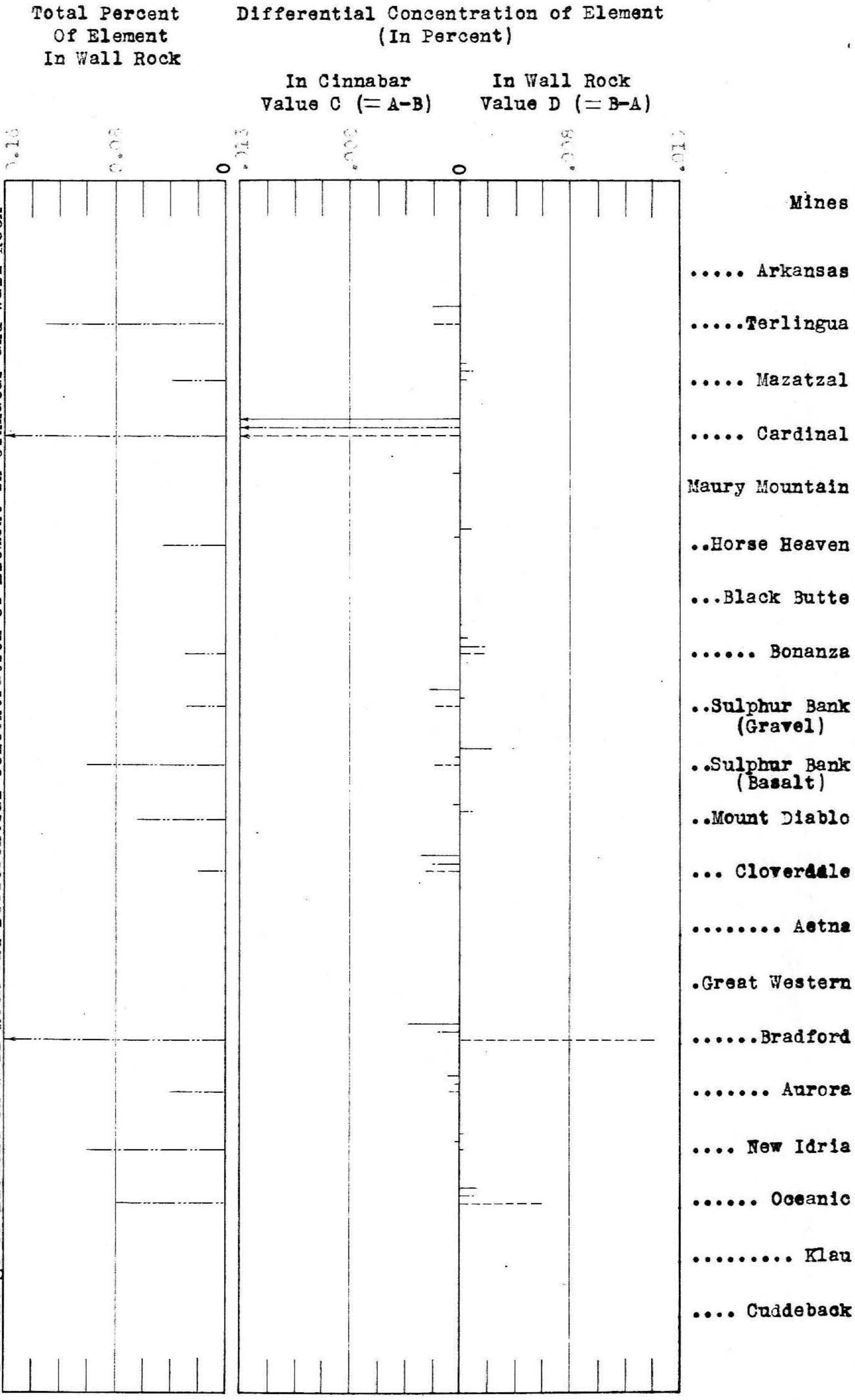


Plate 7 - N 330

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock



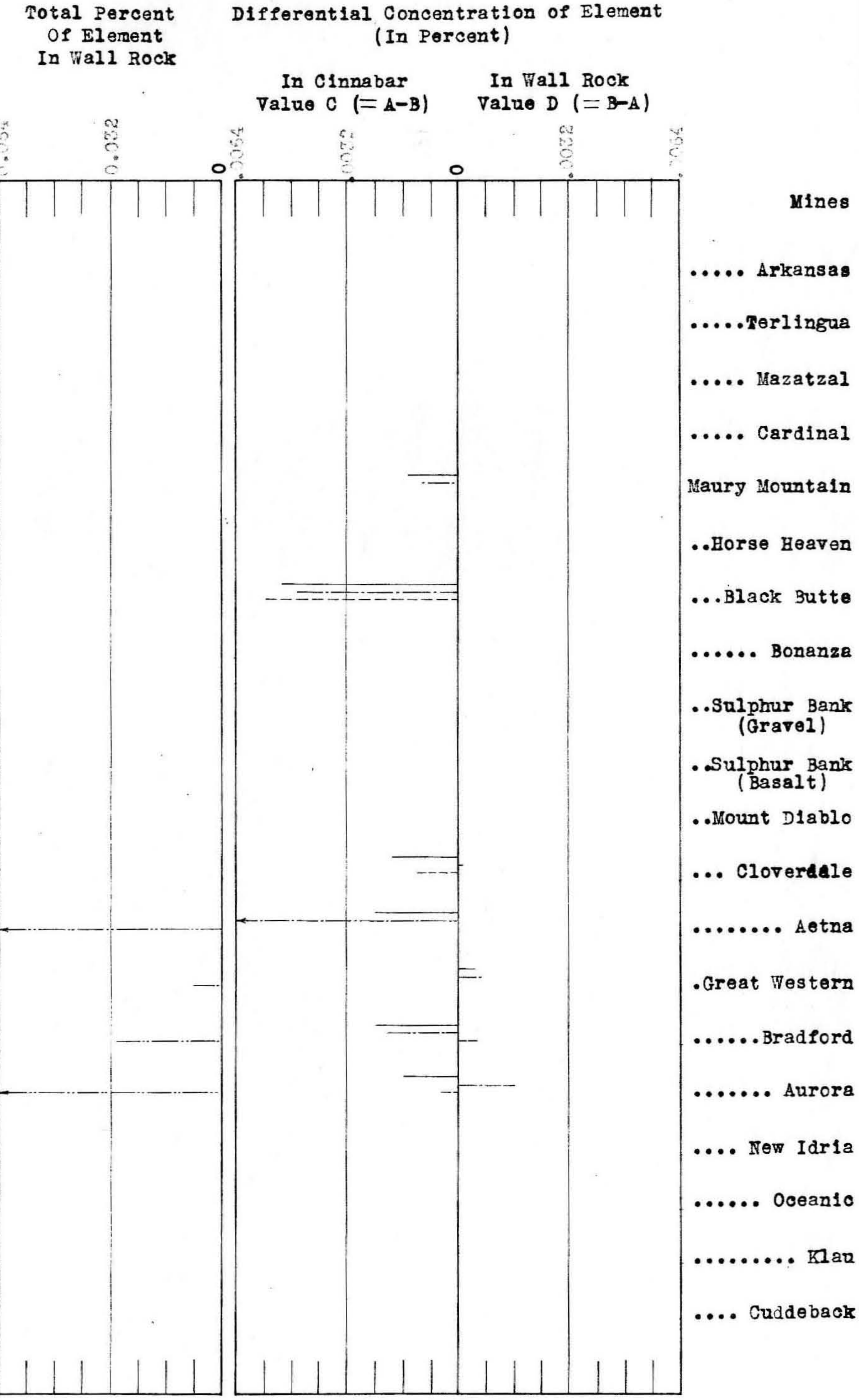


Plate 7 - [illegible]

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

Plate 7 - 2 PbO

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock

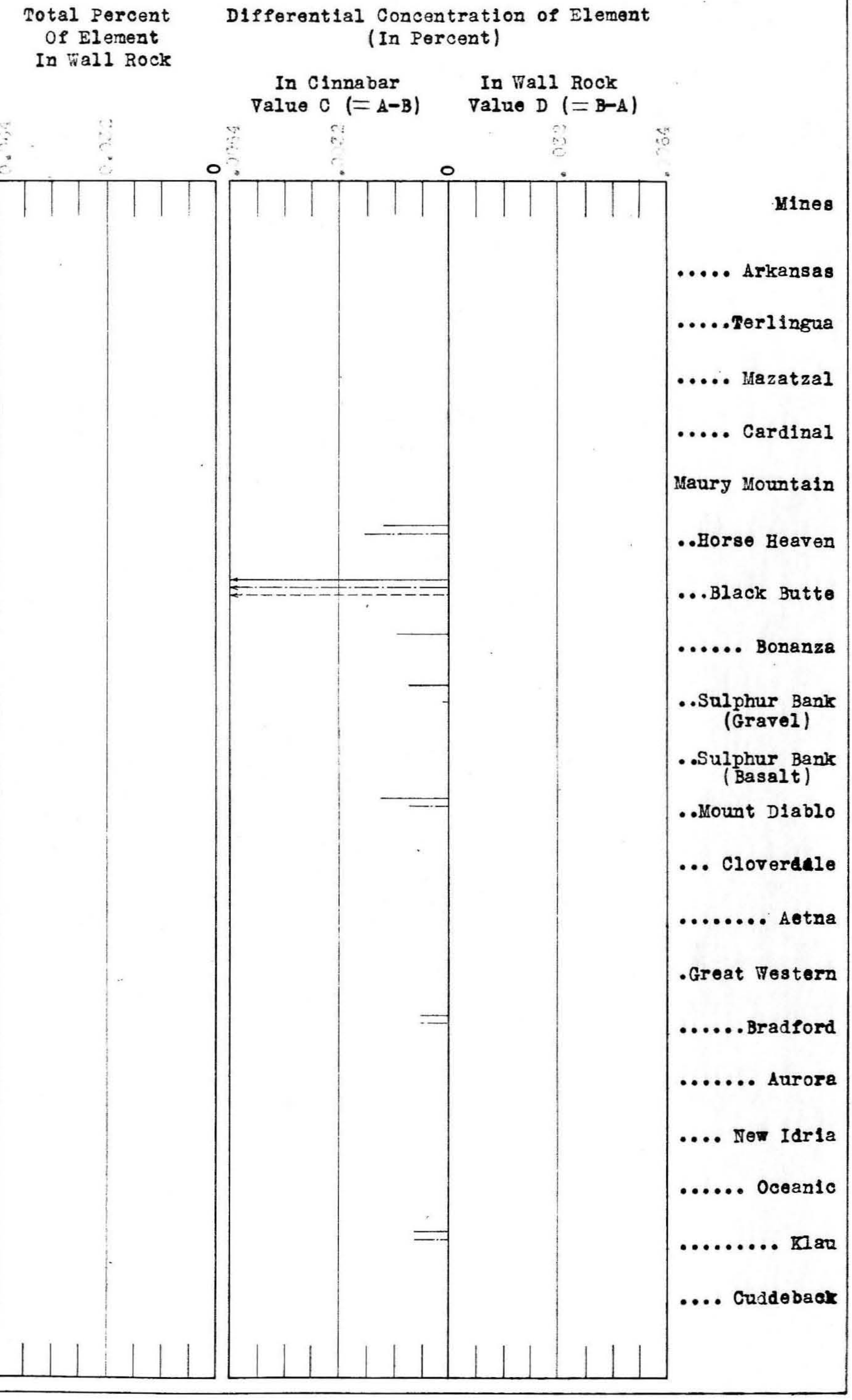
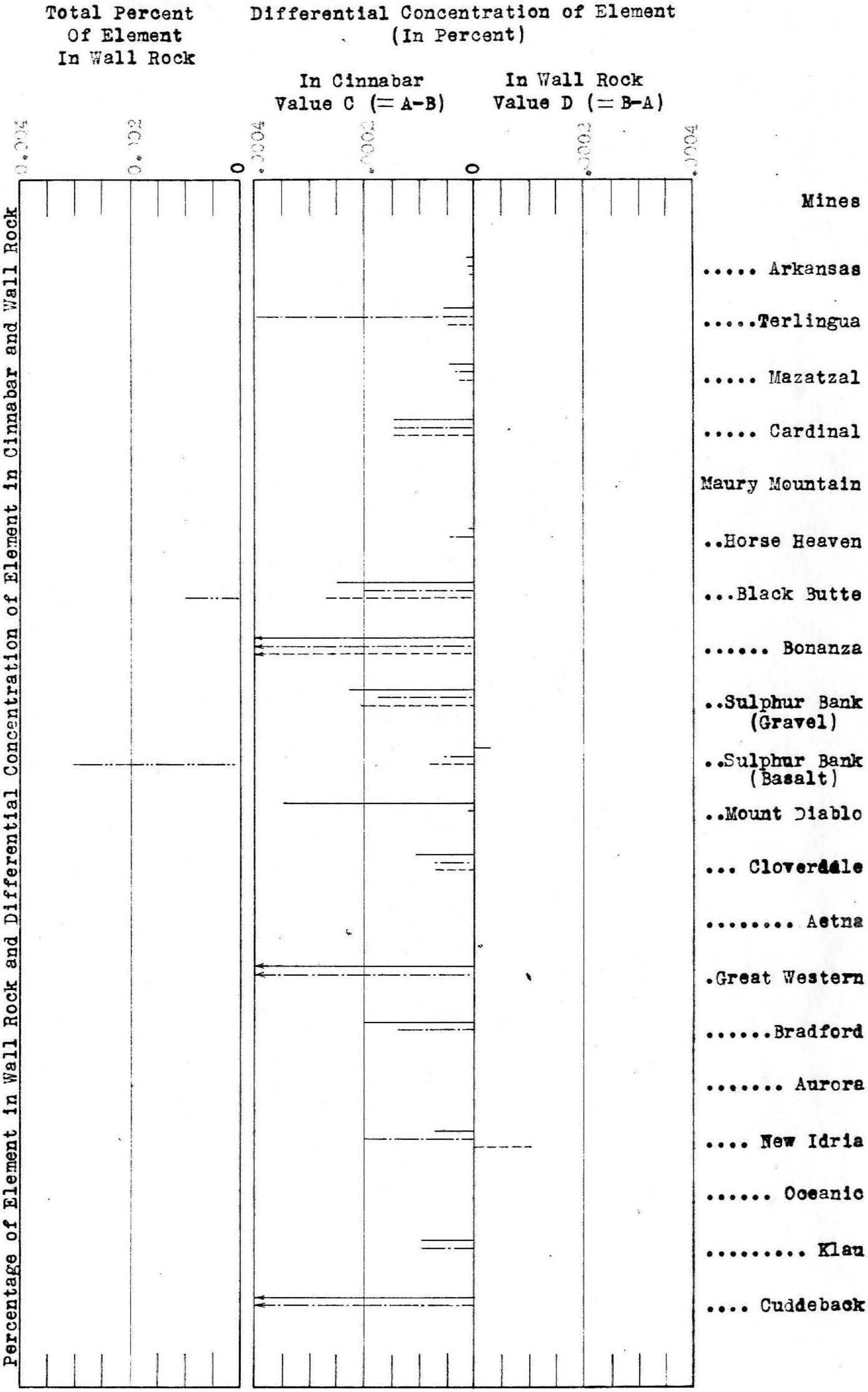


Plate 7 - 9 Ag_2O

Percentage of Element in Wall Rock and Differential Concentration of Element in Cinnabar and Wall Rock



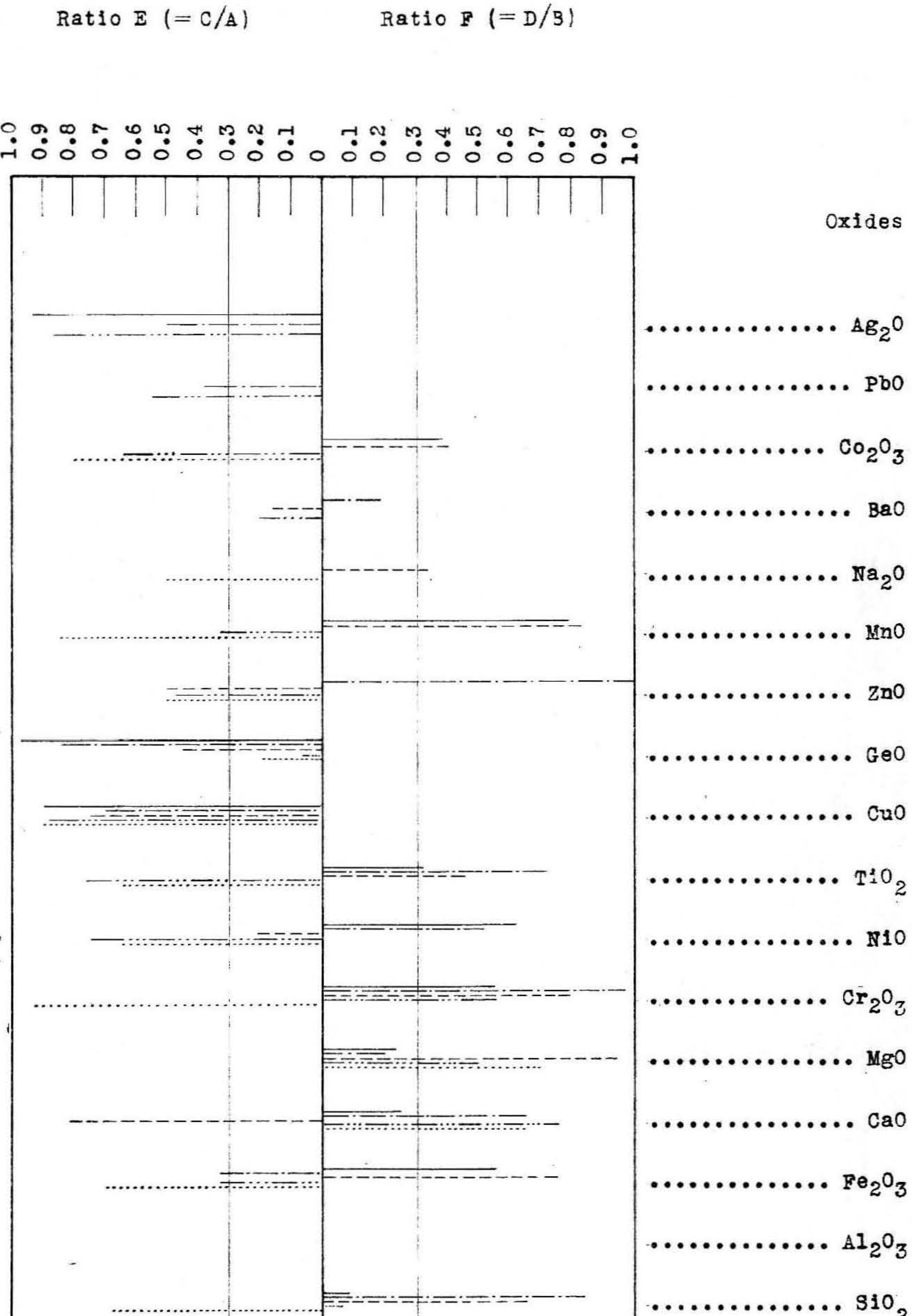


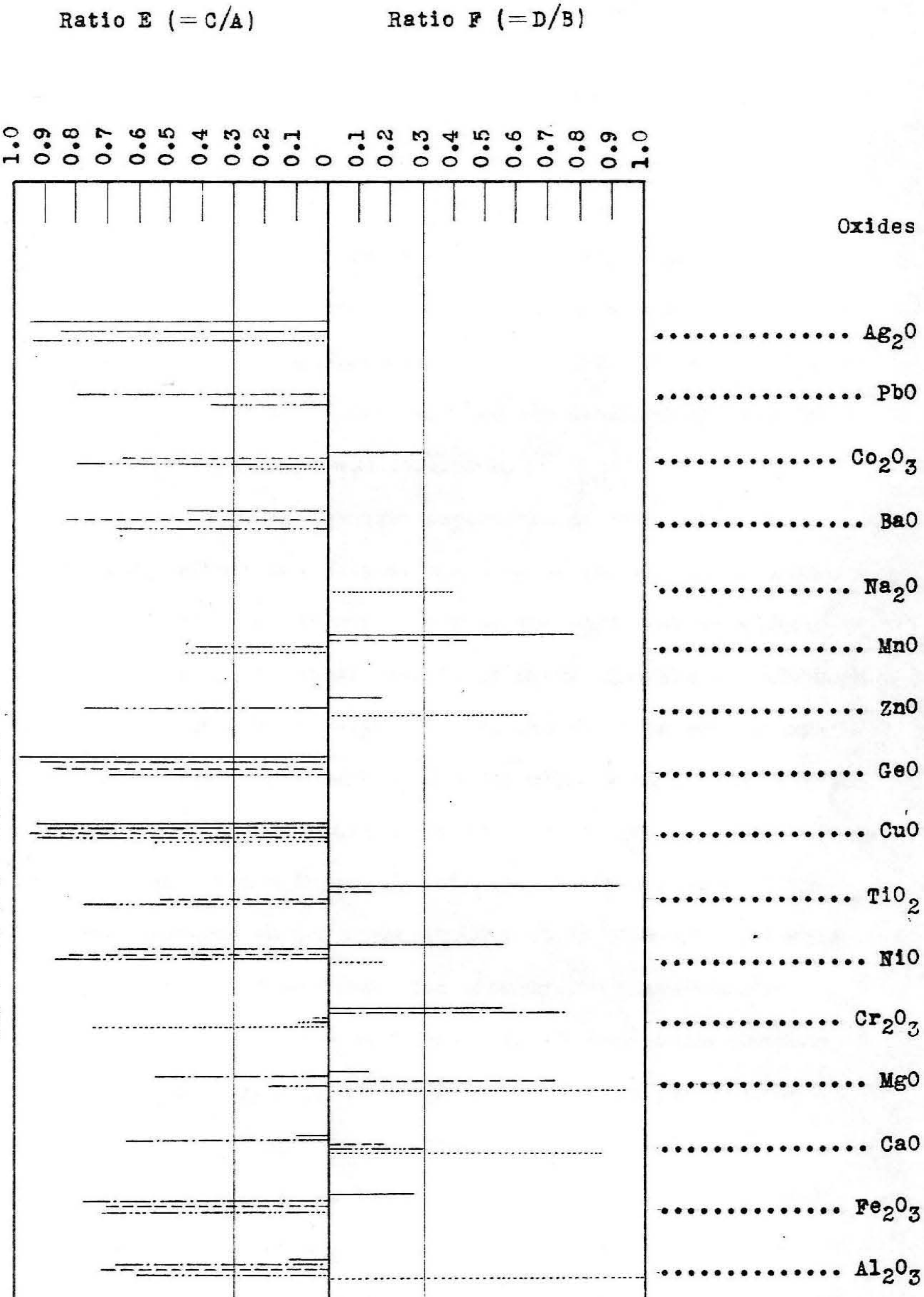
Plate 8

Relative Concentrations of Elements in Cinnabar and Wall Rock for Deposits in Serpentine
(By Alumina Method)

Plate 9

Relative Concentrations of Elements in Cinnabar and Wall Rock for Deposits in Serpentine

(By Total Impurity Method)



Validity of Results

The validity of the results to be derived from this study of elemental concentrations in the cinnabar is dependent on two factors:

(1) The validity of the assumptions used in re-calculating wall rock values. That these assumptions have a high degree of validity will be shown by the similarity of significant results obtained by each of the three methods of wall rock re-calculation.

(2) The efficiency of the gravity separation of cinnabar.

Although every effort was made at the time of separation to insure a complete separation of cinnabar not only from the wall rock as a whole, but also especially from the other associated heavy minerals and although each concentrate was carefully re-purified on the super-panner and examined microscopically to make certain that no differential concentration of heavy minerals occurred with the cinnabar, nevertheless, the efficiency of the separation is of such import in determining the validity of the observable concentrations in the cinnabar that it is likewise advisable to determine from the analyses themselves whether the elemental concentrations in the cinnabar are caused by a differential concentration of heavy minerals during gravity separation. For this purpose, Plate 7 has been prepared. Plate 7 shows the actual differential elemental concentrations, in percent, obtained by each of the three methods of wall rock re-calculation. Each graph represents one element as shown in each of the twenty samples. Plotted above the differential concentrations is the total content of the particular element in the wall rock from which the corresponding cinnabar was concentrated. If, now, the differential elemental concentrations observed in the cinnabar are the result of a differential concentration of other heavy minerals during gravity separation, then those rocks that have the largest total content of a heavy metal in the wall rock should show the greatest differential concentration of that particular metal in the cinnabar. In other words, the greatest differential concentrations on Plate 7 should correspond to a relatively high content of the particular element in the wall rock. Actually no such relationship exists. For example, the serpentine wall rocks have the largest chromium content. Therefore, if the concentrations of elements in the cinnabar are the result only of a differential concentration during gravity separation, the differential concentrations of chromium in the cinnabar should be greatest in the cinnabar concentrated from serpentine wall rock. Yet, on the chromium graph of Plate 7, only one of the differential concentrations of chromium in cinnabar (Aetna) corresponds to the high chromium content of the serpentine. In the other serpentine samples (Aurora, Bradford, Great Western, and Mount Diablo) all of which have a high chromium content, the chromium is actually differentially concentrated in the wall rock rather than in the cinnabar. The graph for iron in Plate 7 shows that, in the wall rocks which have the highest iron content (Oceanic, Aurora, Great Western, and Mount Diablo) there is no marked differential concentration of iron in the cinnabar whereas the largest differential concentration of iron in cinnabar corresponds to a wall rock with a relatively small iron content (Sulphur Bank, basalt). Some of the high differential concentrations of manganese in the cinnabar correspond to a high total content of manganese in the wall rock (Aetna, Cloverdale and Sulphur Bank basalt), but some high differential concentrations in the wall rock likewise correspond to a high total manganese content in the wall rock (Aurora, Bradford). The two southwestern Oregon deposits (Black Butte and Bonanza) show high differential concentrations of zinc in the cinnabar, although there is no abnormally large zinc content in the wall rock. Similarly, there is no relation between the differential concentrations of nickel and cobalt and the corresponding total wall rock content of these elements. Both the Great Western and Aurora samples have a high nickel content in the total wall rock, but the differential concentration of nickel in the Great Western sample is in the wall rock whereas, in the Aurora, it is in the cinnabar. The Cloverdale sample has a low total nickel content, but a marked differential concentration of nickel in the cinnabar. The marked total wall rock content of cobalt in the Aurora sample corresponds to only a minor differential cobalt concentration in the cinnabar. The total wall rock content of copper in the Klau and Mazatzal samples is high whereas that in the Horse Heaven and Bradford samples is low. Nevertheless, the differential copper concentrations are high in the Klau and Horse Heaven samples and low in the Bradford and Mazatzal. For those elements the wall rock content of which is below the limit of spectrographic sensitivity (here, generally, germanium, lead, and silver), but the cinnabar concentration of which is above the limit of sensitivity it is possible to calculate and plot minimum differential concentrations, but it is not possible to plot total wall rock content. Therefore, it is not possible, by direct demonstration, to prove that the concentrations of lead, silver, and germanium are not a result of gravity concentration. On account of the high specific gravity of most compounds of lead and silver, it may be that the observed lead and silver concentrations are the result of gravity concentration. The compounds of germanium, however, are lighter and, by analogy to the relations between differential concentrations and total wall rock content for chromium, cobalt, iron, manganese, nickel, copper, and zinc, it would seem probable that the germanium concentrations, and perhaps the concentrations of lead and silver are likewise real and are not the result of gravity concentration. It is certain that the differential concentrations of copper, chromium, cobalt, iron, manganese, nickel, and zinc, cannot be explained by gravity concentration. This point is further emphasized by the fact that concentrations of heavy metals in cinnabar are not related to any particular cinnabar concentrate. Since each concentrate was made separately, if the differential concentrations observed are the result of gravity concentration, then, in any one sample which shows a marked concentration of one heavy metal, the other heavy metals should also be differentially concentrated in the cinnabar. The observable concentrations should then be related to specific samples. However, Plate 5 shows, for example, that in the cinnabar of the Sulphur Bank gravel sample, there is a marked concentration of copper, lead and silver in the cinnabar, but zinc and manganese are differentially concentrated in the wall rock. In the Great Western sample, there is a differential concentration of copper, germanium, and silver in the cinnabar, but cobalt, nickel, chromium, and iron are differentially concentrated in the wall rock. In the Aurora sample, there is a marked concentration of nickel, copper, and germanium in the cinnabar, but also a marked concentration of iron, chromium, and manganese in the wall rock. The differential concentrations observed are, therefore, real and are in no sense related to artificial gravity concentration.

Similarly, differential concentrations in the wall rock might be explained by the differential separation from the cinnabar during gravity separation of certain constituents of low specific gravity. However, if such a differential separation occurred, the separation should be most marked in those samples that have the largest total content of the particular element in the wall rock. Thus differential wall rock concentration of an element that forms compounds of low specific gravity should likewise coincide with a high content of the particular element in the total wall rock. The graphs for all of the light metals and nonmetals show that no such relationship exists between differential concentrations in the wall rock and the total wall rock content of an element. In the Bradford and Aurora samples, there is a high calcium content in the wall rock, but only in the Bradford is there a marked differential concentration of calcium in the wall rock. The Sulphur Bank basalt sample likewise has a high total calcium content, but, in this instance, the differential concentration of calcium is in the cinnabar. The high differential concentration of sodium in the Oceanic wall rock corresponds to a high total sodium content. However, the Arkansas sample has nearly as great a total sodium content, but only a small differential concentration of sodium in the wall rock. The Bonanza sample has a marked differential sodium concentration in the wall rock, but only a rather small total sodium content. The differential concentrations observed in the cinnabar and wall rocks are thus real concentrations insofar as the methods of wall rock re-calculation give the correct wall rock values. Since only those concentrations shown by all methods of wall rock re-calculation and found in a number of deposits are regarded as significant, it is believed that the results of this study are valid and significant to the extent that will be indicated.

Differential Elemental Concentrations Shown by Analyses

Plate 5 shows deposits plotted against ratios E and F as determined by each of the three methods of wall rock re-calculation. Plate 6 is the average of Plate 5. Both of these plates show well certain salient features.

The most noticeable feature is the similarity of heavy metals associated with all of the deposits. If any of the elements in Table 9 had been present in quantities equal to or greater than the tabulated sensitivities, the elements would have been recorded in the analyses. Table 9 shows that the heavy metals recorded in the analyses are exactly those which are spectrographically most sensitive. Thus, in a sense, the limitation of heavy metals noted in the analyses is somewhat artificial in that the limitation is partially dependent on the spectral sensitivity. Were the sensitivity greater, certain elements which are known to be present in small amounts in many of the deposits such as arsenic, antimony, and gold might appear quantitatively in the analyses. Bismuth is somewhat soluble in alkaline sulphide solutions and stannic tin is highly soluble in such solutions. The absence of both tin and bismuth must indicate that, at the point of origin of quicksilver mineralizing solutions, both tin and bismuth are rare elements.

All of the graphs likewise show certain marked differential elemental concentrations in the cinnabar. The elements which are markedly differentially concentrated in the cinnabar are copper, cobalt, germanium, lead, and silver, but not nickel and zinc. The concentrations of lead and silver may possibly be related to gravity concentration, but the concentrations of copper, germanium, and cobalt are unquestionably real. Only two factors can account for the differential concentration of elements in the cinnabar; viz.:

(1) The particular element concentrated is a pre-mineralization constituent of the wall rock and is especially effective in causing the precipitation of cinnabar. The cinnabar has therefore been differentially precipitated around minerals of which the particular concentrated element is a component and hence the element appears to be concentrated in the cinnabar, or

(2) The elements concentrated in the cinnabar have been carried in by the mineralizing solutions and, because the solubility of the element is governed by physical and chemical variations similar to those which govern the solubility of mercuric sulphide, the particular element is differentially precipitated with the cinnabar and hence is generally concentrated in solid solution in the cinnabar.

On account of the lack of published spectrographic analyses of common rocks, it is not possible to state definitely that the small amounts of lead, cobalt, and germanium in the analyses are not pre-mineralization constituents of the wall rocks. However, the content of copper (0.1-0.5%), zinc (0.3-1.0%), nickel (0.02-0.6%), and silver (0.1-0.5 oz.) is too great to be explained as a primary concentration in the wall rocks. It is, therefore, of distinct interest that, whereas copper and silver are almost always markedly concentrated in the cinnabar, zinc and nickel are, in some samples, differentially concentrated in the cinnabar and, in other samples, in the wall rock. Of all of the elements listed above (copper, zinc, nickel, silver, cobalt, lead, and germanium), the only one that has been known to occur in a mineral at all common in quicksilver deposits is nickel (millerite). Since the quantities of copper and zinc are too large to be regarded as primary constituents of the wall rocks and since copper is always markedly differentially concentrated in the cinnabar whereas such a relationship is not applicable to zinc, this relationship must indicate either (1) that the copper has been preferentially precipitated with the mercuric sulphide whereas the zinc has not or (2) the first phase of quicksilver mineralization is always the deposition of some copper and silver minerals which then subsequently cause a preferential precipitation of mercuric sulphide, but not of zinc. Regardless of the cause of the differential concentrations, it is certain that copper and silver (and, to a lesser extent, cobalt, lead, and germanium) are index elements of nearly all cinnabar. It has been noted that quicksilver mineralization is characterized not only by cinnabar, but also by an abundance of iron disulphide and silica. The spectrographic analyses now show that quicksilver-bearing solutions usually likewise deposit small amounts of copper, zinc, nickel, silver, germanium, cobalt, and lead of which elements the copper, lead, germanium, cobalt, and silver are differentially concentrated in the cinnabar.

These elements associated in small amounts with cinnabar comprise many of the elements which are present in larger amounts in deposits formed at somewhat higher temperatures and pressures. The differences between the various genetic groups of ore deposits is thus, in part, quantitative rather than qualitative. That such quantitative differences in elemental assemblages are not caused entirely by differences in physical conditions, but rather in part by the chemical characteristics of the mineralizing solutions is apparent not only from the varying mineralogy of various types of deposits, but also from the fact that a spectrographic investigation of sphalerite[1] from various types of deposits has shown the presence of indium, bismuth, gallium, and cadmium which are not present in cinnabar. Likewise found in the sphalerite were manganese, iron, copper, lead, silver, and germanium which (except for the manganese) are here shown to be differentially concentrated in the cinnabar. Undoubtedly, as more spectrographic analyses are published, the elemental assemblages here noted will assume added significance. The comparison of the elemental assemblages of deposits of dubious origin with those of known origin must necessarily reveal much concerning the genesis of such deposits of questionable origin.

The graphs show a concentration of sodium and, to a lesser extent, silicon, in the wall rock. A number of elements are sometimes concentrated in the wall rock and sometimes in the cinnabar. This variation in differential concentrations serves to substantiate the fact that quicksilver mineralizing solutions are essentially systems in equilibrium. The mineralizing solutions must, at all times, contain varying amounts of the wall rock constituents in solution. As the amount of each constituent in solution reaches the saturation point, precipitation of that constituent

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[1] Graton, L. C., and Harcourt, G. A., Spectrographic evidence on the origin of ores of the Mississippi Valley type: Econ. Geology, vol. 30, pp. 800-24, 1935.

begins. If the precipitation of any particular element occurs along with the precipitation of cinnabar, there will be a differential concentration of the element in cinnabar. If the same element is re-precipitated in the wall rock at a time when the mineralizing solutions are not saturated with mercuric sulphide or if the element is differentially leached from a place where cinnabar is later deposited, there will be a differential concentration of the element in the wall rock. Since the solutions must remain in equilibrium with the wall rock, the system must contain a number of components and the saturation point of each component would not be reached at the same time nor always at the time when cinnabar was being precipitated. Since soda and silica are highly soluble in hot alkaline solutions, it would be expected that a considerable part of this large-scale solution and re-deposition would involve transfer and differential concentration of these two elements - hence the widespread silicification accompanying many quicksilver deposits. Since differential concentrations are determined only by equilibrium relations in the solutions, it would be expected that many of the differential concentrations found at one point in a particular vein would not be found at another point in the same vein and that the differential concentrations in cinnabar and wall rock would vary as the solutions maintained equilibrium with the physical and chemical environment. Similarly, it would not be expected that parts of the same deposit or of different deposits would show the same type of differential concentrations even when the same major constituents are available in the mineralizing solutions. Such is exactly what is observed. Plate 5 has the deposits arranged geographically, going first from south to north and then from west to east. The Klau and Oceanic mines are only a few miles apart in San Luis Obispo County yet there are no marked features of similarity between the differential concentrations observed in the two deposits other than similarities which are common to all of the deposits. The Aurora mine is in serpentine only a few miles from the New Idria mine, the cinnabar at which occurs in sandstone and slate. Here again there are no essential similarities or differences in the observed differential concentrations. Plates 8 and 9 show the relative differential concentrations for all of the mines in serpentine (Aetna, Aurora, Bradford, Great Western, and Mount Diablo) as calculated by the alumina and total impurity methods respectively. Although all of these deposits are in the same type of wall rock and the Bradford and Great Western mines are only a few miles apart, the differential concentrations bear no more similarity to each other than they do to the differential concentrations of any of the other deposits. The two samples from different rock types at Sulphur Bank show no especial similarities or dissimilarities in differential concentrations. The two southwestern Oregon deposits (Black Butte and Bonanza) are distinguished only by large differential concentrations of zinc. The deposits outside California and Oregon show no markedly dissimilar relative differential concentrations. Therefore, insofar as concerns relative differential concentrations of imputities in the cinnabar and the adjacent wall rock, the geographical and geological occurrence of the deposits is of no importance in effecting the concentrations observed. The marked differential concentrations of certain heavy metals in cinnabar occur regardless of the location or geological environment of the deposit. Such differential concentrations are thus true indices of a distinctive type of mineralization.

Since all of the deposits show marked differential concentrations of certain elements in the cinnabar, the question arises as to the state in which the impurities exist in the cinnabar; i. e., whether the differentially concentrated elements are in solid solution in the cinnabar or whether the elements exist as components of mineral inclusions around which the cinnabar has been preferentially precipitated. For many of the differential concentrations, this question cannot be answered directly, but, insofar as the differential concentrations of heavy metals in cinnabar are concerned, it is possible to note a few salient points. Reasons have been cited for believing that the amounts of many of the heavy metals shown by the analyses are too large to be regarded as pre-mineralization constituents of the wall rocks. Those heavy metals which are present in relatively large amounts (as zinc, nickel, copper, and silver) must have been deposited by the quicksilver mineralizing solutions. Since the copper and silver are always concentrated in the cinnabar, unless the copper and silver are always precipitated before the cinnabar they must exist in solid solution in the cinnabar. There is no petrographic evidence of inclusions of zinc, copper, nickel, silver, cobalt, lead, or germanium bearing minerals in the cinnabar although the content of zinc, nickel, and copper in the ores is relatively large. The evidence thus favors the idea that the observed differential concentrations represent solid solution in the cinnabar.

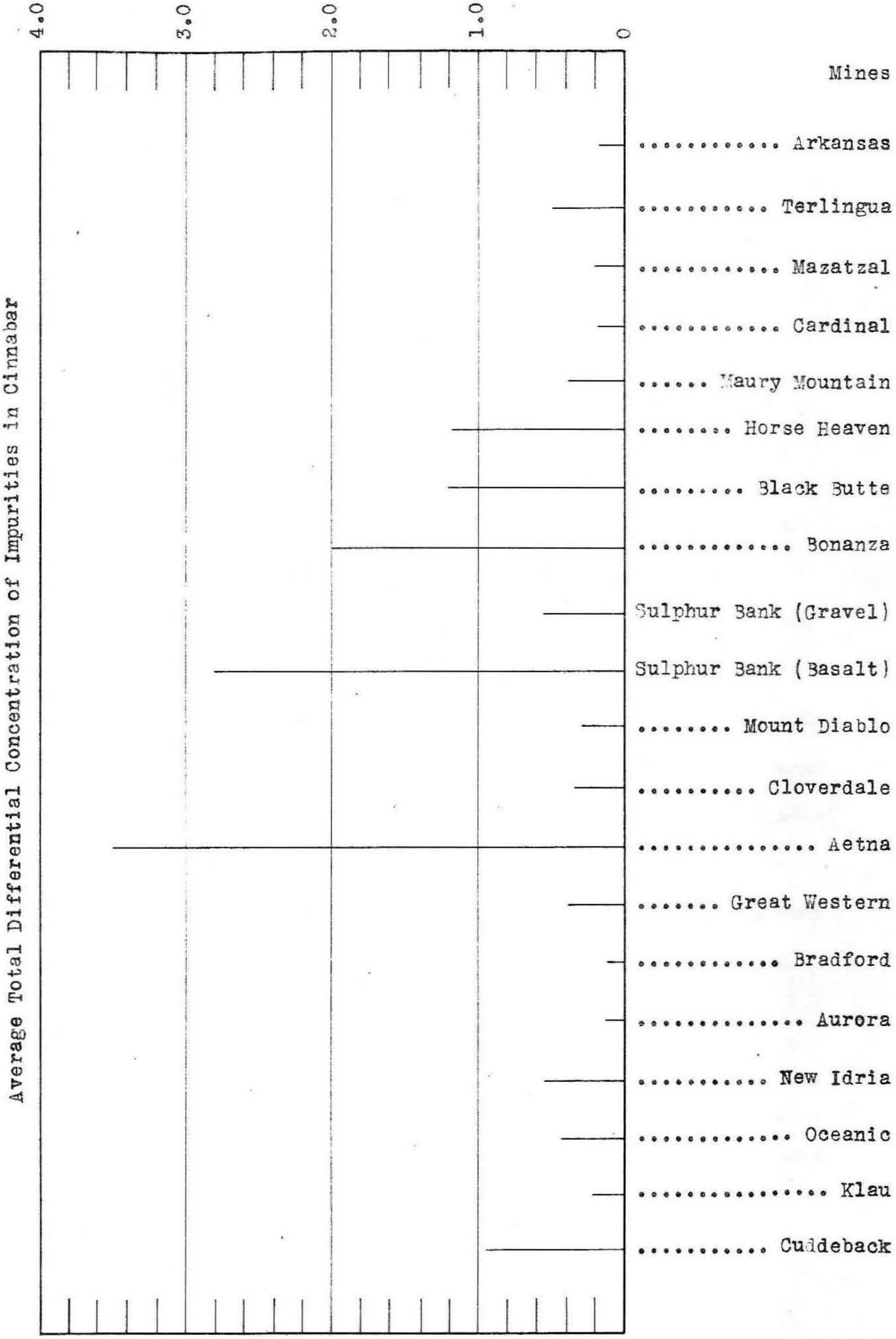
The amount of total differential concentration of elements in the cinnabar (in percent) is shown on Plate 10. The values plotted are the total sum of differential concentrations (C) of all elements in each cinnabar concentrate as averaged by all three methods of wall rock re-calculation. The graph thus gives the total percentage of impurity in each cinnabar concentrate beyond that which could be caused by wall rock contamination. The total amount of impurity is not incompatible with the idea that the impurity may exist in solid solution in the cinnabar. In most cases, the total impurity ranges between 0.1 and 0.5%. The maximum concentration of impurity observed is 3.5% for the Aetna cinnabar - an amount not in excess of that which could be contained in solid solution.

Average Total Differential Concentration of

Impurities in Cinnabar

(In Percent)

Plate 10



Causes of Variation in the Color of Cinnabar

Allen and Crenshaw[1] state that the color of cinnabar is a function of the state of subdivision and that, when two cinnabars of different colors are crushed with a mortar and pestle, the color of the two powders is identical. The writer feels that this statement should be qualified.

As a first experiment, cinnabar was prepared by concentration of an alkaline mercuric sulphide complex solution. The cinnabar was then filtered while hot through a rather porous filter paper which retained only the coarser grains although, of course, the entire precipitate was very fine grained. The cinnabar remaining on the filter paper was a cherry red whereas the cinnabar which passed through the filter paper was orange. This would tend to indicate that color is dependent on the state of subdivision. However, in the preparation of cinnabar for spectrographic analyses, a number of cinnabar ores from mines throughout the country were crushed as finely as possible with a mortar and pestle. The cinnabar was then concentrated by gravity. For purposes of color comparison, some of the concentrates were re-crushed to a fine powder and the colors compared. The color of most of the cinnabar was varying shades of cherry red and the color was little modified by crushing. Typical of the cherry red cinnabar is that from the Mazatzal Mountains of Arizona and those from the New Idria and Aurora mines in San Benito County, California. A sample of crystalline cinnabar from an Arkansas deposit was a very

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[1] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline form and genetic conditions: Am. Jour. Sci., 4th series, vol. 34, p. 368, 1912.

light red in color. A sample of crystalline cinnabar from the Klau mine in San Luis Obispo County, California was a dark purple. Crushing lightened the color of the Klau cinnabar slightly, but it still remained distinctly dark purple in contrast to the other cinnabars. Spectrographic analyses were made of portions of the same concentrates that were used for color comparison. An examination of the relative differential concentrations (Plate 5) will show that there is no significant concentration of any element or group of elements in the Klau sample that is not found in some of the other samples which have a typical cherry red color. Nor are any elements notably present or absent in the Arkansas sample which are not present in the other samples. The total differential concentration of impurities in the cinnabar (Plate 10) does not effect the color since the Aurora sample has less total impurity than the Klau, the New Idria more, and the Mazatzal about the same amount although the Aurora, New Idria, and Mazatzal cinnabars are cherry red in contrast to the dark purple color of the Klau cinnabar. Similarly the Arkansas sample has more impurity than the Aurora and less than the New Idria, but is of distinctly lighter color than either. The spectrographic analyses show no significant difference in elemental assemblage between the Klau and Arkansas or between the Klau or Arkansas and any of the other cinnabars.

The color is thus (1) only very slightly modified by crushing (2) not caused by any spectrographically detectible qualitative or quantitative differences in contained impurity and (3) not wholly related to the size of the crystal aggregates since both the Arkansas and Klau samples were crystalline. The cause of the variation in cinnabar color is not, therefore, readily apparent.

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MAGNETOMETER EXAMINATION OF THE MONTE CRISTO MAGNETITE-ILMENITE DEPOSITS

Robert M. Dreyer

and

Charles A. Dawson, Jr.

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MAGNETOMETER EXAMINATION OF THE MONTE CRISTO MAGNETITE-ILMENITE DEPOSITS

I. Introduction

Situated in the San Gabriel Mountains of Southern California is a large body of anorthosite with which is associated a number of bodies of ilmenitic magnetite. During the summer of 1937, the E. I. duPont de Nemours Corporation obtained options on a group of properties thought to contain several such deposits. In connection with the exploration of the aforementioned deposits, the authors were employed as geophysicists to conduct a magnetic examination of the area. The data contained in this report was collected between August 9 and September 4, 1937. Mr. Dawson is, at the present time, continuing the magnetometer investigation and, in the light of the facts to be presented in the following pages, his work is being watched with considerable interest.

The Monte Cristo area is located a few miles north and west of the head of the Tujunga drainage system in the vicinity of latitude 34°21'N, longitude 118°06'W. The area is one characterized, in general, by a fairly thick cover of brush with few large trees. It was thus both necessary and possible to cut trails along which the magnetometer traverses could be run and on which the position of the magnetometer stations could be subsequently determined with a transit. The area is likewise one of considerable relief. Many of the slopes are quite steep and thus serve to lessen to a certain extent the speed with which the magnetometer work can be executed.

From a purely geophysical viewpoint, however, the area is almost ideal for a magnetic investigation. The anomalies are very high and a high degree of sensitivity is, thus, both unnecessary and unwarranted in the area. The very marked character of the anomalies also renders the interpretation of the results somewhat simpler than is generally the case.

The writers are deeply indebted not only to Dr. Joseph L. Gillson, for permission to use the data comprising this paper, but also to Dr. George H. Anderson, who, as superintendent in charge of exploration, gave liberally of both assistance and advice.

II. General Geology

The area in which the magnetite-ilmenite bodies are found has been stated to be part of a large anorthosite body. In places, the anorthosite consists almost entirely of greyish-white andesine. This facies grades locally into a dioritic phase. These facies are apparently related as derivatives from one original magma. Scattered throughout the anorthosite are bodies of magnetite containing, on the average, about thirty percent ilmenite. Closely associated with such magnetite bodies are dike-like aggregates of actinolite which usually contain a varying amount of magnetite. Field and petrographic evidence would tend to indicate that the actinolite and magnetite are gradational. For this reason it is possible that many bodies which appear to be mainly actinolite on the surface may grade into magnetite-ilmenite bodies with depth. It is, however, notably true that very many large actinolite dikes give relatively small anomalies thus indicating that many such dikes do not grade into magnetite or that the magnetite into which they once graded has now been eroded away. That the latter situation may often well be the case is indicated by the fact that, in the places where the largest broad anomalies are to be found, the outcrops of both magnetite and actinolite are not abundant. It would thus seem to be fairly well established that those areas showing an abundance of magnetite in float or in outcrop are the areas that have been the most deeply eroded and are therefore those in which the smallest anomalies (and hence ore-bodies) can be expected.

Considerable discussion has arisen over the question of whether the magnetite-ilmenite bodies are to be regarded as irregular segregates; as dikes segregated from the same magma as the anorthosite, but intruded later; or as of hydrothermal origin. There is very little evidence for or against the concept of hydrothermal origin. The mere fact that other similar deposits have been regarded as magmatic intrusions or segregates is of very little import since there are some very notable deposits of this type which, in recent years with more careful study, have come to be regarded as hydrothermal. Further mineragraphic study and field mapping of the magnetite-ilmenite bodies might establish the validity of this concept. As to whether these bodies are dikes or irregular segregates, there is a variance of opinion where nearly identical deposits have been studied in other portions of the San Gabriels.[1,2] Suffice it to say that, if the bodies are later intrusives (i. e. dikes) many such dikes are very small and discontinuous in this region. There is a great temptation in any area to line up high anomalies on relatively distant traverses and to regard such an alignment as illustrating a definite trend and thus proving a mode of occurrence. Many more traverses are needed in the area here under discussion before it can be stated definitely that such an alignment exists throughout the area.

The form and continuity of the ore bodies is, however, of the utmost importance in estimating the value of the deposit. For, if the deposit consists of a number of irregularly shaped and heterogeneously distributed aggregates, the cost of mining and the difficulty in exploration would increase tremendously. The difficulties in ascertaining the shape and distribution of such bodies from magnetic profiles will be discussed in a subsequent section.

The entire value of the deposit lies in the titanium content of the ilmenite ($FeTiO_3$) associated with the magnetite in Widmanstätten intergrowth. A small amount of hematite is also present in the ore. Since, with the sensitivity used, only the magnetite is sufficiently magnetic to affect appreciably the magnetometer, the basic assumption on which all of the work is being carried out is that the ilmenite content of the magnetite is fairly constant. Experimentation with surficial ores has tended to substantiate the validity of this assumption. Only diamond drilling, which may be undertaken in the future, can ascertain whether this assumption is also valid for the larger and more deeply buried ore bodies.

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[1] Miller, W. J., Geology of the Western San Gabriel Mountains of California, Univ. of Cal. at Los Angeles Pub. in Math. and Physical Sciences, Vol. 1, pp. 1-114, 1934.

[2] Dawson, C. A., Jr., Petrology of the Igneous Complex Near Lang, California, M. S. Thesis, California Institute of Technology, 1937.

Both of these papers deal with the geology of the San Gabriel anorthosite (and related rocks) in far more detail than is here attempted.

III. Adjustment of Instrument

The primary adjustment in magnetometer work consists of determining the scale constant of the instrument; i. e., the number of gamma equivalent to one scale division. It was determined empirically that, in this particular region, the instrument should be adjusted so that one scale division was equal to approximately thirty three gamma. For this calibration, a single coil, 60.8 inches in diameter, was placed around the instrument. A reading was taken and a current of thirty milliamps was then run through the coil and the deflection caused by the current noted. The bottom screw of the mobile magnet system was then raised and lowered until the constant was a desirable value. The equation used to determine the scale constant was:

$$\text{Gamma} = \frac{20\pi I}{r}$$

I = current in milliamps
r = radius of coil in inches

When the instrument was in final adjustment, the above equation with values substituted was as follows:

$$\text{Gamma} = \frac{20 \times 3.14 \times 30}{30.4} = 62.0$$

The 62.0 gamma were marked by a deflection of the instrument of 1.9 scale divisions. The scale constant was thus 32.6 gamma.

It was also considered desirable, from the viewpoint of facilitating interpretations, that both instruments should have the same reading at a given point. To accomplish this, one instrument was set up at a known point and at a known height and the reading taken. The second instrument was then set up at the same point and height and the two side screws of the mobile magnet system were adjusted until the readings on both instruments were the same.

On account of the size of and wide range in readings it was deemed necessary to make only the temperature corrections. The average range of readings was about 500 gamma and the diurnal, latitudinal, and longitudinal corrections would not amount to more than one-tenth that value. The temperature corrections at times, however, exceeded 200 gamma.

To determine the temperature correction, one instrument was placed in an abandoned mine tunnel, where the temperature was constant and the only variations were due to diurnal fluctuations. The other instrument was placed out in the open. Both instruments were read every twenty minutes for four hours. The diurnal readings were then subtracted from the readings taken in the open air and these corrected instrument readings were plotted against temperature. From this graph it was possible to ascertain the number of scale divisions displaced for each degree change in temperature.

The only other adjustment necessary was the calibration of the auxiliary magnets. This calibration was accomplished by bringing a magnet near enough to the instrument to cause a strong positive deflection. Then another auxiliary magnet was placed in a definite position in the magnet holder with the north pole pointing upwards and the decrease in the former reading was noted. This process was continued until the effect of each magnet was ascertained when the magnet holder was adjusted to each of several positions.

IV. Field Procedure

On account of the dense brush prevailing in the area, it was necessary to have trails cut before the magnetometer work was undertaken. Such trails were first cut at right angles to what a brief examination indicated to be the strike of the ore bodies in the particular area. If the traverse consisted entirely or in part of high anomalies, trails were cut both parallel to and at right angles to the original traverse line until the zone of high anomalies was delimited with reasonable accuracy. The number of traverses used to delimit an area of high anomalies depended on the size of the area. On an area which the first few traverses indicated must be very small, little further work was attempted. Where the area appeared to be one of broad, high anomalies, a number of traverses were run until the limits of the area were well known.

It was the general custom to place all stations as close to sixty feet apart as could be ascertained by pacing. Such paced distances are those indicated on the profiles included with this paper. The position of the stations is now being determined more accurately with a transit, but, for the purpose of the scale used for the profiles, the approximate distance is sufficiently accurate. A variance of a few feet could not be indicated on the graphs. On a few reconnaisance traverses, the stations were placed a hundred feet apart and, on a few of the more detailed traverses, the distances were twenty or forty feet.

Both the distance between stations and the magnetic intensity can be determined from the profiles. The abscissa of the profiles is distance in feet - each millimeter being equal to twenty feet. The ordinate of the profiles is magnetic intensity - each millimeter being equal to thirty three gamma.

Since the anomalies observed were, in general, so high and since the variations in readings between each station were often so large, certain of the corrections commonly applied in regions of smaller anomalies were not here used. Since the average range of readings was over five hundred gamma and since neither the longitudinal nor diurnal corrections would exceed much more than one-tenth that value, these two corrections were not used. However, on account of the high temperature observed, the temperature correction at times reached two hundred gamma. The temperature corrections were thus always applied. Temperatures were read to one-tenth of a degree and magnetic intensity was read to one-tenth of a scale division (3.3 gamma).

The map accompanying this paper is included to show only the approximate areal distribution of the anomalies shown accurately on the included profiles. The anomalies were grouped into various divisions as indicated on the map and very small changes from one group of anomalies to another have been omitted. The position of each of the several trails shown on the map is approximate - many of the trails not yet having been surveyed. The position of the trails and the distribution of the anomalies is, however, in all cases, as close as possible to the correct position as is necessary to show, with reasonable accuracy, the general areal pattern of the magnetic anomalies.

V Discussion and Interpretation of Results

In actual field practice, two types of anomalies were recognized; viz., (a) broad highs or lows in which the large anomaly extended over a wide area and increased or decreased gradually, (b) sharp highs or lows where the actual high anomaly was often larger than in the first type, but occupied only a small area and increased or decreased very rapidly.

In an area in which the main purpose of exploration was the discovery of one or more large ore bodies that could be mined as a unit, the presence of small bodies is of little importance. Hence, it was quickly recognized that a small body, unless near the surface, would cause only a small anomaly. If such a small body is very near to or at the surface, it would cause a marked anomaly that would be very high at one point, but would drop off very rapidly on either side of the marked high. Whether such anomalies were marked highs or lows depended only on the topographic position of the magnetometer station in relation to the pole of the ore body. Many such marked, sharp, local highs were located and were generally associated with surficial exposures of ore. At times there were local outcrops in an area of a broad high and these appear on the profiles as peaks far above the general broad high. The magnetic intensity at the highest point of such sharp highs, unlike the broad highs associated with deeper ore bodies, is inversely dependent on the proximity to and height above an outcrop at which the magnetometer reading was taken.

It might be quite possible that a large ore body could be found near the surface and thus cause a continuous area of extreme highs. Actually, however, no such area was found. Instead the broad highs were all marked by gently increasing and decreasing areas of broad anomalies of moderate size (perhaps 900 gamma in contrast to the sharp highs which at times reached 10,000 gamma and often exceeded 6,000 gamma). Such broad highs could be interpreted in several ways - (1) as one large ore body at considerable depth, (2) as an aggregation of a number of small bodies in one localized area at considerable depth, (3) as one moderate sized body at intermediate depth, or (4) as several fairly small bodies scattered over a wide area at intermediate depth. The possibility of points one, two, and three can be determined only by drilling. It seems quite improbable that point four represents the true situation since, if such were the case, an almost ideal spacing of the numerous small dikes at intermediate depth would be needed to create one broad, consistent high.

Extensive exploration in the Monte Cristo area began with traverse JJ-WW-R-J. (See location of trail on map and also see profile on Plate II.) It will be noted that a broad high commences about 1000 feet west of point R and continues to J. The presence of this high suggested the advisability of extending this traverse to the east. Accordingly, traverse J-E-D-KK-LL was completed. This traverse showed a remarkable continuation of the same broad high (on which were superimposed numerous abrupt highs due mainly to surficial ore pockets) with almost all readings above 600 gamma and many above 1500 gamma (Plate II). It will be noted, however, that from the beginning to the end of this zone of high anomalies, the traverse runs along a topographic ridge. It was therefore, thought possible that a large dike of ore might be the cause of the ridge and that the broad zone of high readings might be due only to the fact that the traverse was conducted parallel to the strike of a dike rather than across a large ore body at considerable depth. Accordingly, a number of traverses were run both parallel to and across traverse JJ-LL to determine the exact cause of the high anomalies. Considering first the parallel trails, it will be noted that none shows a broad, consistent high comparable to traverse JJ-LL. Traverse V-Q-VV (Plate VIII) shows numerous local highs. Traverse WW-O (Plate VIII) also shows only local highs whereas traverse Y-UU-SS-N shows almost no abnormally high anomalies (Plate VIII). Moreover, cross traverses V-W (Plate VII), R-S (Plate VI), G-H-J-K (Plate VI), E-F (Plate VI), and C-D (Plate VI) drop off rapidly after leaving the ridge along which traverse JJ-R-J-E-D-KK-LL was run. These latter cross traverses would thus seem to indicate that the ridge from JJ to LL was actually parallel to and directly above a long dike. However, it will be noted that the readings on traverse A-B (Plate II) and XX-KK-YY (Plate IV) drop off very slowly. Subsequent traverses extended northeast of XX, east of LL, radiating out from KK, and south and east of the XX-KK-A-LL area indicate indeed a broad high somewhat circular in form which centers at KK and extends for at least 1000 feet around KK. All the traverses shown on the map around the KK high area are located on ridges and might reasonably be due to cross dikes. However, traverses run northeast and southeast subsequent to the completion of this map go down a steep slope to the east (more than 700 feet in elevation below the top of the ridge) all the while maintaining the same high readings. Moreover, traverses run on high ridges in other parts of the area often showed very low readings (from perhaps +250 to -250 gamma) thus proving that height alone could not cause the high anomalies. The ore body must thus be broad and at considerable depth. How large an ore body and in what form the ore body exists that causes such a broad circular high some 2000 feet in diameter is problematical and will be disclosed ultimately only by diamond drilling. Traverses V-W, R-S, G-H-J-K, E-F, and C-D as well as Z-HH (Plate III) and MM-NN (Plate I) also served to show the absence of any large ore bodies in the area represented by the southern portion of the map. About a mile south of the southern boundary of this map, however, another broad high, considerably smaller than that centering around KK, has recently been located.

A large part of the area north of the trail going from Z to N showed many surface exposures of ore. For this reason, it was thought wise to run traverses through this northern area. These traverses show excellent examples of small, abrupt highs quite distinct from the broad area centering around KK. Traverses TT-UU, RR-SS, and QQ-U (all on Plate V) all show numerous, small, sharp highs most of which are located at or near surface outcrops of ore. These bodies are thus apparently very small and only surficial in character. Cross trails Y-X (Plate VII), and trails CC-DD and EE-FF (both on Plate IX) show the same situation of a number of narrow, surficial ore bodies indicated by sharp, abrupt highs. Traverse AA-TT-BB (Plate VII) might seem to show near its western extremity an indication of another broad high. However, no such high shows on traverse Y-Z (Plate VII), nor on EE-FF, nor on DD-CC. (The latter has, since the completion of the map, been extended 1500 feet to the east and still shows no indication of this high.) It is thus apparent that the high on AA-TT-BB was caused by paralleling, for a distance, a small, narrow dike.

In conclusion, it may be stated that the valuable discoveries represented by the work summarized in this paper are the area of high anomalies centering at KK with a long, narrow high going to the west, and an area, considerably smaller in size, about a mile south of the southern border of the map. The form, size, and tonnage of these ore bodies can be satisfactorily shown only by diamond drilling supplemented by a large amount of more detailed magnetic prospecting.

EXPLANATION OF PROFILES

Horizontal scale - one millimeter equals twenty feet.

Vertical scale - one millimeter equals thirty three gamma.

Letters above the profile correspond to letters on the map.

Base line (zero line) of each profile is inked in brown.

Where anomalies are too large to be shown on the graph, numbers typed at the point at which such excessively large anomalies leave the graph indicate the magnetic intensity, in gamma, of such anomalies.

Plate I

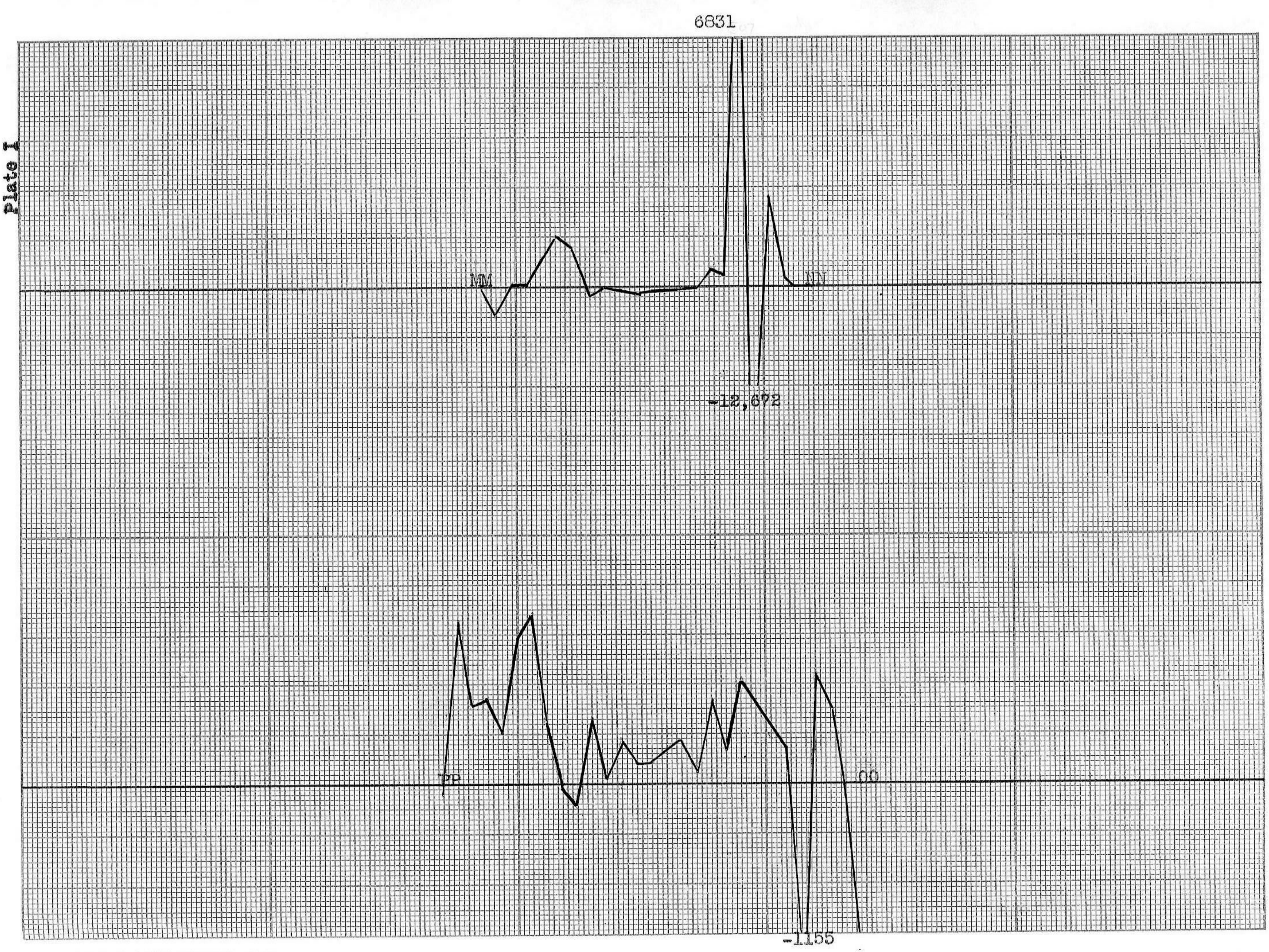
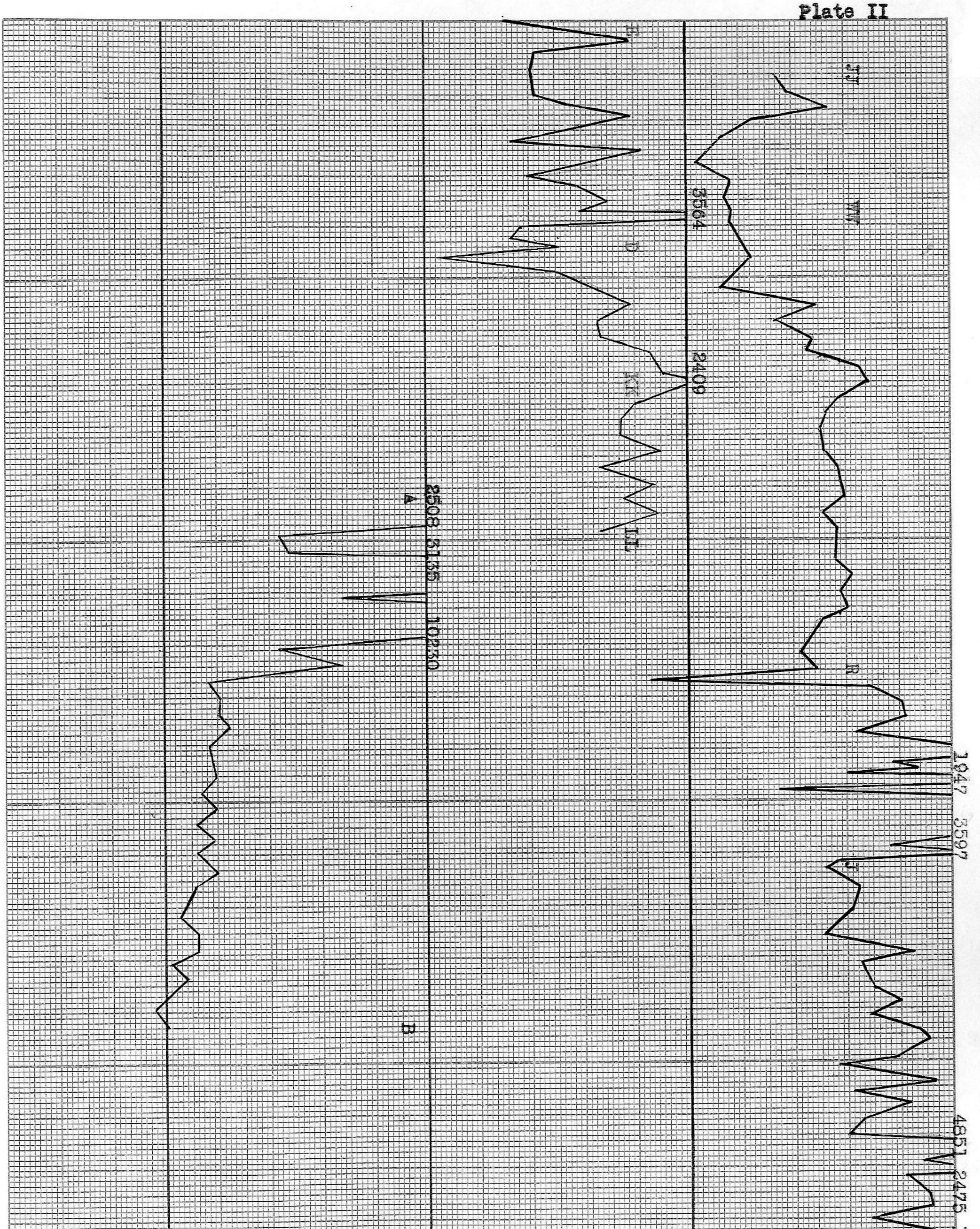


Plate II


E
JJ
3564
WW
D
2409
KK
LL
2508
A
3135
10230
R
1947
3597
J
B
4851
2475
1749
6270
I

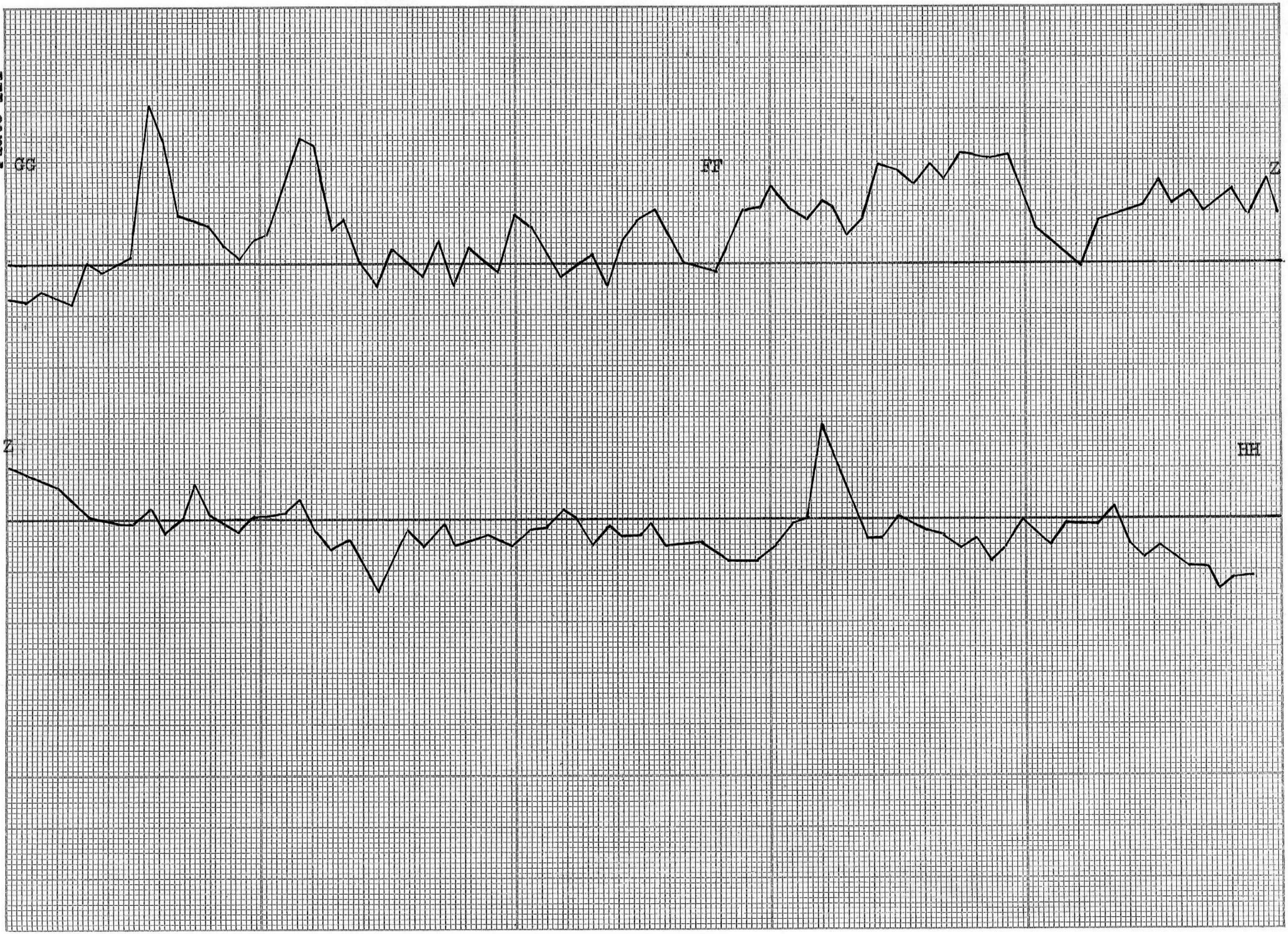

GG
FF
Z
Z
HH

Plate IV

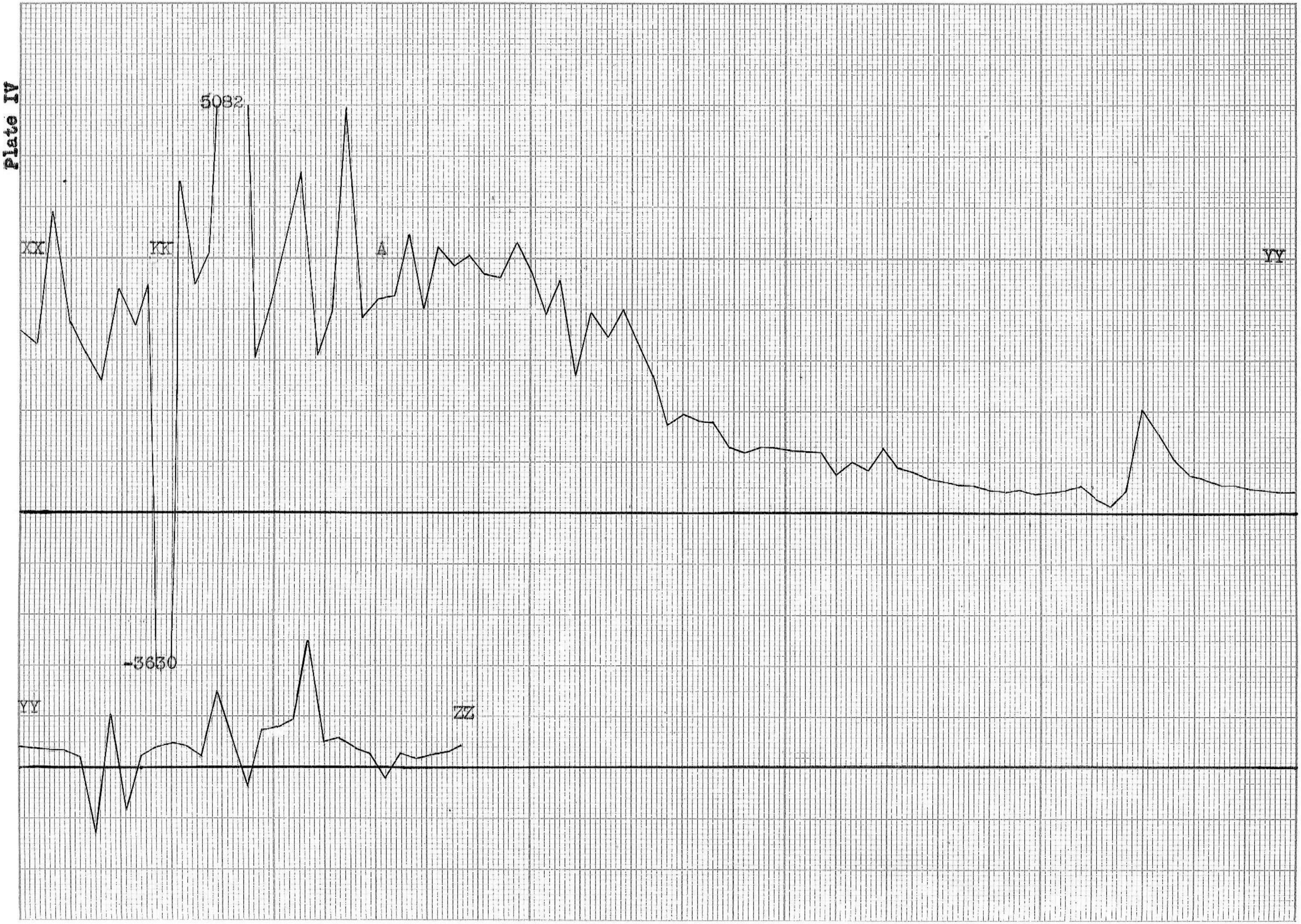


Plate V

Plate VI

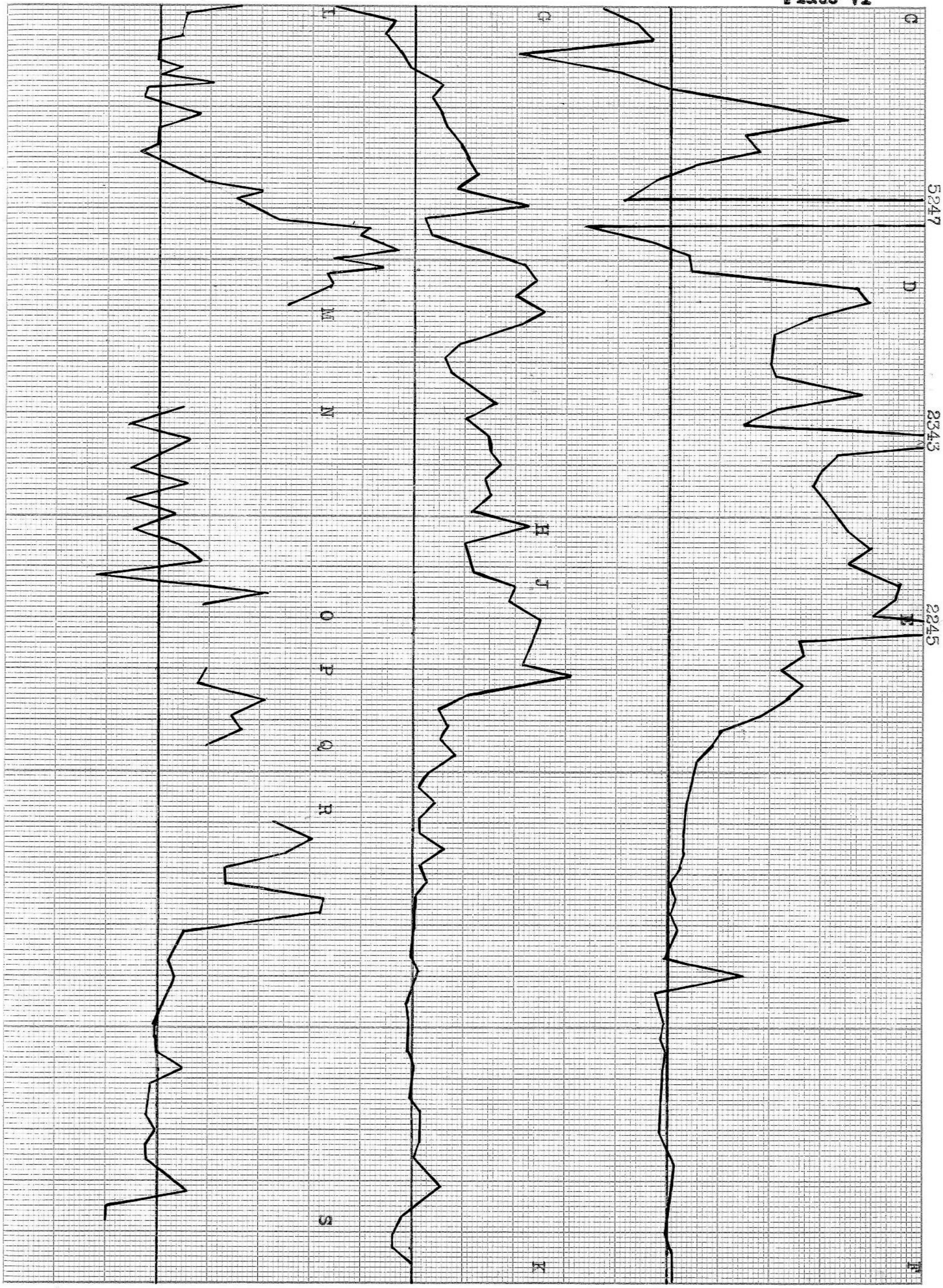


Plate VII

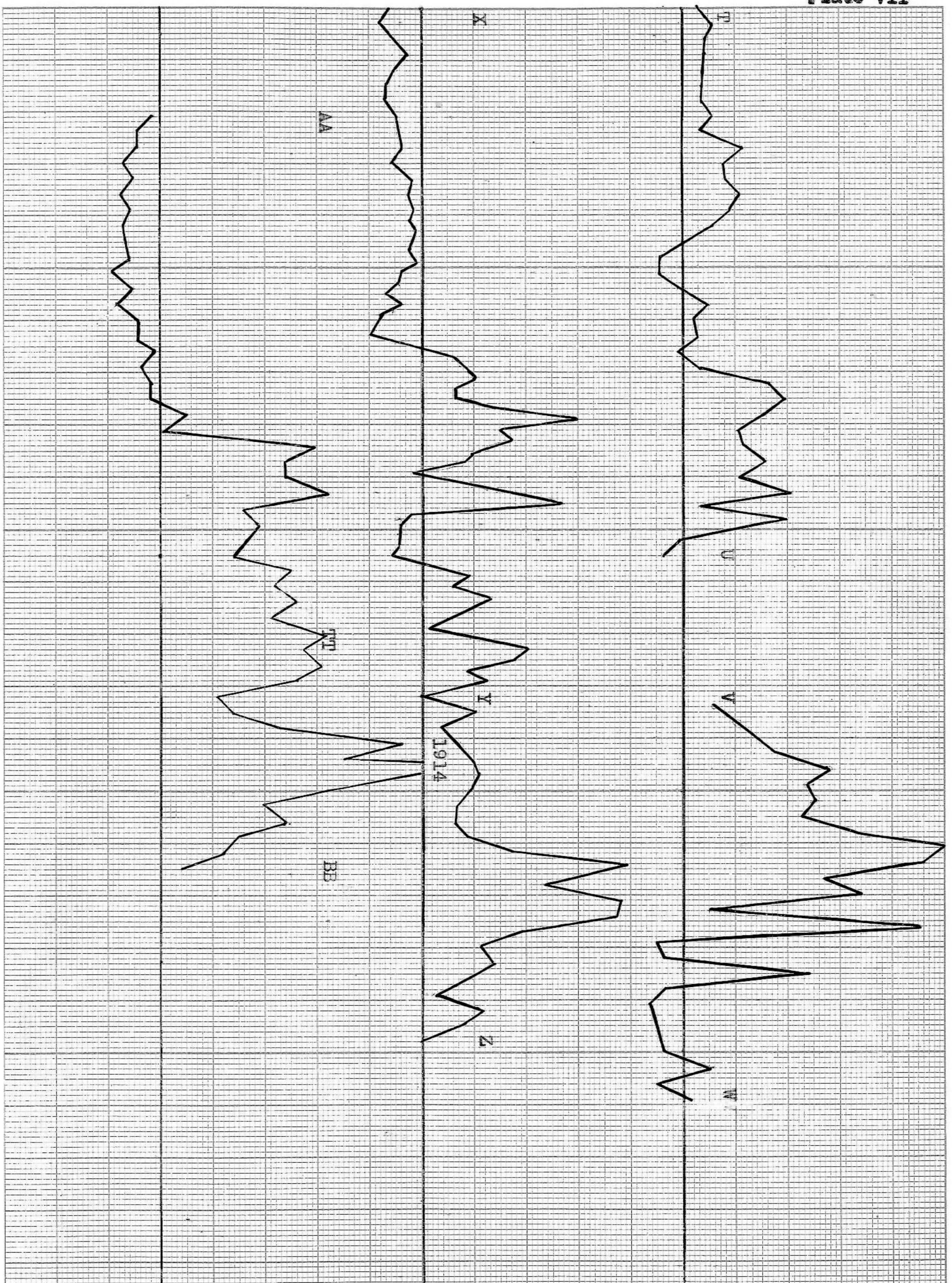


Plate VIII

Plate IX