THE SOURCE OF VANADIUM, MOLYBDENUM, TUNGSTEN, AND CHROMIUM IN OXIDIZED LEAD DEPOSITS

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Introduction

The source of the vanadium and molybdenum in oxidized lead deposits has always been an enigma.

Vanadium is present in small amounts in rocks and residual soils. This is usually considered as the source of the vanadium in the oxidized ores. The presence of molybdenum has been accounted for in several ways. The source usually suggested is microscopic crystals of molybdenite present in the hypogene ore. Other suggestions made are that it is derived from adjoining rocks, or that the wulfenite was formed by hypogene solutions.

The present paper will call attention to the presence of small amounts of these elements in common sulphides. It is the writer's belief that this is the common source for these elements in the oxidized lead deposits, although important contributions may have been made from the wall rocks in some places. Usually these metals, where found, form only small percentages of the oxidized ore.

Distribution and Tenor of Vanadium in Oxidized Lead Ores

Vanadium is widely distributed in small percentages in the oxidized lead and lead-copper ores, in southwest United States, Mexico and part of South America, in certain localities of Spain, and parts of southern Africa.

In western United States,[1] particularly in Arizona, New Mexico, and to a less extent in Nevada and California, lead vanadate is found although seldom in high grade pockets. These deposits almost invariably carry only 0.1 to 0.6 per cent V_2O_5. The deposits[2] are of lead sulphide with some accompanying zinc and copper sulphides which carry vanadium compounds in the oxidized zone. The vanadium compounds include vanadinite, and isomorphous mixtures containing vanadium, arsenic, and phosphorus with lead, zinc, and copper, in varying proportions.

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[1] Conley, J. E., *U. S. Bur. Mines*, Bull. **212**, pp. 239–240, 1923.

[2] Hess, F. L., *U. S. Geol. Survey, Mineral Resources*, vol. **1**, p. 956, 1917.

The deposits are small; none known in 1917 was large enough to furnish ore for a plant of considerable size. In several deposits near Cutter, New Mexico, about 1.0 per cent vanadium oxide is present as vanadinite.[3] Descloizite, wulfenite, galena and other minerals are associated with the vanadinite.

At Kelvin, Arizona, vanadinite ore with associated wulfenite carried 3–5% vanadic oxide[4] while the C and B vanadium mine near Christmas, Arizona, contained 500 tons of ore carrying 1–3% V_2O_5. At the Shattuck Mine, Bisbee, Arizona, 3000 tons of oxidized ore carried 10% vanadic oxide, and a large tonnage carried 1–1.5%. Vanadinite and sometimes cuprodescloizite and wulfenite are found at many places in the Cordilleran of Mexico,[5] in the region extending from Hidalgo to Chihuahua. Some bodies of ore found in Zacatecas carry over 4% vanadic oxide.

Vanadium is widely distributed in small percentages in the oxidized lead ores of Argentina and Bolivia, South America. Almost every oxidized ore tested in this large region was found to contain some, although the amount is usually small.[6] Deposits[7] worked in the Province of Cordoba, Argentina, gave a product of 10% vanadium oxide and copper veins at Talcuna, Chile, contained 6%. Much of the early vanadium ore came from Spanish deposits, apparently from Santa Marta in southwestern Spain.[8] These ores as mined contained four to five per cent vanadic oxide. Lead vanadate and other minerals form the ore. Clays present are also rich in vanadium. Vanadium ores of this type have been found in Northern Rhodesia and also in Southwest Africa; and the Transvaal.

At Broken Hill, Rhodesia[9] a large tonnage, 935,000 tons, of

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[3] Curran, T. F. V., Vanadium ores and uses: *Eng. & Min. Jour.*, vol. **93**, pp 1093–4, 1912.

[4] Vanadium ores monograph, *Imperial Institute*, London, pp. 51–52, 1924.

[5] Curran, T. F. V., *Eng. & Min. Jour.*, vol. **93**, p. 1093, 1912.

[6] Whitehead, W. Oral communication.

See also Bodenbender W., Bleiglanz—Vanadin und Molybdanerzgang in der Provinz S. Luis Argentinen, Süd Amerika: *Zeit. für Prakt. Geol.*, vol. **9**, pp. 51–55, 1901.

[7] De Launay, L., *Traité de Metallogenie.* Gites Mineraux et Metalliferes, vol. **1**, pp. 725–726, 1913.

[8] Smith, J. Kent, The present source and uses of vanadium: *Trans. Am. Inst. Min. Eng.*, vol. **38**, pp. 699–700, 1908. Vanadium ores monograph. *Imperial Institute*, p. 31, 1924.

oxidized ore carries 0.9% V_2O_5 while a very much smaller tonnage carries 3.5%.

In southwest Africa,[10] a number of deposits have been worked, the origin of which is doubtful. Those in the northwest part carry vanadates of lead-copper, with little or no zinc, while those in the southeast carry lead-zinc vanadates with little copper. The deposit at Abanabe is the most important. Small deposits in the Marico district, Transvaal, carry 2.8% vanadic oxide, and one near Messina carries 22% vanadic oxide.[11]

In summarizing, it may be said that there is a fairly wide distribution of vanadium in oxidized lead ores to the amount of 0.1 to 1.0% V and less. It appears to be most commonly found in areas of deep extensive weathering, but it should be observed that so far as the data go, they do not appear to be coextensive with deeply oxidized regions. Rather they are apparently found only within certain areas or parts of deeply oxidized regions. Locally much higher concentrations of vanadium are found. These deposits are commonly present in relatively small tonnages compared with those just mentioned. They usually contain less than 6.0%V.

TESTS FOR VANADIUM

The presence of vanadium in sulphides was determined chemically as well as spectroscopically. Two chemical tests were used; one, the well known hydrogen peroxide test, and the other, the strychnine sulphate test with concentrated sulphuric acid. Complete details of procedure are given in the works cited,[12] and will

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[9] Walker, G. L., *Eng. and Min. Jour.*, vol. **125**, p. 733, 1928.

[10] Wagner, P. A., *Memoir* **7**, *Union of S. Africa, Geological Survey*, pp. 89–90, 1916.

Imp. Inst. Vanadium Monograph, pp. 20–21, 1924.

Stahl, A., Erzlagerstätten des Otavi-Berglandes: *Zeit. für Prakt. Geol.*, pp. 150–151, 1926.

Guide Book **15** *Session Inter. Geol. Cong.*, Excursion C 21, pp. 44–45, 1929.

Clark, Alex. W., The ore deposits of the Otavi Mountains, Southwest Africa: *Min. Mag.*, Vol. **44**, 265–272, 1931.

[11] Vanadium Monograph, *Imperial Institute*, London, pp. 22–23, 1924.

[12] Conley, J. E., Vanadium: *U. S. Bur. Mines*, Bull. **212**, pp. 241–262, 1923.

Gregory, A. W., A colorimetric method for the estimation of small quantities of vanadium: *Chem. News*, vol. **100**, p. 221, 1910.

Fenner, J. A., Determination of tungsten and vanadium in the presence of titanium: *Jour. Soc. Chem. Ind.*, vol. **37**, p. 609A, 1918.

Treadwell and Hall, *Analytical Qualitative Chemistry*, vol. **1**, p. 541, 1930.

not be redescribed here, but certain features may be mentioned. Weighed amounts of sulphides, one to several grams in the several types of procedure used, were dissolved in acid or fused in a nickel crucible and the contents extracted with water.

The hydrogen peroxide test was made on these solutions and also after precipitating the iron in the acid solutions with sodium carbonate and hydrogen peroxide, or with ammonia. The filtrates were tested, after acidifying or after acidifying and concentration by evaporation. Chromium is not present in sufficient amounts to show in the ether ring test, which was made on material from all the localities. Phosphoric acid was added to destroy any color due to iron, NH_4F was added to prevent any color due to titanium. It was known that large quantities of molybdenum and cerium were not present. The residual light yellow, orange to brownish color obtained was compared in tubes with that produced by known concentrations of vanadium, and the results checked against those obtained by the use of strychnine sulphate. The strychnine sulphate test is made in a solution from which the iron has been removed by precipitating with sodium carbonate and hydrogen peroxide. The presence of much water interferes with the test from the quantitative standpoint, and this was overcome by acidifying with large amounts of concentrated sulphuric acid, before adding the strychnine sulphate. This makes the test less desirable than the one using hydrogen peroxide, although the final orange coloration of the solution containing vanadium is very distinctive. Both these tests are very delicate. The coloration due to .001% or less of vanadium may easily be seen when viewed down long tubes against a white background. Numerous blank tests were made on the reagents employed.

The spectroscopic analysis was made by G. E. Claussen in the spectroscopy laboratory of the Massachusetts Institute of Technology under the direction of Professor G. R. Harrison. Two methods were used, first the spark method in which the mineral powders were packed into craters in highest purity graphite electrodes, about 6 mm. in diameter, and subjected to a condensed spark for ten minutes. In addition the arc method was employed on HCl–HNO_3 solutions of the minerals. Wedge shaped graphite electrodes were soaked in the solution and more of it was placed on the hot electrodes. The arc was exposed to the slit of the twenty-one foot concave grating for approximately one minute. The acids used in making the solutions were tested for purity and gave no lines other than those of the graphite electrodes.[13]

VANADIUM IN SULPHIDES

The tests for all elements were made on well crystallized material, mostly large individual crystals. The specimens were chiefly selected from localities which would furnish fresh, clean crystals, in order to avoid the possibility of contamination or "salting" by alteration processes.

The results as given are not considered of good quantitative value, but it is believed that they indicate approximate amounts. The amount of vanadium in the sulphides examined was found to be quite variable.

Five different samples of each of the minerals pyrite, sphalerite and galena from different localities were spectroscopically analyzed. Vanadium was found in the pyrite from Elba, and in galena from Leadville, Colo.; the Utah Apex Mine, Bingham Canyon, Utah; Przibram, Bohemia; Bleiberg, Karnten; and Joplin, Mo. The number of lines present in the spectra suggest that vanadium is present to the amount of .0n–.00n%.

These results are in harmony with those obtained chemically by the writer. The pyrite from Elba was found by the chemical tests to contain about 0.01% V while pyrite from Red Cliff, Colo.; Bingham Canyon, Utah; Leadville, Colo. and Central City, Colo. showed much less. Two of these latter which were examined spectroscopically with negative results, apparently contain the vanadium in amounts below ready spectroscopic detection.[14]

Negative spectroscopic results were obtained on the sphalerite from five different localities, although both chemical tests indicate its presence in four of these in amounts smaller than in the pyrite. This small amount is present in sphalerite from Kisbanya, Ungarn, Oradna, Siebenburgen; Lautenthal, Harz; and Warren, N. H. Less

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[13] Details are given in a paper by Claussen, see *Am. Mineral.*, vol. **19**, pp. 221–225, 1934.

[14] A considerable number of distinctive spectral lines are produced by a chloride solution of vanadium which contains 0.01% V and none from solutions containing 0.001% V.

Twyman, F. and Smith, D. M., *Wavelength Tables for Spectrum Analysis.* Adam Hilger, pp. 78, 100–101, 1931.

It is realized that other factors besides percentage of element may determine the presence or absence of spectral line.

to none was chemically found in the sphalerite from Joplin, Mo.; Santander, Spain; Sonora, Mexico; and Rabenstein in southern Tyrol. The chemical tests on galena check the spectroscopic results. Vanadium ±.1% has been reported [5] in nickeliferous pyrite from the Merensky horizon in the Bushveldt Complex, S. Africa.

SOURCES OF VANADIUM IN THE OXIDIZED LEAD-ZINC-COPPER DEPOSITS

It is evident that several sources contribute vanadium to the oxidized heavy metal deposits. Rocks, circulating waters, and hypogene mineralization probably all furnish their quota each of which may well vary greatly in different localities. The average vanadium content in igneous rocks is .017%V.[16] More is present in the femic than in the silicic or feldspathic rocks. It has been known for some time[17] that clays, residual, limonitic and lateritic soils were more than ordinarily rich in vanadium. This has been confirmed by many new analyses given by Jost[18] who finds less than .001%V in limestomes and dolomites, about .01% in clays and shales, from .03–.05% in bauxites and laterites, and .04–.1% in residual iron and manganese ores. The bulk of the oxidized lead deposits containing vanadinite are found in limestones, dolomites and granitic rocks. These are the lowest in vanadium of all rocks.

Jost advances the hypothesis that the vanadium in the vanadinite deposits is derived from lateritic and other residual soils.[19]

It may well be pointed out that the vanadium has been concentrated in these soils for the same reason that the iron and aluminum have been concentrated, namely due to the insoluble nonfugitive character of the compounds formed. They go into solution and are removed by meteoric waters with difficulty; otherwise, they would not be "residual." Certain deposits, which like the Spanish ones are found in rocks high in vanadium, doubtless re-

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[15] Wagner, P. A., and Schneiderhöhn, H., *Platinum Deposits and Mines of South Africa*, pp. 234–236, 1929.

[16] Clarke, F. W., and Washington, H. S., The Composition of the Earth's Crust: *U. S. Geol. Survey*, Prof. Paper **127**, 20, 40, 1924.

[17] Clarke, F. W., Data of Geochemistry: *U. S. Geol. Survey*, Bull. **770**, pp. 722–723, 1924.

Lindgren, W., Mineral Deposits, pp. 395, 460, 1928.

[18] Jost, Konrad, Über den Vanadiumgehalt der Sedimentgestein Chemie der Erde, vol. **7**, Pt. 2, pp. 280–283, 1932.

[19] Jost, K., *Op. Cit.*, p. 282.

ceive much from that source. The occurrence of vanadium minerals in the Colorado carnotite deposits, and at Mauch Chunk, Pennsylvania, shows that vanadium may migrate at least to some extent in solutions, presumably of meteoric origin. Such circulating waters may at times contribute vanadium to oxidizing lead deposits.

The sulphides, pyrite, sphalerite, and galena, are, however, doubtless the chief contributing source for the more common widely distributed low grade deposits. Rich high grade deposits connected with large bodies of oxidized ore, derived from large original masses of sulphides like those at Broken Hill in N. Rhodesia, may also be in part of this origin.

Obviously, the vanadium must not only be present but also it must be available, i.e. amenable to solution. Femic igneous rocks may be rich in vanadium (0.027%V) where it is probably mainly present in titaniferous magnetite[20] and to a smaller extent in silicates. Magnetite is a relatively insoluble mineral in meteroic waters. As might be expected abundant vanadinite deposits are not found in these rocks. Much the same reasoning will apply to lateritic residual soils as a source. On the other hand, limestones and dolomites, although they contain less vanadium than other sediments, are readily dissolved by the acid solutions from oxidizing pyritic ores, and would hence probably contribute some in most deposits. Sulphide oxidation would precede any extensive lateritization, so these mineral acid solutions would probably not permeate the lateritic soils to any extent.

THE OCCURRENCE AND TENOR OF MOLYBDENUM IN OXIDIZED LEAD ORES

The oxidized ores of lead carry molybdenum chiefly as the mineral wulfenite[21] ($PbMoO_4$) which may contain some tungsten, chromium, vanadium, copper and calcium.

Wulfenite is widely distributed in varying but generally small amounts in lead ores that have been subjected to prolonged oxidation. In most places where found it has furnished specimens

[20] Pope, F. J., Investigation of magnetic iron-ores from Eastern Ontario: *Trans. Am. Inst. Min. Eng.*, vol. **29**, pp. 395–397, 1899.

[21] Dana, *System of Mineralogy*, pp. 989–991, 1914.
Hintze, *Handbuch der Mineralogie*, Bd. 1. Abt. 3, Hft. 2, pp. 4044–4059, 1930.
Rastall, R. H., Molybdenum ores. Monograph, *Imper. Inst.*, **1922.**
Hess, F. L., Molybdenum deposits: *Bull. U.S.G.S.* **761,** pp. 6–31, 1924.

only of mineralogical interest. Hess has mentioned the fact that wulfenite is generally not present in any considerable amounts in the oxidized zones of large lead deposits in most of our mining centers. Deposits of commercial interest have been worked in Spain, in southwestern United States, Mexico, Austria, Germany and Yugo-Slavia.

Among the localities which contained wulfenite and were worked to some extent in past years are, Bleiberg, Carinthia; Rezbánya, Hungary; Przibram, Bohemia; Eureka, Nevada; and the Wheatley Mine, Pennsylvania. Considerable variation in the tenor of the molybdenum is found. The following brief review is intended to give some idea of its quantity. At the Mammoth and Collins Mines, Schultz, Arizona, the oxidized ore bodies contain about 1–2% wulfenite.[22] One shoot averaging 10–12 inches wide contained 20–30% wulfenite. The average run of ore from the Old Yuma mine, Pinal County, Arizona, contains not over 2–3 per cent wulfenite.[23] A vein 25 miles west of Tucson is said to show 2–3 per cent,[24] and one about 29 miles from the same city is said to carry 3 per cent wulfenite. A deposit near Twin Bridges, Montana,[25] carries 1/2–1 per cent wulfenite. Pure wulfenite contains 26.15 per cent molybdenum, so these deposits generally run about 0.15–0.80% Mo. In the provinces of Granada and Almeria, Spain, oxidized lead ores in limestone average about 1% Mo[26]. An average of 0.08% Mo is present in some Carinthian wulfenite ores.[27] According to Hess the wulfenite ores of the United States, Mexico, Austria and Spain carry greatly varying percentages of molybdenum but the average is probably less than 1%.[28]

TEST FOR MOLYBDENUM IN SULPHIDES

The presence of molybdenum in sulphides was determined spectroscopically and by means of two chemical tests. The chemical

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[22] Horton, F. W., Molybdenum; its ores and their concentration: *U. S. Bur. Mines*, Bull. **11**, p. 47, 1916.

[23] Horton, *Op. Cit.*, p. 49.

[24] Horton, *Op. Cit.*, p. 50.

[25] Horton, *Op. Cit.*, p. 76.

[26] Rubio, D. J., and Gavala, J., Yacimentos de Molibdeno en las provincias de Granada and Almeria: *Boletin Instituto Geologico de Espana,* **39,** 2nd Ser. 19, pp. 167–193, 1918.

[27] Doelter, *Handbuch der Mineralchemie*, vol. **4,** Pt. 2, pp. 798–99, 1929.

[28] Hess, F. L., *Min. Res., U. S. Geol. Surv.*, Pt. 1, p. 907, **1917.**

tests are, first, the well known ammonium or potassium thiocyanate test in which, after the addition of this reagent, metallic zinc or stannous chloride is added, the red color due to the presence of iron will disappear and the reddish color indicative of the presence of molybdenum will appear. The writer prefers to use stannous chloride as a reducing agent where small amounts of both iron and molybdenum are present. The color due to the molybdenum may be collected and concentrated in a little ether, which after shaking forms a ring containing the color on top of the solution. This test is delicate and is said to be infallible.[29]

The other test which was used is one given by Feigl. It is a spot plate[30] test in which a drop or two of neutral or slightly acid test solution is placed on a spot plate and then a fragment of potassium ethyl xanthate is added followed by two drops of 2N HCl. A red-blue color develops when a molybdate is present. This test is very delicate and according to Feigl, the leading authority in that field, is completely specific.

MOLYBDENUM IN SULPHIDES

Molybdenum was found present by the chemical tests described in pyrite and galena from a number of localities. The amount varies in material from different places.

An attempt was made to find the approximate percentage of molybdenum present by varying the concentration of the solutions obtained from the sulphides, and finding the limiting concentration between positive and negative tests for the element. Similar work was done on known solutions of molybdenum. Pyrite from five localities was spectroscopically examined and molybdenum was found present in four of them.[31]

The pyrite containing spectroscopic amounts of molybdenum came from near Philipsburg, Montana; French Creek, Pa.; the

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[29] Bonardi, J. P., *U. S. Bur. Mines*, Bull. **212,** Molybdenum, p. 72, 1923.
Treadwell and Hall, *Analytical Chemistry, Qualitative Analysis*, vol. **1,** p. 543, 1930.
Roscoe, H. E., and Schorlemmer, C., *A Treatise on Chemistry*, vol. **2,** p. 1121, 1923.

[30] Feigl, Fritz, Qualitative analyse mit hilfe von Tupfel Reaktionen. *Leipzig*, p. 176, **1931.** The potassium thiocyanate test is also used by Feigl to obtain a spot plate reaction, pp. 175–176.

[31] A considerable number of diagnostic or distinctive spectral lines are produced by solutions containing 0.01% and few by solutions containing 0.001% Mo.

Commercial Mine, Bingham Canyon, Utah; and Central City, Colo. Pyrite from Elba gave much weaker chemical tests for molybdenum than the others just mentioned, and negative spectroscopic results were obtained on it since the percentage of molybdenum, was probably too low to give spectral lines. Galena from Przibram, Bohemia, contains spectroscopic molybdenum while none was found by this means in galena from Leadville, Colo.; Utah Apex Mine, Bingham Canyon, Utah; Bleiberg, Carinthia; and Joplin, Missouri. Chemical tests on these last four indicate the presence of the element to the amount of approximately 0.000n% Mo. Sphalerite from six localities gave negative spectroscopic results although several gave faint chemical reactions for the element.

Urbain[32] found molybdenum in five samples of sphalerite out of sixty-four samples examined.

There can be no doubt that the Mo is commonly present—as are also the V, W and Cr,—in solid solution in the sulphides, rather than as separate compounds such as molybdenite (MoS_2). A careful microscopic examination was made of the crystals analyzed but no molybdenite was found. It is known that molybdenite is present with these sulphides in some localities.

SOURCE OF MOLYBDENUM IN OXIDIZED LEAD ORE

Traces of molybdenum are present in igneous rocks, particularly the silicic ones,[33] and this source may contribute in some places. Certain organisms apparently take in molybdenum and accumulate it in their life processes.[34] Sedimentary rocks containing such organic remains would doubtless contribute some molybdenum, if they formed the wall rock of an oxidizing lead ore body. The presence of molybdenite accounts for the wulfenite in some oxidized lead deposits.[35]

Twyman, F., and Smith, D. M., *Wavelength Tables for Spectrum Analysis*, Adam Hilger, pp. 78, 93, 1931.

[32] Urbain, G., Analyse spectrographique des blendes: *Compt. Rend.*, Vol. **149,** pp. 602–603, 1909.

[33] Hillebrand, W. T., Distribution and quantitative occurrence of vanadium and molybdenum in rocks of the United States: *Am. Jour. Sci.*, vol. **6,** pp. 209–212, 1898.

Ferguson, J. B., Molybdenum in rocks: *Am. Jour. Sci.*, **37,** pp. 399–402, 1914.

[34] ter Meulen, H., Accumulation of molybdenum in some aquatic plants: *Chem. Abst.*, vol. **26,** p. 4628, 1932.

[35] Lindgren, W., *Mineral Deposits*, p. 985, **1928.**

The fact remains that in others the presence of molybdenite has not been demonstrated, although careful search for it has been made.[36]

It is the writer's opinion that a common partial source of the molybdenum is the small amount contained isomorphously in the primary sulphides such as pyrite, sphalerite and galena. The molybdenum present in these would be readily available to form wulfenite during the processes of oxidation. Galena has been suggested as a possible source before.[37]

TUNGSTEN AND CHROMIUM

These two elements are present in small amounts in many oxidized lead deposits. Neither of these, so far as is known, commonly forms separate compounds, but are both contained in wulfenite,[38] while chromium is also found in vanadinite,[39] and other minearls.

The separate compounds such as crocoite ($PbCrO_4$) and stolzite ($PbWO_4$) are more rarely found in oxidized zones. Tungsten is present in most of the vanadium bearing oxidized lead deposits in the southwestern states.[40] It rarely exceeds 2%.

Hartley and Ramage found[41] chromium spectroscopically in a specimen of sphalerite, and the spectroscopic work on sulphides done at Massachusetts Institute of Technology shows its presence in galena from Leadville, Colo.; the Utah Apex Mine, Bingham Canyon, Utah; Przibram, Bohemia; Bleiberg, Carinthia and Joplin, Missouri. The amount is estimated as roughly 0.0n–0.00n%Cr.

The spectroscopic work further demonstrated the wide occurrence of tungsten in small amounts in sulphides. It was found in pyrite from near Philipsburg, Montana; Elba, French Creek, Pa.; Commercial Mine, Bingham Canyon, Utah; Central City, Colorado, and in sphalerite from Kisbanya, Hungary; Oradna, Sieben-

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[36] Emmons, W. H., Enrichment of ore deposits: *U.S.G.S.*, Bull. **625**, p. 425, 1917.
Butler, B. S., San Francisco Region, Utah: *U.S.G.S.*, Prof. Paper **80**, pp. 110, 195–96, 1913.

[37] Curtis, J. S., Silver lead deposits of Eureka, Nevada: *U.S. Geol. Surv.*, Mon. **7**, pp. 54–56, 64–71, 1884.
Butler, B. S., Geol. and Ore deposits of the San Francisco Region, Utah: *U.S.G.S.*, Prof. Paper **80**, pp. 110, 195–196, 1913.
Schmidt, C., Vorkommen von Gelbbleierz: *Zeit. für Prakt. Geol.*, p. 102, **1915.**

[38] Hess, F. L., Molybdenum deposits: *U.S.G.S.*, Bull. **761**, pp. 6–7, 1924.

[39] Hintze, C., *Handbuch der Mineralogie*, vol. **1**, No. 22, p. 618, 1924.

[40] Hess, F. L., Mineral Resources, *U.S.G.S.*, vol. **1**, p. 956, 1917; *U.S.G.S.*, Bull. **761**, p. 6, 1924.

[41] Hartley, W. N., and Ramage, H., *Jour. Chem. Soc.*, vol. **71**, p. 540, 1897.

burgen; Lautenthal, Harz; and in the galena from Leadville, Colorado; Utah Apex Mine, Bingham Canyon, Utah; Przibram, Bohemia; Bleiberg, Carinthia and Joplin, Missouri. The amount is estimated as 0.0n–0.00n% W.

CONCLUSION

In most of the lower grade and probably some of the higher grade deposits of vanadium and molybdenum in the oxidized zones of lead and lead-zinc-copper deposits, the vanadium and molybdenum are largely derived from small amounts present in the original sulphides.[42] Careful examination may later show that other hypogene minerals also contain these elements in small percentages.

The source of chromium and tungsten in the oxidized zones of lead deposits is also probably largely due to the small amounts of these elements present in the original sulphides.

The areal distribution of the oxidized lead deposits containing these elements is thought to be largely dependent upon the presence or absence of these metals and strong oxidation. The presence or absence of these metals in the primary sulphides, is presumably dependent on space lattice requirements to some extent, but the temperature of deposition and source of the solutions are probably more important factors. Careful study would probably show zonal relations of these metals within single districts.

The general lack of wulfenite and vanadinite in any considerable amounts in the oxidized zones of large lead deposits in many mining centers, is probably because these metals are not present in magmatic solutions from a source that yields large amounts of lead. If it were purely temperature control, occurrences would be expected somewhere in the vicinity of the large lead deposits, in some kind of zonal relation.

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[42] After this paper was in press, H. Moritz (a) reported vanadium in sulphide ore from Tsumeb, South Africa. Tennantite, enargite, sphalerite, and other sulphides, as well as calcite and dolomite, contain around 0.001% vanadium. Pyrite may contain as much as 0.01% vanadium. Molybdenite is present in germanite and sphalerite to the amount of 0.01–0.001% molybdenum. Galena from this locality contains very small inclusions of patronite, the aggregate running 0.01–0.005% vanadium. The writer re-examined, with oil immersion objective, the material used in the present study, and was unable to find any patronite. It is believed that most or all of the vanadium, as well as the molybdenum, chromium, and tungsten, are present in solid solution in the material used in the present study.

[a] Moritz, H., Die Sulfidschen Erze der Tsumeb Mine, *Neues Jahrb. f. Min., B.B.* **67A,** pp. 130–134, 1933.