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UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

TRACE ELEMENTS INVESTIGATIONS

THE OCCURRENCE OF INDIUM

BY

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Trace Elements Investigations -- Report No. 10

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TRACE ELEMENTS INVESTIGATIONS

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ABSTRACT

Indium has been found to occur most abundantly in sphalerites. The amount ranges from traces to a maximum of 1.0 percent. Dark sphalerites are reported richer in indium than light-colored sphalerites. Up to 0.1 percent indium has been reported in chalcopyrite and bornite, but these minerals generally contain very little indium. Some sulfo-salts of tin from Bolivia contain up to 1.0 percent indium. There is an unverified report of a pegmatite in Utah containing 1.0 to 2.8 percent indium.

Some residues in zinc smelting contain more than 1.0 percent indium and are the present source of indium. No better source can be suggested but steps should be taken to ascertain that this source is being fully exploited. Tin sulfide smelter products should be checked. An effort should be made to check the Utah pegmatite occurrence.

INTRODUCTION

This report on the occurrences of indium is the third in a series of similar reports to be prepared by the Geological Survey discussing possible sources of several rare or uncommon elements for which there are war uses. Other elements will be discussed in forthcoming reports.

Indium is a chemical element with the atomic number 49 and the atomic weight 114.76. It belongs to the third group of the periodic table, midway

between gallium and thallium, and is similar in its chemical behavior to these elements. Indium is trivalent in most of its compounds. The element's history, its properties and those of its compounds are summarized in detail by Gmelin (29) and Heller (31), briefly by others (26, 28, 46, 61). Several bibliographies of indium are available (16, 49, 54, 62).

GEOCHEMICAL CONSIDERATIONS

General statement

Indium is one of the very rare elements. All the recent estimates (8, 20, 31, 56, 57) give 1 x 10^{-5}% In for its abundance in the earth's crust, which makes it sixty-fourth in abundance of the ninety known elements. These estimates were, however, based on very scanty data. Indium is a dispersed element, and is not a major constituent of any mineral, 1 percent In being the maximum recorded percentage. It is a strongly chalkophilic element, concentrated almost exclusively in sulfides.

The empirical ionic radius of trivalent indium is given by Goldschmidt as 0.92. One might therefore expect that indium might be associated with the following elements, whose ionic radii are close to 0.92: divalent manganese 0.91, zinc 0.83, divalent iron 0.83, cobalt 0.82, cadmium 1.03 and trivalent thallium 1.05. Zirconium and scandium have ionic radii in this range, but do not occur in sulfide deposits. Actually, indium is found to be associated especially with zinc, also with divalent iron, quadrivalent tin (ionic radius 0.74) and copper, and only very rarely with divalent manganese. This suggests that the ionic radius of indium is lower than 0.92, perhaps about 0.85.

Occurrences in specific minerals and rocks

Sulfides.--Indium was first detected in 1863 in sphalerite from Freiberg, Germany, and has since been detected in sphalerite from many localities. The early work is summarized by Heller (51). Qualitative data have been published by many workers (2, 4, 9, 10, 21, 33, 36, 38, 42, 58, 63, 64, 65, 73, 74, 75, 76). Quantitative determinations have been published for many sphalerites, with studies of paragenesis and associations (1, 12, 19, 25, 64, 68, 69). The indium content of sphalerite varies from none to 1 percent In. About 5 percent of the analyses reported, including one sample from Leadville, Colo., show over 0.1 percent In, and about 30 percent, including samples from Georgetown, Colo., Nevada City, Colo., and Bingham Canyon, Utah, show 0.01 to 0.1 percent In. There is general agreement in the literature (1, 10, 12, 64, 69, 74) that sphalerite from low-temperature deposits is low in indium, whereas sphalerite from mesothermal to hypothermal deposits is likely to contain appreciable indium. However, this does not check with results from the Geological Survey mill products study which indicates no such correlation (see section--Results of mill products studies). Sphalerite from contact deposits of scheelite or magnetite and sphalerite from wolframite deposits are likely to have high indium contents (12, 64). Dark-colored, i.e., iron-rich sphalerites are generally richer in indium than light-colored sphalerites (1, 12, 25, 58).

Indium has been detected (9, 12, 25, 36, 58, 64, 65) in many other sulfides including chalcopyrite, stannite, chalcocite, covellite, bornite, galena, pyrite, pyrrhotite, cobaltite and bismuthinite. The concentrations of indium in these minerals are generally very low, in the thousandths of a percent, but up to 0.1 percent In has been reported in chalcopyrite and bornite.

Sulfosalts.--The tin-bearing sulfosalts, cylindrite and franckeite, from Bolivia have been reported to contain 0.1 to 1.0 percent In (14, 15). Indium

has been detected in traces in tetrahedrite (25), in germanite (30) and in teallite (14).

Oxides.--Indium has been detected in cassiterite from many localities (7, 14, 25, 31, 36, 45, 47, 58, 63, 64, 65, 73), but the concentration is always very low, perhaps 0.01 percent In as a maximum. Commercial tin metal likewise contains traces of indium (14, 15, 23, 27, 34, 73). Other oxides that have been reported to contain traces of indium include columbite (up to 0.01 percent In), hematite, limonite, magnetite, zincite and samarskite.

Carbonates, Phosphates.--Indium has been reported to occur in traces and small amounts (no figures given) in cerussite (9), rhodochrosite (10), smithsonite (14, 71), siderite (30, 36, 63) and in triplite (31). One sample of siderite gave a strong test for indium (36).

Tungstates, Sulfates.--Indium has been reported (3, 10, 31, 41, 63, 64, 65, 76) to occur in wolframite from many localities, but apparently is generally present in very low percentage. The only quantitative analysis (41) gave 0.02 percent In. Indium has also been reported to occur in traces in alunite (76) and in jarosite (9, 65).

Silicate minerals.--The indium content of most silicates examined (see especially 25) has been very low. Hemimorphite (31, 71), rhodonite (76), muscovite (31), garnet (25), vesuvianite (25) and allanite (25), the last three from an ore deposit at Pitkäranta, Finland, unusually rich in indium, have been reported to contain traces of indium. Helvite from Pitkäranta contained up to 0.005 percent In, serpentine from Pitkäranta up to 0.05 percent In, and an unusual tin-bearing amphibole from Pitkäranta contained 0.1 to 1.0 percent In (25), although other amphiboles contained none. Cordierite has been reported (67) to contain probably several percent of indium, but this has not been substantiated.

Rocks.--The few published determinations (11, 30, 31, 37, 64, 67) of the indium contents of rocks are all below 0.001 percent In, excepting the unverified report (67) that a pegmatite dike in western Utah contained 1.0-2.8 percent In.

RESULTS OF MILL PRODUCT STUDIES

The indium content of zinc smelter products varies with varying sources of ore, and also depends on the metallurgical treatment. However, some generalizations can be made from the published data (5, 8, 13, 17, 24, 39, 40, 44, 52, 70, 72). Indium is concentrated in the residues from spelter retorts (17, 24, 39), which may contain up to 1 percent In, in the sludge precipitated in purifying zinc sulfate in the manufacture of lithopone (40), in flue dusts (up to 0.1 percent In) (13, 52, 58, 59, 72), in residues from cadmium recovery (8, 44, also 60), and in certain ore slimes whose exact nature is not specified (8, 58, 59).

Appreciable percentages of indium have been reported in various products of lead smelters (8, 58) and copper smelters (6, 9, 37). Traces of indium have been reported in the flue dust of gas works (37, 53), in coal ashes (30), in flue dust of iron works (37), in commercial aluminum and alumina (35), and in metallic tin; see under Oxides above.

Over a thousand samples from more than 200 mines and mills have been tested for indium by the Geological Survey as part of the mill products study. Table 1 (page 11) lists 39 of the samples which contained 0.01 percent or more of indium. It is noteworthy that all but one of the samples came from zinc producing plants. The exception is a calcine from titanium pigment and it is not clear whether it also contains zinc or not. There are many more samples containing indium in the range of 0.002 to 0.008 percent which have not been listed, almost all of which are from zinc plants. The information available to us does not indicate specific quantities of the indium-bearing products. However,

in the case of flue dusts and comparable smelter by-products which are comparatively rich in indium the amounts are certain to be relatively small, probably considerably less than one ton per day even in smelters of moderate size. The sphalerite concentrates would of course be available in large tonnages but they contain rather small quantities of indium. The concentration of indium comes in the smelting process.

The experience in the mill products testing does not clearly support the indication from the literature that high-temperature sphalerite contains more indium than low-temperature sphalerite. However, the mill products testing is on various zinc concentrates with no knowledge of the degree of concentration of the product by various mines.

Concentrates from the Wisconsin area were lowest (0.002 percent In) but concentrates from the Metaline district in Washington where the ore is a relatively low-temperature type contained the most (up to 0.020 percent In) of any zinc concentrates. Only certain smelter products were higher, notably special residues such as Cottrell dust from Dwight-Lloyd furnaces, some of which contained more than 1.0 percent In. Concentrates from the Tri-State area which is a very low-temperature deposit contain about 0.004 percent In whereas concentrates from Brittania, B. C. at 4000 feet depth and presumably a relatively high-temperature deposit also contain 0.004 percent In. Thus there seems to be no general agreement.

No other source than by-products of zinc treatment has so far been indicated by the mill products work. Manganese samples tested were very low and copper ores and concentrates in general were also very low. However, some large plants have not yet been tested. Tungsten concentrates tested in the mill products study did not contain any indium.

RECOVERY OF INDIUM

Indium is now being recovered from some plants by several of the largest American companies, namely, American Metal Co., Ltd., American Smelting and Refining Co., Anaconda Copper Mining Co., and National Zinc Co., Inc. Early work on the recovery of indium is summarized by Mellor (51); more recent methods have been reviewed briefly (24, 26, 46, 77). A number of other papers are concerned with the recovery of indium from various types of zinc by-products (13, 15, 19, 22, 43, 44, 55).

BEST SOURCES OF INDIUM

The best known source for indium continues to be zinc smelter by-products, particularly some of the residues and flue dusts. For the present, the only apparent way to increase supplies of indium is by more complete recovery from these by-products at all zinc smelters. Data are not available to indicate the possibilities of such a plan which may already have reached fulfillment. No supplementary source is so far suggested in the mill products study.

SUGGESTIONS FOR FURTHER INVESTIGATIONS

Waste products of smelters handling Bolivian tin sulfide ores should be worth study, in view of the reported high indium content of cylindrite.

Waste and by-products of copper smelters might be worth investigation, especially those handling ore that contains much covellite or secondary chalcocite.

The fate of the small indium content of wolframite during th recovery of tungsten metal is not known. Possibly indium could be recovered from these operations. However, no indium was found in tungsten concentrates tested in the mill products study.

Steps should be taken to ascertain that all zinc smelters are making all the indium recovery that is possible or practicable.

Some large copper smelters have not been tested in the mill products program, and although some of the copper tested has not been of interest, these large plants should be tested.

The reported indium-bearing pegmatite in Utah should be investigated.

Table I. Best indium values resulting from mill products spectrography
(Unpublished data of the Geological Survey)

Name of plant	Location	Material treated	Indium-bearing product	Percent In_2O_3
Bartlesville Smelter	Bartlesville, Okla.	Zn ore	Special residue Dwight-Lloyd flue dust	1.0
Dumas Smelter	Dumas, Texas	..Do..	Blackwell Cottrell dust	1.0
.....Do.....	.....Do.....	..Do..	Cadmium plant, lead sludge	0.4
.....Do.....	.....Do.....	..Do..	Cottrell dust (D.-L)	0.4
.....Do.....	.....Do.....	..Do..	Zinc conc. (Ozark)	0.01
.....Do.....	.....Do.....	..Do..	Zinc conc. (Potosi)	0.01
Bartlesville Smelter	Bartlesville, Okla.	..Do..	Flue dust	0.06
.....Do.....	.....Do.....	..Do..	Car residue	0.06
.....Do.....	.....Do.....	..Do..	Pb residue	0.04
Granby Smelter	E. St. Louis, Ill.	..Do..	Zn furnace residue	0.04
.....Do.....	.....Do.....	..Do..	Herreshoff Cottrell dust	0.03
.....Do.....	.....Do.....	..Do..	Cottrell dust	0.02
.....Do.....	.....Do.....	..Do..	Cd furnace residue	0.02
.....Do.....	.....Do.....	..Do..	Waelz clinker	0.01
Monsanto Smelter	.....Do.....	..Do..	Ozark calcines	0.02
.....Do.....	.....Do.....	..Do..	Moore filter cake	0.02
.....Do.....	.....Do.....	..	Potosi calcine	0.02
.....Do.....	.....Do.....		Calcine from Ti pigment	0.02
.....Do.....	.....Do.....	Zn ore	Fresnillo calcine	0.01
Grand View mill	Metaline Falls, Wash.	..Do..	Zinc conc.	0.02
Newcastle Acid Plant	Newcastle, Pa.	1/	Flue dust (some Zn)	0.02
Bartlesville Smelter	Bartlesville, Okla.	Zn ore	Flue dust	0.01
Columbus Smelter			Cottrell dust	0.01
Mammoth-St. Anthony mill	Tiger, Ariz.	2/	Zn conc. & moly. conc.	0.01
Hillsboro Smelter	Hillsboro, Ill.	..Do..	Clinker from oxide plant	0.01
Mathiessen-Hegeler	La Salle, Ill.	..Do..	Flue dust	0.01
Sierra Zinc mill	Aladdin, Wash.	..Do..	Zinc conc.	0.01
Deshaner mill	Versailles, Mo.	..Do..	Zinc con.	0.01

1/ Various ores
2/ Pb-Zn-Mo ore.

ANNOTATED BIBLIOGRAPHY OF OCCURRENCES OF INDIUM

Note: The original papers were seen except those for which reference to an abstract journal is given.

1. Abramov, F. I. and Husanov, A. K. Spectroscopic investigation of sphalerites for germanium, indium, cadmium and gallium. (in Russian). Problem. Soviet Geol. 8, No. 5, 64-73 (1938).

A summary of results on 236 sphalerites from the U.S.S.R. Of these, 2 contained 0.1-1.0% In, 12 contained 0.1%, 7 contained 0.01%, 54 contained 0.01%, 31 contained less than 0.01%, 35 contained traces and indium was not detected in 94. Sphalerites of hypothermal, mesothermal and sulfide-magmatic deposits were, in general, highest in indium content. Dark sphalerites generally contained more indium than light-colored sphalerites.

2. Andersen, J. S. Chemistry of the earth. J. Proc. Roy. Soc. New South Wales 76, 329-346 (1943).

A general account, including a table of the abundance of the elements. Indium is estimated to be 1×10^{-5}% of the earth's crust which places it as sixty-fourth in order of abundance of the elements. Sphalerite and galena from Broken Hill, New South Wales, contain minute but detectable amounts of indium. It is estimated that about one ton of indium annually passes through this one smelter.

3. Atkinson, E. A. Indium in tungsten minerals. J. Am. Chem. Soc. 20, 811-813 (1898).

Indium was detected in wolframite from Zinnwald, Bohemia, but not in two other wolframites or in two scheelites.

4. Beck, G. Der Nachweis seltener Elemente in den Anstegger und Walliser Erzen. (The detection of rare elements in ores from Anstag and Wallis). Abstract in Mitt. naturforsch. Ges. Bern 1937, V-VI.

Lead-zinc ores from two Swiss localities contained approximately 0.2% In.

5. Bibikova, V. I. and Gornova, Z. A. Investigation of the products and the wastes of the Chelyabinsk zinc plant for minor elements. (in Russian). Tsvetnye Metal. 1940, No. 5-6, 121-133 (from an English summary by T. Stadnichenko).

Spectroscopic study of various mill products. The ore concentrates treated were all low in indium (0.004% maximum), and most of the products studied had very low indium contents, the maximum recorded being in ZnO (0.007-0.01% In).

6. Borovick, S. A. Spectroscopic investigation of the products of an arsenic plant.
Compt. rend. acad. sci. U.R.S.S. 25, 210-211 (1939).

Five samples from the arsenic plant of a copper smelter were studied. Four samples of Cottrell and bag-filter dusts contained small quantities of indium (no figures given).

7. Borovick, S. A. and Gotman, J. D. Content of rare and other elements in the cassiterites of different genesis from U.S.S.R. deposits according to spectrum analysis data.
Compt. rend. acad. sci. U.R.S.S. 23, 351-354 (1939).

Spectrographic study of 27 cassiterites. Indium lines were absent in most samples, weak in cassiterite from sulfide-cassiterite veins, strong in two wood-tin samples.

8. Borovick, S. A. and Kalinin, S. K. Spectroscopical analysis of the products of lead and zinc plants.
Compt. rend. acad. sci. U.R.S.S. 19, 257-258 (1938).

Indium was found (figures not given) in Cottrell dusts and in dry ore slime of the Chimkent lead works. Copper-cadmium cake from the Ridder plant contain about 0.005% In; slimes and spongy cadmium from this plant contained somewhat less indium.

9. Borovick, S. A. and Prokopenko, N. M. New data on the distribution of indium in Kazakhstan.
Compt. rend. acad. sci. U.R.S.S. 24, 926-928 (1939).

Indium was detected in sphalerites from several deposits, in some pyrite, chalcocite, and chalcopyrite (thousandths of a percent). Traces of indium were found in some jarosite and cerussite. Traces of indium were found in the slag and dust of the reverberatory furnace flue, in Dorr thickener tailings and in black copper, all from the Karsakpai copper smelter. In the Kyzyl-Espe deposit, the indium content varies directly with the tin content.

10. Borovick, S. A. and Prokopenko, N. N. Distribution of indium in Ural ore deposits.
Compt. rend.acad. sci. U.R.S.S. 31, 22-23 (1941).

No quantitative data are given. Indium was found spectroscopically in many sphalerites, especially in those from high-temperature deposits. Indium was noted in low concentrations in chalcopyrite, rhodochrosite, wolframite and native gold.

11. Borovick, S. A., Prokopenko, N. N. and Pokrovskaya, T. L. Distribution of indium in rocks.
Compt. rend.acad. sci. U.R.S.S. 25, 618-621 (1939).

Spectrographic analysis following chemical concentration was used. A mixture of 12 Russian granites contained 5 x 10^{-6}% In. Another granite contained 1.5 x 10^{-4}% In, a nepheline syenite contained 9 x 10^{-6}% In and a monzonite contained 1.9 x 10^{-4}% In. No indium was detected in gabbros and dunites. Traces of indium were detected in clays and in one sample of pyrrhotite.

12. Borovick, S. A., Vlodavets, N. I. and Prokopenko, N. N. The occurrence of indium in the lead-zinc deposits of Middle Asia.
Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Sér. ghol. 1938, 335-339 (in Russian), 339-340 (in English).

Spectrographic analyses of 52 minerals are given. Up to 0.3% In was found in sphalerite. Sphalerites containing much iron and little germanium and cadmium were highest in indium and tin. Sphalerites richest in indium were those from hypothermal deposits, also those from skarn scheelite deposits and from wolframite deposits. Indium was also detected in chalcopyrite, arsenopyrite and pyrite.

13. Boettger, R. Ueber das Vorkommen des Indiums in sogenannten Ofenrauche der Zink-Röstöfen auf Juliushütte bei Goslar am Harz. (The occurrence of indium in the furnace fumes of the zinc-roasting furnaces of the Julius smelter near Goslar in the Harz).
J. prakt. Chem. 98, 28-29 (1866).

Flue dusts from furnaces roasting Rammelsberg ore contained 0.1% In_2O_3. The extraction of indium from these dusts is described.

14. Brenner, F. M. and Baker, Enid. Arc spectrographic determination of indium in minerals, and the association of indium with tin and silver.
J. Chem. Soc. (London) 1935, 1286-1290.

Spectrographic determinations of indium in many minerals. Traces were found in metallic tin (up to 0.01% In), in some cassiterites, in zincite from Franklin, N. J., in argentite, in tenallite and in smithsonite. Cylindrite from Bolivia contained 0.1-1% In, franckeite from Bolivia 0.1% In. Two chalcopyrites contained approximately 0.1% In; two others contained none.

15. Brewer, F. M. and Baker, Enid. Extraction of indium from cylindrite, chalcopyrite and metallic tin.
J. Chem. Soc. (London) 1936, 1290-1294.

Laboratory-scale extraction is described. Spectrographic analysis after chemical concentration gave 0.003% In in metallic tin and 0.1% In in cylindrite from Bolivia.

16. Browning, P. E. Index to the literature of indium (1863-1903).
Smithsonian Misc. Coll. 46, 1-15 (1905).

17. Browning, P. E. and Uhler, H. S. On a gallium-indium alloy.
Am. J. Sci. 41, 351-354 (1916).

The alloy, containing 10% In, was found as liquid globules on the surface of the residue from the distillation of zinc spelter in the Tri-State district. The residue contained 95.6% Pb, 1.2% Sn, 3% Ga + In and a little copper.

18. Burkser, E. S. Rare elements in the wastes of sulfuric acid and zinc plants. (in Russian).
Redkie Metally 6, No. 4, 34-36 (1937); through Chem. Abs. 32, 3099 (1938).

The recovery of indium from zinc retorts is discussed.

19. Cambi, L. and Malatesta, L. Germanio, gallio, indio nelle blende di Sardegna. (Germanium, gallium and indium in Sardinian sphalerite).
Rend. Ist. Lombardo Sci. Lett. Milano 69, 369-374 (1936); through Mineralog. Abs. 7, 107 (1938).

Calcined sphalerite from Sardinia contained 0.007-0.012% In.

20. Clarke, F. W. and Washington, H. S. The composition of the earth's crust.
U. S. Geol. Survey Prof. Paper 127, 117 pp. (1924).

The indium content of the earth's crust was estimated, from very few data, to be 10^{-9}%.

21. DeLaunay, L. and Urbain, G. Recherches sur la métallogénie des blendes et des minéraux qui en dérivent. (Research on the metallogeny of sphalerite and minerals derived from it).
Bull. Geol. Soc. France [4] 10, 787-795 (1912).

Qualitative spectrographic study. Indium was detected in many sphalerites and in some hemimorphites (calamines).

22. Druce, J. G. F. Occurrence of indium in commercial iron sulfide and its extraction. (in German).
Z. Angew. Chem. 41, 79 (1928); through Chem. Abs. 22, 3022 (1928).

Commercial iron sulfide contained about 0.006% In.

23. Eastman, E. D. Indication of a genetic relation between indium and tin.
Phys. Rev. 52, 1226-1227 (1937).

A review of the literature indicates marked association of indium with tin. Possible transitions are discussed.

24. Enselin, Fritz. Gewinnung des Indiums aus den zwischenprodukten des Zinkhüttenprozesses. (Recovery of indium from the intermediate products of zinc smelting).
Metall u. Erz 37, 401-403 (1940).

Previous methods for extracting indium are reviewed. In the distillation of zinc, indium is concentrated in the residue (Waschzink), a lead-zinc alloy that separates into two layers. The lead-rich layer contains 0.5-1.0% In, the zinc-rich layer 0.05-0.1% In.

25. Ermetsä, Olavi. Ueber die Verbreitung in finnischen Mineralen und ueber seine Trennung von anderen Metallen. (The distribution of indium in Finnish minerals and its separation from other metals).
Annales Acad. Sci. Fennicae (Suomalaisen Tiedeakatemian Toimituksia) A51, No. 1, 92 pp. (1938).

Spectrographic determinations of indium are given for several hundred mineral specimens. Forty sphalerites contained from none to 1% In, the mineral from Pitkäranta being especially rich in indium. In general, dark-colored and coarsely crystallized sphalerites were highest in indium. Most chalcopyrites contained little or no indium, but four samples from Pitkäranta contained 0.05-0.1% In. Bornite from this deposit contained 0.1% In. Traces of indium (up to 0.001%) were found in some tetrahedrites and cassiterites. Columbites contained up to 0.01% In. All silicates tested contained no indium except for samples from Pitkäranta. Garnet, vesuvianite and allanite from this deposit

contained up to 0.001% In, helvite up to 0.008% In, serpentine up to 0.00% In and single unusual amphibole contained 0.1-1.0% In, although other amphiboles contained only traces of indium.

26. French, S. J. A story of indium.
J. Chem. Education 11, 270-272 (1934).

A popular general account, including a highly glamorized account of the search for indium ore by W. S. Murray of the Indium Corporation of America. It is stated that at an unnamed locality (stated elsewhere to be near Kingman, Ariz.), 35,000 tons of ore have been blocked out that contain an average of 1.93 oz./tons In (=0.006% In). Methods of treatment of the ore are described.

27. Garrett, M. W. Experiments to test the possibility of transmutation by electronic bombardment.
Proc. Roy. Soc. London 114A, 289-292 (1927).

It is stated that "considerable difficulty was experienced in obtaining tin free from all traces of indium."

28. Geckler, R. F. and Marchi, L. E. Indium.
J. Chem. Education 21, 407-411 (1944).

A general review.

29. Gmelin's Handbuch der Anorganische Chemie.
System No. 37. Indium. 116 pp. (1936).

30. Goldschmidt, V. M. The principles of distribution of chemical elements in minerals and rocks.
J. Chem. Soc. (London) 1937, 655-673.

A general account. The indium content of the earth's crust is estimated to be 1×10^{-5}% In. It is stated without details that indium has been found to be somewhat concentrated in oceanic phosphate sediments, in sedimentary and hydrothermal siderite and in some coal ashes (up to 2×10^{-4}%).

31. Goldschmidt, V. M. Geochemische Verteilungsgesetze der Elemente (IX). Die Mengenverhältnisse der Elemente und der Atom-Arten. (The principles of the geochemical distribution of the elements. (IX). The abundance of the elements and isotopes.

Skrift. Norsk. Videnskaps-Akad. Oslo. Mat.-Nat. Klasse 1927. No. 4. 148 pp.

The most detailed recent account. It is stated that unpublished work shows indium to be somewhat concentrated in basic pyroxene-rich rocks (5 to 10 x 10^{-5}% In), in muscovites (about 5 x 10^{-5}% In), especially high in tin and tungsten minerals of pneumatolytic origin (5 x 10^{-5}% to 1 x 10^{-3}% In), also in stannite, cassiterite, wolframite and triplite (no figures given). Indium is also concentrated in iron and manganese-rich sediments (no figures given).

33. Goldschmidt, V. M., Barth, T. F. W. and Lunde, G. Geochemische verteilungsgesetze der Elemente V. Isomorphie und Polymorphie der Sesquioxyde. Die Lanthaniden-Kontraktion und ihre Konsequenzen. (The principles of the geochemical distribution of the elements. V. The lanthanide contraction and its consequences).
Skrift. Norsk. Videnskaps-Akad. Oslo. Mat.-Nat. Klasse 1925, No. 7, 59 pp.

Indium has close crystallochemical relations with scandium, less close relations with thallium and gallium. Indium might be expected to be present in rare earth minerals, especially those high in scandium.

33. Graton, L. C. and Harcourt, G. A. Spectrographic evidence on origin of ores of Mississippi Valley type.
Econ. Geol. 30, 805-824 (1935).

Qualitative spectrographic study of 18 sphalerites. Indium was present in some.

34. Green, J. R. Occurrence of indium in tin.
Nature 119, 893 (1927).

Nearly all samples of metallic tin examined contained indium.

35. Hartley, W. N. and Ramage, Hugh. On the spectrographic analysis of some commercial samples of metals, of chemical preparations, and minerals from the Stassfurt potash beds.
J. Chem. Soc. (London) 71, 547-580 (1897).

Commercial Al_2O_3 and aluminum metal contained traces of indium.

36. Hartley, W. N. and Ramage, Hugh. The wide dissemination of some of the rarer elements, and the mode of their association in common ores and minerals.
J. Chem. Soc. (London) 71, 533-547 (1897).

Qualitative spectrographic study. Indium was detected in 9 of 14 sphalerites, 3 of 9 pyrites, 1 of 2 pyrrhotites, 1 of 1 chalcopyrite, 1 of 1 stannite, 4 of 4 cassiterites, 1 of 6 brown hematites (limonites ?), 3 of 18 red hematites, 1 of 7 magnetites, 1 of 12 manganese ores, 3 of 5 siderites (strong test in one).

37. Hartley, W. N. and Ramage, Hugh. The mineral constituents of dust and soot from various sources.
Proc. Roy. Soc. London 68, 97-109 (1901).

Qualitative spectrographic study. Indium was detected in the flue dust of a copper works, in the flue dust of a gas works, in traces in flue dust of four iron furnaces, and in pumice from Krakatoa.

38. Heinrich, F., Laubmann, H. and Prell. Ueber eine indiumhaltige Zinkblende aus dem Oberpfalzer Walde (Bayern). (An indium-bearing sphalerite from the Oberpfalz Forest, Bavaria).
Z. angew. Chem. 37, 877-878 (1924).

A black sphalerite from pegmatite at Hagendorf contained somewhat less than 0.1% In.

39. Hillebrand, W. F. and Scherrer, J. A. Recovery of gallium from spelter in the United States.
Ind. Eng. Chem. 8, 225 (1916).

The presence of indium was noted in a spelter residue from the Tri-State district.

40. Hirschel, W. N. Cadmium, thallium, indium and gallium as byproducts of the lithopone industry.
Chemistry and Industry 1933, 797-798.

Zinc sulfate solutions to be used in manufacturing lithopone are treated with metallic zinc to remove elements whose sulfides are colored. The precipitate obtained may contain 10-30% Cd, also thallium, gallium and indium. One such precipitate contained 0.15% In.

41. Hoppe-Seyler, E. Ueber das Vorkommen von Indium in Wolfram. (The occurrence of indium in wolframite).
Annalen der Chemie 140, 247-248 (1866).

Wolframite from an unknown locality contained 0.023% In_2O_3. Wolframite from Zinnwald also contained indium.

42. Imaizumi, Yoshio. Occurrence of indium in Japan. (in Japanese). J. Chem. Soc. Japan 54, 771-772, 1009-1010 (1933); through Chem. Abs. 28, 583 (1934).

Indium was present in many Japanese sphalerites, the maximum percentage found being 0.006% In.

43. Izbekov, V. O. and Vovk, M. T. The separation of indium from the dust of the Konstantinovsky zinc plant.
Univ. état. Kiev, Bull. sci., Rec. chim. 2, No. 2, 21-27 (1937) (in Ukrainian 21-25, in Russian 26-26, in English 26-27).

In the electrolysis of furnace dust, cadmium, lead and indium remain in the slime and can be recovered chemically. The recovery from 1.5 kg. of dust was 0.156 g. In_2O_3 or 0.006% In.

44. Kvantkina, N. A. Recovery of indium from the waste products in cadmium production. (in Russian).
Novosti Tekhniki 1940, No. 17-18, 27-28; through Chem. Abs. 37, 5317 (1943); see also Russian Patents 50,448 and 50,479 (1937); Chem. Abs. 31, 8848 (1937), 32,1415 (1938).

Chemical and electrolytical recovery of indium is described for secondary cadmium sponge containing 29.7% Cu, 14.4% Cd and 0.045% In.

45. Larionov, J. and Tolmachev, J. M. On the chemical composition of cassiterites Compt. rend. acad. sci. U.R.S.S. 14, 303-306 (1937).

Qualitative spectrographic study. Indium was present in five pegmatite cassiterites.

46. Lawrence, R. W. and Westbrook, L. R. Indium--occurrence, recovery and uses. Ind. Eng. Chem. 30, 611-614 (1938).

A review.

47. Liebisch, Th. Ueber den Schichtenbau und die elektrischen Eigenschaften des Zinnerzes. (The zonal structure and electrical properties of cassiterite).
Sitzber. Kon-Preuss. Akad. Wiss. 1911, 414-422.

Qualitative spectrographic study. Indium was detected in one of five cassiterites.

48. Lopez de Azcona, J. M. Geochemical study of the lead minerals (in Spanish). Ion (Revista espanola de quimica aplicada) 2, 446-457 (1942); through Chem. Abs. 37, 1670 (1943).

Qualitative spectrographic study. Indium was detected in 18% of the 924 lead ores examined.

49. Ludwick, H. T. A bibliography of indium, 1934-1940. Supplement to the bibliography of indium, 1941-1942.
Indium Corporation of America, Utica, N. Y.

50. Lunt, Joseph. A spectrographic analysis of the new germanium-gallium mineral germanite.
S. African J. Sci. 20, 157-166 (1923).

Indium was detected spectrographically in germanite.

51. Meller, J. W. A comprehensive treatise on inorganic and theoretical chemistry Volume V, Longmans, Green and Co. (1924).

Pages 387-405 deal with indium.

52. Meyer, R. E. Zur Kenntnis des Indiums.
Annalen der Chemie 150, 137-160 (1869).

Flue dust of a lead-zinc furnace contained very little indium. Sphalerite from Freiberg contained 0.014% In.

53. Morgan, Gilbert and Davies, G. R. Germanium and gallium in coal ash and flue dust.
Chemistry and Industry 56, 717-721 (1937).

Traces of indium were detected in flue dusts of gas works.

54. Murray, W. S. A preliminary indium bibliography (1863-1932).
W. S. Murray, Inc., Utica, N. Y., 25 pp. (1933).

55. Nishnik, O. T. Thermal method of enriching cadmium dust.
Zapiski Inst. Khim., Akad. Nauk U.R.S.R. 7, 179-191 (1940); 179-189 in Ukrainian, 190 in Russian, 190-191 in German.

The cadmium and indium contents of zinc furnace dust were increased by paper control of addition of NaCl.

56. Noddack, Ida and Noddack, Walter. Die Häufigkeit der chemischen Elementen. (The abundance of the chemical elements).
Naturwissenschaften 18, 757-764 (1930).

A general account. The indium content of the earth's crust was estimated to be $1x10^{-5}$% In.

57. Noddack, Ida and Noddack, Walter. Die geochemischen Verteilungskoeffizieten der Elemente. (The geochemical distribution coefficients of the elements).
Svensk Kemisk Tidskrift 46, 173-201 (1934).

A general account. The indium content of the earth's crust was estimated to be 8×10^{-6} In.

58. Novokhatsky, I. P. and Kalinin, S. K. Indium and its distribution (in Russian Redkie Metally 1937, No. 5-6, 24-28 (from an abstract by T. Stadnichenko).

Many ores and minerals from Kazakhstan and Northern Kirgisia were examined. Dark-colored sphalerites generally are highest in indium (up to 0.07% In). Indium was also detected in cassiterite and stannite. Chalcopyrite contained up to 0.01% In. A study was made of the products of the Chimkent lead works, which was treating ore containing less than 0.001% In. Indium was found to be concentrated in Cottrell dusts (up to 0.1% In) and in dry slimes (over 0.1% IN).

59. Novokhatsky, I. P. and Kalinin, S. K. Indium in the waste of the Chimkent lead works.
Compt. rend. acad. sci. U.R.S.S. 22, 425-426 (1939).

See No. 58 above.

60. Papish, Jacob and Holt, E. A. Indium (I). Detection and estimation of indium from the arc spectrum (in German).
Z. anorg. allgem. Chem. 192, 90-96 (1930), through Chem. Abs. 24, 3619 (1930).

A commercial sample of cadmium oxide contained about 0.1% In.

61. Peter, A. V. Gallium, germanium, indium and scandium.
U. S. Bur. Mines Inf. Circ. 6401, 17 pp. (1930).

A brief review of occurrences and uses with an incomplete bibliography.

62. Potratz, H. A. and Exeley, J. B. A bibliography of indium, 1863-1933.
Univ. Colorado Studies 21, 151-157 (1934).

63. Prokopenko, N. M. Occurrence of indium in various metallogenetic cycles of the U.S.S.R.
Compt. rend. acad. sci. U.R.S.S. 31, 19-21 (1941).

No numerical data are given. Indium occurs in young, as well as in old metallogenetic cycles. It has been found in sphalerites from many deposits, in cassiterite and wolframite from high-temperature tin deposits and in manganuside ite.

64. Prokopenko, N. M. Principal stages in the history of indium in the earth's crust.
Compt. rend. acad. sci. U.R.S.S. 31, 903-906 (1941).

A discussion of the occurrence of indium as related to genesis. No numerical data are given and high, low and trace concentrations are not defined. Magmatic Stage (see all above). Indium is found only in traces in sulfides genetically related to basic and alkaline rocks, whereas some sulfides genetically related to intermediate and acid rocks may have appreciable indium contents. Pegmatitic Stage. Indium is not typical of pegmatites. It occurs in low concentrations in several silicates from pegmatites. Pneumatolytic Stage. Few data are available. Indium may be present in low concentration in cassiterite, wolframite and stannoidite. Ore Deposits. (a) Contact Type. Sphalerite from contact deposits of scheelite--molybdenite, magnetite, lead-zinc and tungsten-tin-arsenic are rather high in indium. Chalcopyrite and arsenopyrite from such deposits generally have low concentrations of indium. (b) Lead-zinc deposits. The indium content of sphalerite varies widely, but, in general, sphalerite from hypothermal and hypo-mesothermal deposits is rich in indium, sphalerite from mesothermal deposits is low in indium; sphalerite from epithermal deposits contains none or very little indium. Cobaltite from a hypothermal deposit was enriched in indium. (c) Tin deposits. Indium is typically associated with tin in tin sulfide deposits. It may also be present in cassiterite and wolframite and in sulfides of metals other than tin. (d) Tungsten-molybdenum deposits. Indium is generally present in wolframite, usually in low concentrations, but sometimes in increased concentrations. Sulfides associated with tungsten deposits, such as galena, sphalerite and chalcopyrite, may contain increased concentrations of indium. Supergene Stage. Indium seldom accumulates in the oxidation zone of sulfide deposits, but is further disseminated. It occurs in traces and small concentrations in minerals such as hemimorphite, cerussite and jarosite. However, indium appears to be precipitated at places where acid

waters of the oxidation zone are neutralized, and should be looked for in zones of secondary sulfide enrichment, particularly in covellite and chalcocite. Sedimentary Rocks. Indium has been found in low concentrations and traces in some manganese ores, bauxites and clays.

65. Prokopenko, N. M. Distribution of indium in Transbaikal.
Compt. rend. acad. sci. U.R.S.S. 31, 907-908 (1941).

Qualitative data on minerals from many deposits. Indium was detected in sphalerite, pyrite, chalcopyrite, covellite, cassiterite, wolframite, stannite, galena, bismuthinite and jarosite.

66. Ramage, Hugh. Gallium in flue dust.
Nature 119, 783 (1927).

Indium was detected in flue dust from a gas works.

67. Rosenn, Hendrik, Jr. Indium and scandium in pegmatite.
J. Am. Chem. Soc. 55, 3899-3900 (1933).

Analyses of samples taken at random along a pegmatite dike in Western Utah indicated 1.0-2.8% In and 0.5-1.2% Sc. The chief minerals of the deposit were cordierite, actinolite, antigorite, calcite and molybdenite. Apparently indium occurred as a partial replacement of the aluminum in cordierite. [Note - This brief note has never been substantiated and must be regarded with suspicion - Abstractor].

68. Siniakova, S. I. Polarigraphic determination of indium and cadmium.
Compt. rend. acad. sci. U.R.S.S. 29, 376-379 (1940).

Four sphalerites from Kirghisia contained 0.026 to 0.083% In.

69. Stoiber, R. E. Minor elements in sphalerite.
Econ. Geol. 35, 501-519 (1940).

Spectrographic study of 75 sphalerites, of which 2 contained 0.1-1% In (one of these from Leadville, Colo.), 11 contained 0.01-0.1% In, 26 contained less than 0.01%, 36 contained no indium. The indium content was lowest in sphalerites from low-temperature deposits, highest in sphalerites from intermediate-temperature deposits.

70. Streng, A. Ueber das Vorkommen von Thallium und Indium in einigen Erzen und Hüttenprodukten des Harzes. (The occurrence of thallium and indium in some ores and furnace products of the Harz).. Berg. - u. Hüttenmänn Ztg. 24, 191 ((1865).

In a mill treating Rammelsberg ore, much thallium and indium present in (1) the mother liquor of vitriol preparation from furnace residues, (2) the mother liquor of copper sulfate manufacture and (3) the gold- and silver-rich slime left after solution of copper in dilute sulfuric acid.

71. Tanner, J. A. Examination for indium of smithsonite from southwestern Virginia and eastern Tennessee. Chem. News 30, 141-142 (1874).

Traces of indium were found in ore containing smithsonite and hemimorphite.

72. Thiel, A. Studien ueber das Indium. Z. Anorg. allgem. chem. 40, 280-338 (1904).

The lead fumes from tapping lead-zinc slag contained 0.2% In.

73. Tongeren, W. van. Contributions to the knowledge of the chemical composition of the earth's crust in the East Indian Archipelago. II. On the occurrence of rarer elements in the Netherlands East Indies. Amsterdam, 1938, pp. 122-161.

Zinc ore from West Borneo contained 0.008% In. Malayan cassiterite contains somewhat less than 0.01% In, and indium is always present in commercial tin.

74. Urbain, G. Analyse spectrographique des blendes. (Spectrographic analysis of sphalerites). Compt. rend. 149, 602-603 (1909).

Indium was detected in 41 of 64 sphalerites examined. It was lowest in those samples containing much germanium.

75. U. S. Geological Survey. Unpublished spectrographic data by George Steiger, K. J. Murata and J. C. Rabbitt.

76. Vernadsky, V. I. Notes on the distribution of the chemical elements in the earth's crust. (in Russian). Bull. acad. sci. St. Petersburg 4, 1129-1148 (1910); 5, 187-193 (1941).

Qualitative spectrographic study of many minerals. Indium was detected in sphalerite, pyrrhotite, franklinite, rhodonite, tantalite, wolframite, samarskite and alunite.