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GEOLOGICAL SURVEY

THE OCCURRENCE OF GERMANIUM

by

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The Occurrence of Germanium

ABSTRACT

Germanium is found to occur most abundantly in sphalerites of low temperature deposits. The amount ranges from traces to tenths of a percent. Cinnabar sometimes contains germanium in tenths of a percent and enargites contain up to 0.1 percent. Pyrargyrite contains up to 1.0 percent and some tin-bearing sulfides have 0.5 percent germanium. Many other minerals have germanium in hundredths of a percent.

Some residues in zinc smelting contain more than 1.0 percent germanium. Dusts and ashes from burning of certain coals contain germanium in amounts from tenths to more than 1.0 percent. Zinc smelter residues are believed to offer the best immediate chance for recovery of germanium, but copper smelters and plants burning large quantities of coal should be investigated.

INTRODUCTION

This report on the occurrences of germanium is the first 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.

Germanium is a chemical element with the atomic number 32 and the atomic weight 72.60. It belongs to the fourth group of the periodic table, midway between silicon and tin, and in its chemical behavior shows many similarities to these elements. Germanium may be quadrivalent, as in GeO_2, or bivalent, as in GeO. The element's history, its properties and those of its compounds are summarized in Keller (51).

GEOCHEMICAL CONSIDERATIONS

(by Michael Fleischer)

General statement

Germanium was formerly regarded as a very rare element. Clarke and Washington (18) estimated in 1924 that the earth's crust contained $n \times 10^{-9}$% Ge, a value in good agreement with earlier estimates. Spectrographic study since then has shown that this estimate was much too low. The most recent estimates (34, 35, 37, 55, 57) range from 1×10^{-4}% to 7×10^{-4}% Ge in the earth's crust, and 4×10^{-4}% may be taken as a fair average. This may be compared to the following estimates (35) for the percentage of more familiar elements in the earth's crust: 100×10^{-4}% Cu; 40×10^{-4}% Zn; 16×10^{-4}% Pb; 0.1×10^{-4}% Ag; and 0.005×10^{-4}% Au.

Studies of the distribution of germanium among the metallic, sulfide, and silicate portions of meteorites (37, 38, 56) show that germanium is, according to Goldschmidt's classification, siderophilic and chalkophilic, i.e. it tends to be concentrated in the metallic and sulfide phases rather than in the silicate phase. The outer crust of the earth should therefore have a lower content of germanium than the earth's interior. Furthermore, sulfide ores should be richer in germanium than silicate rocks, and this has been found to be true.

From the size of the ionic radii, it might be predicted that quadrivalent germanium would occur as an isomorphous replacement of silicon in silicates, of quadrivalent tin, and of quinquevalent arsenic, antimony and vanadium. The first three replacements listed have been observed and data are lacking for the others. However, the occurrence of germanium in sphalerite and

cinnabar is not explicable on this basis, but would fit well with the assumption that germanium is present in these minerals as bivalent germanium.

Occurrences in specific minerals and rocks

Germanium is an essential constituent of only two minerals, argyrodite + canfieldite and germanite, see under sulfosalts below. Associations in which germanium has been reported are discussed below.

Native metals.- Germanium is relatively concentrated in the nickel-iron of meteorites, whose average content is reported to be 0.02-0.05% Ge (26, 35, 37, 38, 43, 55, 56). Terrestrial native iron also is relatively high in germanium (37). Native arsenic was reported to contain 0.013% Ge (56), and native copper to contain traces (32, 59).

Sulfides.- Germanium has been detected spectrographically by many workers (2, 8, 9, 11, 12, 18, 40, 42, 45, 64, 65, 66, 69, 76, 77, 79) in sphalerite and wurtzite from many localities. Quantitative spectrographic determinations are given for 75 sphalerites by Stoiber (72), for 18 sphalerites and wurtzites by Goldschmidt and Peters (37) and there are individual determinations by others (14, 56). A summary of the results on 237 Russian sphalerites has been published (1). The germanium contents determined range from traces to tenths of a percent. There is general agreement (9, 18, 40, 72) that the germanium content is highest in sphalerites of low-temperature deposits such as those of the Tri-State district and Wisconsin.

Unpublished spectrographic determinations in the Chemical Laboratory of the U. S. Geological Survey show that germanium is present in many samples of cinnabar and metacinnabar in amounts up to tenths of a percent. No examination of these minerals for germanium has been reported previously.

Chalcocite from Butte has been reported to contain 0.03% Ge (56). Secondary chalcocite from Tsumeb, South West Africa, contained up to 0.02% Ge, whereas primary chalcocite from the same deposit contained no germanium (53). Germanium has been detected in chalcopyrite (37, 56, 64, 79), the maximum content recorded being 0.009% Ge. Geroldorffite from Loos, Sweden, contained 0.03% Ge (56), marcasite from Westphalia was reported to contain 0.009% Ge (56); many other sulfides and arsenides examined (37, 56) had less than 0.005% Ge or none.

Sulfosalts.- The only two minerals known in which germanium is a major constituent are sulfosalts. These rare minerals are the argyrodite-canfieldite series (Ag_8GeS_6–Ag_8SnS_6) and germanite [perhaps (Cu,Ge,Fe) (As,S)]. A third mineral, ultrabasite, reported to contain germanium, has been discredited (17). Argyrodite-canfieldite occurs at several mines in Bolivia and near Freiberg, Saxony (17), and perhaps in Switzerland (4). Germanite is known only from Tsumeb, South West Africa (17). All these occurrences are from low temperature sulfide deposits.

Quantitative spectrographic determinations have been reported for sixteen enargites (37, 56, 61). Most contain 0.01-0.1% Ge, including samples from Butte, Montana, Central City, Colo., Red Mt., Colo., and Tintic, Utah. A sample from the Santa Fe mine, Chiapas, Mexico, contained more than 0.1% Ge. The tin-bearing sulfosalts franckeite, cylindrite, and teallite from Bolivia have been reported (2, 56) to contain up to 0.5% Ge, but stannite contained only 0.01% or less. Chalcostibite from Colquechaca, Bolivia, contained 0.54% Ge (2). Of seven pyrargyrites examined, five contained no germanium, one contained 0.07% and one contained more than 1% Ge (39). Tetrahedrite contained traces to 0.02% Ge (37, 56). The rare tin-bearing mineral colusite from Butte, Montana, has not been studied spectrographically, but might well contain germanium.

Oxides.- Germanium has been reported (7,23,37,41,49,58,61) to occur in cassiterite, especially in pegmatite cassiterite (49), but none have been found to contain as much as 0.01% and most contain less than 0.005% Ge. Many other oxide minerals contain traces of germanium (37, 56, 78), but the percentages reported are less than 0.005% Ge, except for the columbium-tantalum minerals blomstrandine (0.006%) and euxenite (0.015%) (56), a sample of rutile (0.01%) (56) and some hematites (0.001-0.01%) (37). Chromite was reported to contain up to 0.045% Ge (56), but this has not been verified by later work (37, also 77). Silica sinters and iron-manganese-rich deposits from hot springs may contain up to 0.01% Ge, exceptionally 0.~~005~~.05% Ge (37).

Carbonates, halides, sulfates, phosphates, etc.,- There are few data on these minerals (56). With few exceptions, the samples examined contained 0.001% Ge or less. The germanium content of smithsonite is apparently lower than that of sphalerite (45, 56); the highest content reported is 0.01% Ge in smithsonite from Marion Co., Kentucky (54). Vanadinite from Arizona is reported to contain 0.007% Ge (56), huebnerite from Gladstone, Colo., to contain 0.009% Ge (56).

Silicate minerals.- Many silicates have been analyzed quantitatively for germanium (37, 56), and many qualitative tests have been made (60, 77). The only minerals found to contain appreciable percentages of germanium are some of pneumatolytic or pegmatitic origin. Qualitative tests (58, 60, 77) show that most topazes contain germanium. Quantitative determinations (6, also 23, 37) showed contents of more than 0.01% Ge in 18 of 29 topazes studied; the maximum percentage recorded is 0.04% Ge. Lepidolite (37, 60, 77), spodumene (37, 60, 77), tourmaline (37, 60) and garnet (37, 77), all from pegmatite, show appreciable germanium contents, 0.01% Ge being the

highest percentage recorded. Most hemimorphites (calamine) examined gave negative or weak tests for germanium, but a few gave good tests (59). Two samples of dioptase contained about 0.01% Ge (36).

Rocks.- Germanium is similar to silicon in its chemistry and in ionic radius (29, 30, 68), so that it might be expected to occur in silicates. It is, however, rather evenly distributed and no very high concentrations have been reported. The germanium content of igneous rocks increases with increasing silicon content, gabbros averaging 0.00014% Ge, granites 0.00035% Ge (32, also 37, 46, 56, 80). Greisen from cassiterite veins is distinctly enriched in germanium and may contain up to 0.005% Ge (37). Clays and schists have a slightly higher average germanium content than the igneous rocks, but none is reported to contain over 0.005% Ge (37, 56).

Coal, coal tar, coal ashes, and flue dusts.- Since 1930, when Goldschmidt (27) reported that coal ashes were enriched in germanium, many analyses have been published of coals and ashes from Germany (33, 37, 39), England (37, 52), Bohemia (71), Russia (20, 48, 67, 78, 81, 82), and Australia (16). No data on American coals have been published, but germanium has been detected in coal from Clyser, Pa. (77). A review of the literature has recently been published (25).

There is general agreement that the germanium content is highest in coals with the lowest ash content, and that lignites are low in germanium. Vitrain and clarain are highest in germanium (20, 67). The behavior of germanium during the burning of the coal varies with the conditions of burning. Germanium is concentrated in the ash, whose germanium content is for most samples a few hundredths of a percent, although up to 1.2% Ge has been reported. Flue

dust is also enriched in germanium (37, 39); a study (53) of 72 flue dusts from English gas works showed that many contained tenths of a percent of germanium. The tarry residues left in coking also may contain germanium concentrations up to one percent (37, 48, 81).

RESULTS OF MILL PRODUCT STUDIES

Germanium has been found in several smelter products particularly in zinc smelters. The residues from spelter retorts, in which zinc is reduced to metal and volatilized, are particularly enriched in germanium (12, 21, 45) and may contain up to 0.5% Ge. Under oxidizing treatment, germanium is concentrated in the zinc oxide (12, 54) which may contain up to 0.18% Ge (12, 19). Data on the occurrence of germanium in products of zinc smelters are also given in other papers (8, 13, 74).

Products of many American zinc smelters have been studied spectrographically by the Geological Survey (77). Some spectrographic results are shown in table 1 at the end of this report. The germanium contents of various types of mill products vary, as would be expected, with different sources of ore, but some generalizations can be made. The best sources of germanium appear to be residues from cadmium furnaces (up to 0.3% Ge), lead sludge from the cadmium plant (up to 0.4% Ge) and zinc oxide from the Waelz process (up to 0.5% Ge). Some Cottrell dusts are rich in germanium (up to 0.06% Ge). Coarse zinc and flotation zinc concentrates from the Tri-State district contain 0.01 to 0.02% Ge; Waelz zinc oxide from the Tri-State smelters averages about 0.14% Ge.

Copper smelters (8, 59) yield flue dusts and slags which contain germanium. It is also reported in mill products of non-ferrous metallurgy (8, 74) and in the waste products of sulfuric acid plants (73).

Two gold mines in South Dakota produced concentrates which contained 0.014% Ge (77).

RECOVERY OF GERMANIUM

The literature contains many references to methods for recovering germanium. Most of the work has been done on a laboratory scale, but many of the proposed methods are relatively simple and probably could be adapted to large scale operations. Methods of recovering germanium from spelter and zinc oxide have been published (13, 15, 19, 22, 45, 54), and it has been stated (44) that workable methods for the recovery of germanium from zinc-plant residues have been developed at the Anaconda plant at Great Falls, Montana.

The extraction of germanium from germanite has been studied; the most recent reports (21, 47, 62, 70) give references to earlier work. Possible methods of recovery have also been discussed for flue dusts of gas works (16, 62), for coal by-products such as tars (48), and for waste products of a sulfuric acid plant (73).

BEST SOURCES OF GERMANIUM

The by-products of zinc smelters should be the best source of germanium and would also yield gallium and thallium. Cadmium and indium are now being recovered from this source. The percentage of germanium contained in the best of the zinc smelter by-products ranges from 0.2% to more than 1%. No quantitative data are available regarding amounts of such material; but since most are residues and sludges, the quantities are probably not large. It is not known whether or not germanium is now being recovered from these sources.

Suggestions for Further Investigations

Flue dusts from the manufacture of producer gas is a possible source, if American coals are similar to other coals in their germanium content. Only a few coals have been examined in the mill products study investigation of the U. S. Geological Survey (77). No germanium was found in them. Slurry residues from coke ovens are also worth more investigation.

Some cinnabar contains germanium and it is possible that flue dusts from mercury retorts might contain concentrations of germanium; but none of those tested by the Geological Survey (Ark., Ariz., Calif.) have shown any germanium concentration.

Copper smelting waste and by-products should be investigated particularly in the Butte district, where enargite is common.

Waste products of smelters handling Bolivian tin sulfide ore would also be worth study.

Flue dust and ashes from oil burners might be worth investigation.

Table 1
Best germanium values resulting from mill products spectrography
(Unpublished data of the U. S. Geological Survey)

Name of plant	Location	Material treated	Germanium-bearing product	Germanium percent
Bartlesville Smelter	Bartlesville, Okla.	Zn ore.	Special residue Dwight-Lloyd flue dust	1.0
Granby Smelter	E. St. Louis, Ill.	"	Cadmium plant lead sludge	0.5
"	"	"	Oxide, zinc oxide	0.5
"	"	"	Cadmium furnace residue	0.2
Mathiessen & Hegler Smelter	LaSalle, Ill.	"	Oxide, zinc oxide	0.2
"	Danville, Ill.	"	" "	0.2
Granby Smelter	E. St. Louis, Ill.	"	Dwight-Lloyd Cottrel dust	0.08
Monsanto Smelter	"	"	Ozark calcines	0.08
Granby Smelter	"	"	Zn furnace residue	0.06
Monsanto Smelter	"	"	Moore filter cake	0.05
"	"	"	Fresnillo calcine	0.05
Granby Smelter	"	"	Herreshoff furnace Cottrell dust	0.5
Bartlesville Smelter	Bartlesville, Okla.	"	Car residue	0.04
Monsanto Smelter	E. St. Louis, Ill.	-	Calcine from Ti pigment	0.04
Tennessee-Schuylkill Mill	Chloride, Ariz.	Zn ore	Zn concentrates	0.04

More than 100 samples of zinc concentrates from many mills, mostly Tri-State, contain 0.01 to 0.02% Ge.

ANNOTATED BIBLIOGRAPHY OF OCCURRENCES OF GERMANIUM

(by Michael Fleischer)

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

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

Of 237 samples studied, 30 had 0.1% Ge, 7 had 0.01 to 0.1% Ge, 61 had 0.01% Ge. The germanium content was slightly higher in light-colored varieties, and particularly high in the "schalenblende" type of sphalerite (or wurtzite). The samples studied are classified according to type of deposit; those from "sulfide-magmatic" and "metasomatic" deposits have the highest germanium contents.

2. Ahlfeld, Freidrich and Morita, H. Beitrag zur Kentniss der Sulfostannate Bolivions. Neues Jahrb. Mineral. Geol., Beil.-Bd. 66A, 179-212 (1933).

Chemical and spectrographic analyses are given of wurtzite, stannite, chalcostibite, teallite, franckeite, cylindrite, and argyrodite from Bolivia. The occurrence and parageneais of argyrodite-canfieldite are described.

3. Anon. Needless waste of metals said to occur in smelting Tri-State ores. Eng. Mining J. 129, 64 (1930).

Germanium, indium, cadmium, gallium, and thallium are said to be wasted by present methods of ore roasting.

4. Beck, G. Der Nachweise seltener Elements in dem Anstegor und Valliser Erzen. Abstr. in Mitt. naturforsch. Ges. Bern 1937, V-VI.

Ore from Anstag contained germanium corresponding to 0.8% argyrodite (= 0.03% Ge). Lead-zinc ores from mines in Wallis contained germanium and about 0.2% indium.

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

Samples, collected from the arsenic recovery plant of a copper smelter, included Cottrell dust, bag filter material obtained after removing As_2O_3, dross from roasting Cottrell dust, coal dust, boiler dust, etc. Germanium was found to be concentrated (no figures given) in all the samples excepting the Cottrell dust.

6. Borovick, S. A. On the content of germanium and other rare elements in topazes and beryls of the U.S.S.R.
Compt. rend. acad. sci. U.R.S.S. 31, 24-26 (1941).

Twenty-seven topazes were examined. Seven contained 0.04 to 0.03% Ge, four contained 0.03 to 0.02% Ge, six contained 0.02 to 0.01% Ge, seven contained 0.01 to 0.001% Ge, three contained no germanium.

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, 381-384 (1939).

Qualitative spectrographic study of 27 cassiterites. Only one wood-tin contained germanium and that one only traces.

8. Borovick, S. A. and Kalinin, S. K. Detection of germanium in ores and industrial wastes. (in Russian).
Problem. Soviet Geol. 9, Nos. 4-5, 140-141 (1939); from English abstract by T. Stadnichenko.

Spectrographic data are given for ores and for products of zinc, lead, copper, and cadmium smelters. Only 8 of 204 samples contained germanium. "Speise" from a zinc plant had strong germanium lines.

9. Borovick, S. A. and Prokopenko, N. N. Germanium in some sulfide ores in U.S.S.R. (in Russian).
Bull. acad. sci. U.R.S.S., Ser. geol. 1938, No. 2, 341-344; Chem. Abstr. 34, 691 (1940).

Qualitative spectrographic study. Of 58 sphalerites examined, 19 contained germanium in small amounts. Sphalerites containing germanium are mostly found with low-temperature meso- and epithermal deposits. These are usually light-colored and contain very little or no indium. In zones of oxidation, no germanium was found..

10. Brandes, Wilhelm and Geller, Adolf. Seltner Elements.
Z. prakt. Geol. 41, 153-163 (1933).

A brief review of occurrences of germanium is included.

11. Buchanan, G. H. The occurrence of germanium in zinc materials.
Ind. Eng. Chem. 8, 585-586 (1916).

Germanium was found in Joplin ores and in some Mexican ores, but none in Franklin ore. A by-product of Wisconsin sphalerite (see 12, below) contained 0.18% Ge.

12. Buchanan, G. H. The occurrence of germanium in Missouri and Wisconsin blendes.
Ind. Eng. Chem. 9, 661-663 (1917).

Germanium is concentrated in the residue left in spelter retorts. When these residues are heated under oxidizing conditions to recover ZnO, germanium accompanies the oxide which may contain 0.18% Ge (see above). A method is given for recovering the germanium.

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

"The recovery of tellurium and bismuth from the Cottrell dust of H_2SO_4 plants and of germanium, indium, and thallium from zinc retorts is discussed."

14. Cambi, L. and Malatesta, L. Germanio, gallio, indio nella blende di Sardegna.
Rend. Ist. Lombardo Sci. Lett. Milano 69, 369-374 (1936); Mineralog. Abstr. 7, 107 (1938).

Spectroscopic analysis of calcined sphalerite from Sardinia gave 0.009 to 0.016% Ge, 0.007 to 0.012% In.

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

A summary.

16. Cooke, W. T. The occurrence of gallium and germanium in some local coal ashes.
Trans. Roy. Soc. South Australia 62, 318-319 (1938).

Chemical analyses showed up to 0.03% Ge in flue dusts from coal burners. The germanium can be leached out of the flue dusts by hot caustic soda, but too much silica accompanies it.

17. Dana's System of Mineralogy, Seventh Edition, Volume I. John Wiley and Sons (1944).

For an account of the occurrences of argyrodite-canfieldite, see pp. 356-358; for the occurrence of germanite, see pp. 385-386; on ultrabasite, see p. 415.

18. DeLaunay, L. and Urbain, G. Recherches sur la métallogénie des blendes et des minéraux qui en dérivent.
Bull. Geol. Soc. France (4) 10, 787-795 (1912).

Qualitative spectrographic study of sphalerite with the conclusion that germanium is highest in sphalerite from low-temperature deposits.

19. Dennis, L. M. and Johnson, E. B. Germanium V. Extraction from germanium-bearing zinc oxide. Direct preparation of germanium dioxide free from arsenic. Detection of minute amounts of arsenic in germanium dioxide.
J. Am. Chem. Soc. 45, 1380-1391 (1923).

Crude ZnO from the New Jersey Zinc Co. contained 0.18% Ge (compare 12). A method for the extraction of germanium is given.

20. Egorov, A. I. and Kalinin, S. K. Distribution of germanium in the coals of Kazakhstan.
Compt. rend. acad. sci. U.R.S.S. 26, 925-926 (1941).

Germanium was present in the ashes of coal from eleven of thirty-five deposits studied, the highest concentration being 0.5% Ge. Coals with low ash had the highest germanium content. Vitrain and clarain were much higher in germanium than other coal constituents.

21. Foster, L. S. and Tompson, E. Y. The extraction of germanium and gallium from germanite. III. The recovery of germanium from the arsenious sulfide sublimates.
J. Am. Chem. Soc. 61, 936-937 (1939).

22. Gable, H. S. The extraction of germanium from germanium-bearing spelter retort residues.
Rec. trav. chim. Pays-Bas 52, 225-228 (1933).

Spelter residues from Missouri zinc ores contain fused silicates, much coke and iron sulfide. The germanium, apparently present as metal, varies from 0.1 to 0.5% Ge. It can be recovered by a simple distillation with HCl.

23. Geilmann, W. and Brünger, K. Zum Nachweis von Germanium.
Z. anorg. allgem. Chem. 196, 312-320 (1931).

Details are given of methods of chemical concentration and spectrographic determination. Analyses for germanium are listed for topaz, cassiterite, and native copper.

24. Geilmann, W. and Brünger, K. Die Aufnahme von Germanium durch Pflanzen.
Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1932, Heft 3, 249-253.

Authors found that plants grown on soil to which germanium had been added contained appreciable amounts of germanium in their ashes. This may explain the concentration of germanium in coal.

25. Gibson, F. H. and Selvig, W. A. Rare and uncommon chemical elements in coal.

U. S. Bur. Mines, Techn. Paper 669, 23 pp. (1944).

A review, with bibliography, including a section on germanium.

26. Goldschmidt, V. M. Ueber das Vorkommen des Germaniums in Meteoriten von Cranbourne.
Z. physikal. Chem. A 146, 404-406 (1930).

Troilite from this meteorite contained approximately 0.1% Ge.

27. Goldschmidt, V. M. Ueber das Vorkommen des Germaniums in Steinkohlen und Steinkohlen-Produkten.
Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1930, Heft 3, 398-401.

Germanium occurs in many coals in percentages of 0.001 to 0.01% Ge. Germanium is also concentrated in the flue dust, which contains much arsenic.

28. Goldschmidt, V. M. Geochemische Verteilungsgesetze und kosmische Häufigkeit der Elemente.
Naturwissenschaften 18, 999-1013 (1930).

A general review of geochemical principles with some data on germanium.

29. Goldschmidt, V. M. Ueber die Kristallchemischen Beziehungen zwischen Gallium und Aluminum, Germanium und Silicium.
Norsk. Geol. Tidsskrift 12, 247-264 (1931).

Nearly the same as #30 below.

30. Goldschmidt, V. M. Kristallchemie des Germanium.
Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1931, Heft 2, 184-190.

The close similarity between silicon and germanium, which have ionic radii respectively 0.39 and 0.44 A., is further shown by synthesis of various germanium compounds which have crystal structures close to those of the analogous silicates.

31. Goldschmidt, V. M. Grundlagen der quantitaven Geochemie.
Fortschr. Mineral., Krist., Petrog. 17, 112-156 (1933).

A review of geochemical principles, with some applications to the occurrence of germanium.

32. Goldschmidt, V. M. Drei Vorträge ueber Geochemie.
Geol. För. Förh. (Stockholm) 56, 385-427 (1934).

A general review. The germanium content of silicate rocks is roughly proportional to the content of silica. Gabbros average 0.00014% Ge, nepheline syenites 0.00021%, granites 0.00035%.

33. Goldschmidt, V. M. Rare elements in coal.
Ind. Eng. Chem. 27, 1100-1102 (1935).

About the same as #39 below.

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

A general account, with a table of the content of the earth's crust for all the elements.

35. Goldschmidt, V. M. Geochemische verteilungsgesetze der Elemente. (IX). Die Mengenverhaltnisse der Elemente und der Atom-Arten.
Skrift. Norsk. Videnskaps-Akad. Oslo, Mat.-Nat. Klasse 1937, No. 4. 148 pp.

The most detailed recent work giving a discussion of the occurrences of the elements and the content of the earth's crust for all the elements.

36. Goldschmidt, V. M. and Peters, Cl. Geochemie des Galliums.
Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1931, Heft 2, 165-183.

A detailed spectrographic study, with some data on germanium. Two samples of dioptase contained about 0.01% Ge. Determinations of germanium are given for a number of meteorites. Germanium is highest in the metallic portion, lowest in the stony portion of meteorites. Sedimentary iron oxide ores nearly always show enrichment in germanium, with contents of 0.001 to 0.004% Ge.

37. Goldschmidt, V. M. and Peters, Cl. Zur Geochemie des Germaniums.
Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1933, Heft 2, 141-166.

An elaborate study, with spectrographic determinations of the germanium content of two hundred or more rocks and minerals of all types.

38. Goldschmidt, V. M. and Peters, Cl. Zur Kentniss der Troilit-Knollen des Meteoriten. Ein Beitrag zur Geochemie von Chrom, Nickel und Zinn.
Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1933, Heft 3, 278-287.

Data are given on the germanium content of metal and troilite phases of several meteorites.

39. Goldschmidt, V. M. and Peters, Cl. Ueber die Anreicherung seltener Elemente in Steinkohlen.
Nachr. Ges. Wiss. Göttingen. Math.-Phys. Klasse, 1933, Heft 4, 371-387.

Data on many elements. The germanium determinations on coal ashes are repeated from #37. Coal ashes average 0.05% Ge. The mode of concentration of germanium in coal is discussed.

40. Graton, L. C. and Harcourt, G. A. Spectrographic evidence on origin of ores of Mississippi Valley type.
Econ. Geol. 30, 800-824 (1935).

Qualitative spectrographic data are given for 18 sphalerites. Conclusion that the germanium content is highest for low-temperature deposits.

41. Hadding, Assar. Ueber das Vorkommen des Germaniums im Kassiterite.
Z. anorg. allgem. Chem. 183, 171-172 (1929).

Qualitative spectrographic study of four cassiterites showed that two contained traces of germanium.

42. Hassler, E. L. and Hoye, H. C. Rare elements in Oklahoma sphalerite.
Proc. Okla. Acad. Sci. 14, 67-68 (1934).

Germanium was detected in Oklahoma sphalerite.

43. Heide, F., Merschkewitz, E. and Preuse, E. Ein neuer Hexahedrite von Cerros del Buei Muerto, Chile.
Chem. Erde 7, 483-502 (1932).

Germanium was detected in the iron of this meteorite.

44. Hess, F. L. Rare metals and minerals.
Mining and Metallurgy 19, 8-9 (1938).

A brief review. The statement is made, "Workable methods for the recovery of indium and germanium from zinc-plant residues have been developed at the Anaconda plant at Great Falls, Montana."

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

Qualitative spectroscopic tests for germanium were made on four zinc sulfide ores and three zinc carbonate ores.

46. Hybinette, A.-G. and Sandell, E. B. Determination of germanium in silicate rocks.
Ind. Eng. Chem., Anal. Ed. 14, 715-716 (1942).

A method is given for chemical concentration and colorimetric determination of traces of germanium. A granite contained 0.00026%, a diabase contained 0.00014% Ge.

47. Johnson, W. C., Foster, L. S. and Kraus, C. A. The extraction of germanium and gallium from germanite. I. The removal of germanium by the distillation of germanous sulfide.
J. Am. Chem. Soc. 57, 1828-1832 (1935).

This includes references to previously suggested methods for recovery of germanium.

48. Kostrikin, V. N. Germanium in the tar by-products of the coking process. (in Russian).
J. Applied Chem. U.S.S.R. 12, 1449-1454 (1939); from English abstract by T. Stadnichenko.

Germanium is generally present in the light ash found in gas flues. All samples of coal tar and carbonaceous residues left after distilling tar are enriched in germanium. Two methods of extracting germanium from these products are described.

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

Qualitative spectrographic study showed germanium to be present in five cassiterites from pegmatites and absent in two cassiterites from hydrothermal deposits.

50. López de Azcona, J. M. Geochemical study of the lead minerals. (in Spanish).
Ion (Revista española de química aplicada) 2, 446-457 (1942); Chem. Abstr. 37, 1670 (1943).

Qualitative spectrographic tests were made of 924 samples of lead ores, mostly from Spain. Germanium was present in 3% of the samples.

51. Meller, J. W. A comprehensive treatment on inorganic and theoretical chemistry. Vol. VII, Longmans, Green and Co. (1927).

Pp. 254-275 deal with germanium.

52. Morgan, Gilbert and Davies, G. R. Germanium and gallium in coal ash and flue dust.
J. Soc. Chem. Industry 56, 717-721 (1937).

Germanium is present in the ashes of many English coals, also in tarry residues from coke ovens. It is particularly concentrated in the flue dusts of gas works. Many analyses are given, with a discussion of possible methods of recovery of germanium and gallium.

53. Moritz, H. Die sulfidische Erze der Tsumeb-Mine von Ausgehenden bis zur XVI Sohle.
Neues Jahrb. Mineral. Geol., Beil.-Bd. 67A, 118-153 (1933).

Secondary chalcocite from Tsumeb contained 0.005 to 0.02% Ge, primary chalcocite and other sulfides contained none.

54. Müller, J. H. Germanium in smithsonite and mine waters from the Hudson mine, Livingston Co., Kentucky.
Ind. Eng. Chem. 16, 604-605 (1924).

Chemical analysis showed 0.01% Ge in smithsonite and 0.3 parts per million Ge in the mine waters. At the Trenton, N. J., plant that treated this ore, the furnace clinker contained 0.006%, the flue deposit 0.003%, ZnO from pipes near the bag house 0.007%, and the finished product (ZnO) 0.011% Ge. Recovery of germanium from zinc oxide is described.

55. Noddack, Ida and Noddack, Walter. Die Häufigkeit der Chemischen Elemente Naturwissenschaften 18, 757-764 (1930).

Tables are given of the occurrence of the elements in the earth's crust and in meteorites. The percentage of germanium in the earth's crust is given as 0.0001% Ge.

56. Noddack, Ida and Noddack, Walter. Die Geochemie des Rheniums.
Z. physikal. Chem. A154, 207-244 (1931).

Quantitative spectrographic determinations are given of the germanium content of about 200 rocks and minerals.

57. Noddack, Ida and Noddack, Walter. Die geochemischen Verteilungskoeffizienten der Elemente.
Svensk Kemisk Tidsskrift 46, 172-201 (1934).

A general discussion. Tables are given of the occurrence of germanium in the earth's crust, in meteorites, and in minerals.

58. Papish, Jacob. Occurrence of germanium in topaz.
Science 68, 350-351 (1928).

Qualitative spectrographic tests showed germanium to be present in many topazes, in appreciable amounts in some. Cassiterites contained only traces of germanium.

59. Papish, Jacob. New occurrences of germanium. I.
Econ. Geol. 23, 660-670 (1928).

Qualitative spectrographic tests. Four samples of stannite contained traces of germanium. Five samples of pyrargyrite gave negative tests, one contained 0.07% Ge, and one over 1% Ge. Seven samples of native copper contained traces of germanium. Five hemimorphites gave negative tests, six gave weak tests, four gave good tests for germanium. It is stated that some flue dusts and slags from copper smelters contained germanium.

60. Papish, Jacob. New occurrences of germanium. II. The occurrence of germanium in silicate minerals.
Econ. Geol. 24, 470-480 (1929).

Qualitative spectrographic tests on nearly two hundred silicates. Germanium was found especially in topaz, tourmaline, lepidolite, spodumene, and some muscovites.

61. Papish, Jacob, Brewer, F. M. and Holt, D. A. Germanium. XXV. Are spectrographic detection and estimation of germanium. Occurrence of germanium in certain tin minerals. Enargite as a possible source of germanium.
J. Am. Chem. Soc. 49, 3028-3033 (1927).

Spectrographic analyses of twelve cassiterites showed two with 0.005% Ge or more. Of fourteen enargites, two contained 0.1% Ge or more; six additional contained 0.01 to 0.1% Ge.

62. Patnode, W. I. and Work, R. W. Germanium XXXVI. Extraction of germanium and gallium from germanite.
Ind. Eng. Chem. 23, 204-207 (1931).

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

Brief reviews of occurrences and uses of these elements. Bibliography.

64. Pilipenko, P. P. Investigations of the paragenesis of chemical elements in the sulfide ores of copper, lead and zinc. (in Russian).
Trudy Moskov. Geol.-Razved Inst. 8, 3-16 (1937) Chem. Abstr. 33, 7240 (1939).

Germanium was found in traces in some chalcopyrites.

65. Pina des Rubies, S. and López de Azcona, J. M. Análisis espectral de la Blende por concentración pirroeléctrica.
Anal. soc. Espan. fís. quím. 34, 307-314 (1936); Neues Jahrb. Mineral. Geol. 1938, Ref. I, 166.

Qualitative spectrographic detection of germanium in sphalerite.

66. Pina des Rubies, S. and López de Azcona, J. M. The relation between color and spectrochemical composition of sphalerite from Aliva, Picos de Europa. (in Spanish).
Anales. soc. Espan. fís. quím. 35, 180-186 (1937); Chem. Abstr. 32, 2462 (1938).

Qualitative spectrographic detection of germanium in sphalerite.

67. Ratynsky, V. M. Accumulation of germanium in coals. Compt. rend. acad. sci. U.R.S.S. 40, 198-201 (1943).

Analyses of about 100 Russian coals show 0.001 to 1% Ge in the ashes. Low-ash material is, in general, highest in germanium content but there is much variation even within a single field. Vitrain coals contain 10 to 100 times as much germanium as average coals.

68. Schütz, Wolfram. Kristallchemische Beziehungen zwischen Germanium und Silicon.
Z. physikal. Chem. B31, 292-306 (1936).

X-ray study of some germanates shows them to correspond closely in crystal structure to the analogous silicates.

69. Scott, Walter. Germanium in a British mineral.
Phil. Mag. (7) 1, 1007-1009 (1926).

Qualitative spectrographic detection of germanium in sphalerite from Wales.

70. Sebba, F. and Pugh, W. Gallium. II. The extraction of gallium and germanium from germanite.
J. Chem. Soc. (London) 1937, 1371-1373.

71. Simek, B. G. The germanium content of coals of the Ostrau-Karwin basin.
Chem. Listy 34, 181-185 (1940); Chem. Abstr. 37, 4036 (1943).

Spectrographic determinations on coal ashes gave 0.0001% Ge for most of the coals, 0.001% Ge for some.

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

Spectrographic determinations on seventy-five sphalerites gave: 0.01 to 1% Ge two, 0.01 to 0.1% Ge nine, less than 0.01% Ge thirty-two, not detected thirty-two. Germanium is highest in sphalerite from low-temperature deposits.

73. Syrokomsky, V. S. and Sherova, A. K. The presence of the rare elements thallium and germanium in the waste products from sulfuric acid factories. (in Russian).
J. Chem. Ind. U.R.S.S. (Zhurnal Khimicheskoi Promishlennosti) 15, No. 2, 23-30 (1938); from an abstract prepared by Telsie Stadnichenko.

The thallium and germanium contents of waste products of sulfuric acid plants are low when flotation tailings are used as a source of sulfur. Cottrell dusts may contain 0.01 to 0.03% Ge. Leaching these dusts with 35% H_2SO_4 dissolves only 25 to 40% of the germanium content. The recovery of germanium would be profitable since other elements would be recovered. It is mentioned that Cottrell dust from the Chelyabinsk zinc plant (7 tons daily) contained 0.004 to 0.008% Ge.

74. Syrokomsky, V. S. and Sharova, A. K. The content of the dispersed rare elements thallium, indium, gallium and germanium in the intermediate and the waste products of the nonferrous metallurgy of Ural. (in Russian).
Tsvetnye Metally 1938, No. 11, 23-27; Chem. Abstr. 34, 895 (1940).

No specific data are given.

75. Ulrich, Frantisek. Brookite from Bobrovka.
Rozpravy Ceske Akak., Classe 2, 31, No. 8(1922); Mineralog. Abstr. 2, 141 (1923).

Brookite from albite pegmatite contained germanium.

76. Urbain, G. Analyse spectrographique des blendes.
Compt. rend. 149, 802-803 (1909).

Qualitative spectrographic study showed that germanium was present in thirty-eight of sixty-four sphalerites examined.

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

78. Vakhrushev, G. V. Exploration of rare elements in Bashkiriya (southern Ural) (in Russian).
Uchenye Zapiski Saratov Gosudarst Univ. N. G. Chernyshevskogo 15, No. 1, 124-146 (1940); Chem. Abstr. 35, 6541 (1940).

The upper horizon of the Krasnaevka coal deposits contains 0.06 to 0.2% V_2O_5 and approximately 0.1% Ge.

79. Veselovsky, B. E. High-vacuum sublimation as a method for detecting and concentrating rare elements. (in Russian).
Zavodskaya Lab. 10, 372-374 (1941); Chem. Abstr. 35, 7873 (1941).

A method is described for fractional sublimation of mineral sulfides under high vacuum. A sphalerite contained 0.0001% Ge, a chalcopyrite 0.001% Ge.

80. Wager, L. R. and Mitchell, R. L. Preliminary observations on the distribution of trace elements in the rocks of the Skaergaard intrusion, Greenland.
Mineralog. Mag. 26, 283-296 (1943).

The germanium content of average gabbro is listed as 0.00014% Ge, of average granite as 0.00035% Ge.

81. Silberminz, V. A. Germanium in the coals of the Donetz Basin. (in Russian).
Mineral. Syre 11, No. 6, 16-26 (1936); from an English abstract by Taisia Stadnichenko.

Nearly 300 samples from 250 coal fields were studied. The percentage of germanium varies, even in a single bed. Of the samples studied, the ashes of 7% of the samples had 0.1 To 1% Ge, of 12% had 0.01 to 0.1% Ge. The ashes of carbonaceous residues and pitch from coke ovens contained about 1% Ge.

82. Silberminz, V. A., Busanov, A. K. and Kostrikin, V. M. The question of the distribution of germanium in fossil coals. (in Russian).
Akad. V. I. Vernadskomu Pyatidesyatiletiyu Nauch. Deyatelnosti 1, 169-190 (1936); Chem. Abstr. 33, 8384 (1939).

Spectrographic determinations of germanium in the ashes of coals from all over the U.S.S.R. Thirty-four had 0.1 to 1% Ge, fifty-eight had 0.01 to 0.1% Ge. Most coals rich in germanium had low ash content.