

Germanium geochemistry and mineralogy

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Abstract—Germanium is enriched in the following geologic environments: (1) iron meteorites and terrestrial iron-nickel; (2) sulfide ore deposits, particularly those hosted by sedimentary rocks; (3) iron oxide deposits; (4) oxidized zones of Ge-bearing sulfide deposits; (5) pegmatites, greisens, and skarns; and (6) coal and lignitized wood. In silicate melts, Ge is highly siderophile in the presence of native iron-nickel; otherwise, it is highly lithophile. Among silicate minerals, Ge is concentrated in those having less polymerized silicate tetrahedra such as olivine and topaz. In deposits formed from hydrothermal solutions, Ge tends to be enriched mostly in either sulfides or in fluorine-bearing phases; it is thus concentrated both in some hydrothermal sulfide deposits and in pegmatites, greisens, and skarns. In sulfide deposits that formed from solutions having low to moderate sulfur activity, Ge is concentrated in sphalerite in amounts up to 3000 ppm. Sulfide deposits that formed from solutions having higher sulfur activity allowed Ge to either form its own sulfides, particularly with Cu, or to substitute for As, Sn, or other metals in sulfosalts. The Ge in hydrothermal fluids probably derives from enrichment during the fractional crystallization of igneous fluids, or is due to the incorporation of Ge from the country rocks, particularly from those containing organic material. Germanium bonds to lignin-derivative organic compounds that are found in peat and lignite, accounting for its common concentration in coals and related organic material. Germanium is precipitated from water together with iron hydroxide, accounting for its concentration in some sedimentary and supergene iron oxide deposits. It also is able to substitute for Fe in magnetite in a variety of geologic environments. In the oxidized zone of Ge-bearing sulfide deposits, Ge is concentrated in oxides, hydroxides, and hydroxy-sulfates, sometimes forming its own minerals. It is particularly enriched in some iron- and manganese-bearing oxides and hydroxides, including goethite (up to 5300 ppm) and hematite (up to 7000 ppm).

INTRODUCTION

GERMANIUM IS A geologically intriguing element, being distinctly lithophile, siderophile, chalcophile, and organophile in different environments. In the earth's crust, most germanium is dispersed through silicate minerals in amounts up to a few parts per million. This is due to the isomorphous substitution of Ge(IV) for the chemically similar Si(IV). The highest germanium concentrations occur, however, in two distinct non-silicate crustal environments: (1) zinc-rich and copper-rich sulfide ore deposits, and (2) coal and lignitized wood. Additionally, concentrations of hundreds of ppm Ge are commonly found in iron-nickel meteorites. This enrichment suggests that most of the earth's Ge resides in the iron-nickel core.

In this report, the distribution, crystal chemistry, and mineralogy of Ge will be reviewed and the geochemical behavior of Ge will be discussed in light of recent analytical, mineralogical, and thermochemical data.

DISTRIBUTION

Cosmos and meteorites

The cosmic abundance of germanium has been estimated at 1.71 atoms Ge/10,000 atoms Si (MASON and MOORE, 1982), based largely on the composition of chondritic meteorites. The germanium content of ordinary chondrites is fairly homogeneous, averaging 7.6 ppm (SHIMA, 1964) to 10.6 ppm (ONISHI, 1956). SHIMA (1964) found Ge to be slightly enriched in the Abee enstatite chondrite (29.3 ppm) and in the Murray

carbonaceous chondrite (17.3 ppm). CLARKE *et al.* (1970) found 15 ppm in the Allende carbonaceous chondrite.

In composite stony-iron meteorites, Ge is always found to be enriched in the metal fraction by factors of 10 to 70 relative to the silicate-oxide fraction (ONISHI, 1956; SHIMA, 1964; EL WARDANI, 1957). In the Brenham stony-iron, for example, the Ge concentration was found to be 56 ppm in the metal, 0.85 ppm in the silicate-oxide fraction, and 17.3 ppm in troilite (SHIMA, 1964).

Germanium is generally enriched in iron meteorites, though the content is highly variable. The Ge content usually ranges from less than 0.1 ppm up to several hundred ppm, though concentrations of several thousand ppm have been reported (WASSON, 1966). The current classification of iron meteorites utilizes this variability, being based largely on Ge/Ni and Ga/Ni values, with germanium being "probably the most useful single trace element for classifying irons" (SCOTT and WASSON, 1975). The classification scheme of Scott and Wasson based on Ge and Ni concentrations is shown in Fig. 1.

Terrestrial materials

GANAPATHY and ANDERS (1974) calculate that the earth has roughly the cosmic abundance of Ge (0.96 atoms Ge/10,000 atoms Si; 13.8 ppm). This calculation is based mainly on the chemical composition of meteorites and a theoretical model for the condensation of the solar nebula. In this model, the earth and moon are proposed to have co-evolved, with the earth accreting most of the iron-nickel (and associated Ge) and the moon accreting mostly silicates. The bulk moon composition is therefore calculated to be depleted in Ge (0.09

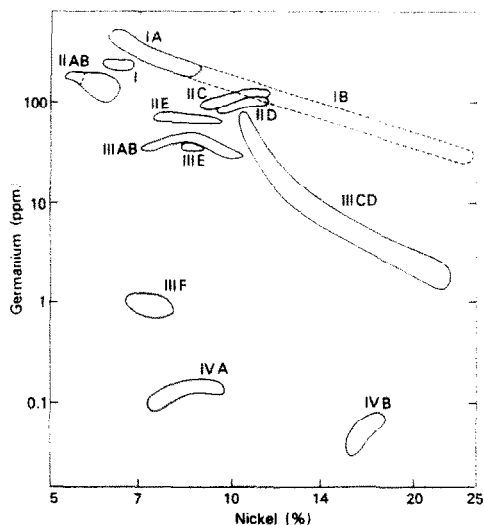


FIG. 1. The classification of iron meteorites based on their Ge and Ni contents (after SCOTT and WASSON, 1975).

atoms Ge/10,000 atoms Si; 1.66 ppm). The crustal abundance of Ge in the earth is estimated at 1.0–1.7 ppm by various authors. Average Ge contents for the crust and for various terrestrial materials are shown in Table 1.

Igneous rocks. As can be seen in Table 1, no significant difference has been found in the Ge content of mafic and granitic igneous rocks. This result has been noted by ONISHI (1956), EL WARDANI (1957), BURTON *et al.* (1959), VINOGRADOV (1962), and HÖRMANN (1963). Enrichment of Ge in some nepheline syenite pegmatites was observed by GOLDSCHMIDT (1954), with GeO₂ contents ranging from less than 5 ppm up to 10 ppm. Germanium is also commonly concentrated in some of the minerals of granitic pegmatites and grei-

sens, particularly in topaz, micas, and spodumene. Data on the bulk compositions of these rocks are presently lacking.

Sedimentary rocks. The Ge content of siliceous sedimentary and metasedimentary rocks is closely comparable to that of igneous rocks (Table 1). Shales are sometimes slightly enriched in Ge, particularly those containing organic material (EL WARDANI, 1957; BURTON *et al.*, 1959; BREGER and SCHOPF, 1955). Sedimentary carbonate rocks are depleted in Ge, averaging only 0.09 ppm. In deep sea sediments, Ge appears to be slightly enriched in siliceous clays and manganese nodules, and slightly depleted in calcareous clay and ooze (Table 1).

The enrichment of Ge in many coals, and particularly in coal ash, is well known and has been extensively studied. The Ge content of these materials varies over several orders of magnitude, both regionally and within particular deposits. The highest concentrations have been found in isolated lignitized logs near Washington, D.C., in which STADNICHENKO *et al.* (1953) reported up to 0.2% Ge with 7.5% Ge in the ash. BREGER and SCHOPF (1955) reported up to 760 ppm Ge in thin coaly stringers within the Chattanooga shale; the shale itself contains only up to 18 ppm. In bedded coal deposits, the highest Ge contents are almost invariably reported from the top and bottom of beds and along partings, rather than from the interior of beds (*e.g.* GLUSKOTER *et al.*, 1977; MANSKAYA and DROZDOVA, 1968; BREGER, 1958). The interior of a large coal bed often contains less than one ppm Ge, while the margins of the same bed can contain several tens of ppm Ge.

The Ge in coals has long been thought to concentrate in the organic fraction (*e.g.* GOLDSCHMIDT and PETERS, 1933). This conclusion originally was based on the rough inverse correlation between total ash content and Ge content, and the frequent enrichment of Ge in the vitrain (vitreous woody) component. Subsequent studies, including "washability" measurements where organic and inorganic fractions are separated, have shown that Ge indeed has one of the highest organic affinities of all the elements in coal with very little Ge occurring in the mineral fraction (GLUSKOTER *et al.*, 1977).

Iron oxide ores. The enrichment of Ge in iron oxide ores has often been noted. BURTON *et al.* (1959) found 43 and 83 ppm Ge in two samples of hematite from unspecified localities

Table 1. Abundance of germanium in various terrestrial materials.

	Mean (ppm* Ge)	Range (ppm Ge)	Number of samples	References
Bulk earth	13.8	---	---	1
Crust	1.4	1.0 - 1.7	---	2,3,4,5
Igneous rocks				
Granitic & intermediate	1.5	0.5 - 4.0	173	2,3,6,7,8
Mafic	1.4	0.7 - 3.1	114	2,3,6,7,8,9
Ultramafic	0.91	0.55 - 1.6	20	2,6,7,8,9
Sedimentary rocks				
Siliceous	1.4	0.2 - 3.3	34	2,3,7
Carbonate	0.09	0.03 - 0.17	6	2
Metamorphic rocks				
Siliceous	1.7	0.08 - 8.0	57	2,8
Deep sea sediments				
Siliceous ooze	1.7	1.1 - 2.2	6	2
Carbonate ooze	0.3	0.0 - 1.4	7	2,3
Clays	2.1	1.4 - 2.8	41	2,3
Manganese nodules	2.5	1.8 - 3.2	2	2
Ocean water				
Total Ge	60	50 - 70	11	2,3
Inorganic Ge	7	0 - 8	34	10
Methylgermanium	39	35 - 43	75	11

*ppm = parts per million

**ppt = parts per trillion

References: 1. Ganapathy and Anders, 1974; 2. Burton *et al.*, 1959; 3. El Wardani, 1957; 4. Vinogradov, 1962; 5. Taylor, 1964; 6. Hörmann, 1963; 7. Onishi, 1956; 8. Schrön, 1968; 9. Baedecker and Wasson, 1970; 10. Froelich and Andreae, 1981; 11. Lewis *et al.*, 1985.

in Cumberland, England, though they found only <0.02 to 3.1 ppm in 11 other samples of iron oxide minerals from other localities. In an extensive study of the Ge content of magnetite, VAKHRUSHEV and SEMENOV (1969) found an average 10.34 ppm Ge in 32 samples from what they call "volcanogenic-sedimentary magnetite-hematite deposits", and 2.50 ppm Ge in 628 samples from skarn deposits. BEKMUKHAMETOV *et al.* (1973) also noted Ge enrichment in volcanogenic-sedimentary magnetite-hematite deposits (up to 70 ppm) compared to that in iron oxides of skarns (few ppm), hydrothermal vein deposits (up to 20 ppm), and sedimentary limonites (few ppm). GRIGOR'YEV and ZELENOV (1965) observed a similar pattern, and also found 11–15 ppm Ge in Fe-Mn oxide-hydroxide particles collected from submarine hot springs near the Banu-Wuhu volcano, Indonesia.

Sulfide ore deposits. The primary commercial production of Ge is currently from carbonate- and shale-hosted sphalerite-rich sulfide deposits. These include the upper Mississippi Valley district (up to 420 ppm Ge in sphalerite; HALL and HEYL, 1968), and the Saint-Salvy sphalerite deposit in France (up to 3000 ppm; BARBANSO and GELDRON, 1983). Studies on the Ge content of sphalerite from a variety of localities have repeatedly found that the highest Ge concentrations occur in low-temperature, late-formed sphalerite (discussed further under "Mineralogy").

Germanium is also produced from the Kipushi Zn-Cu-Pb sulfide deposit in Zaire, and the Tsumeb Pb-Cu-Zn deposit in Namibia. At these deposits, Ge-rich zones occur within high-grade Cu ore; these contain concentrations of the Ge sulfide minerals renierite, $Cu_{10}(Zn_{1-x}Cu_x)Ge_{2-x}As_xFe_4S_{16}$, germanite, $Cu_{11}Ge(Cu,Zn,Fe,Ge,W,Mo,As,V)_{4-6}S_{16}$, and lesser briartite, $Cu_x(Fe,Zn)GeS_4$. These minerals also occur dispersed as microscopic inclusions through much of the hypogene ore. The orebody at Kipushi forms a highly irregular subvertical pipe at the faulted boundary of dolomitic shale and marine dolomite, with sulfide replacement zones extending along bedding planes and fracture zones; renierite in particular is locally abundant (INTIOALE and OOSTERBOSCH, 1974). The ore at Tsumeb consists of an irregular pipe-like body within late-Precambrian dolomite; masses of germanite weighing up to 28 tons have been reported (SÖHNGE, 1964).

JOHAN *et al.* (1983) describe the occurrence of several minerals with exceptionally high concentrations of Ge that are present as microscopic inclusions within sphalerite. These minerals occur in several metamorphosed sphalerite deposits in the central Pyrenees of France. The deposits contain argutite (tetragonal GeO_2), brunogeierite (Fe_2GeO_4), and traces of briartite, as well as the germanate equivalents of the silicates chloritoid (carboirite) and lepidomelane (Table 2). As can be seen in the lower part of Table 3, titanite, allanite, zoisite, quartz, and chlorite from these deposits can contain considerable Ge as well, far more than previously reported from natural samples of these minerals. Sphalerite from these deposits contains a moderate 60–150 ppm Ge (GELDRON, 1983).

Submarine hydrothermal sulfide deposits. BISCHOFF *et al.* (1983) analyzed nine samples containing mixtures of sulfides, sulfates, and silica from hydrothermal vents at 21°N., E. Pacific Rise, the Juan de Fuca Ridge, and the Galapagos Rift. Sphalerite- and wurtzite-rich samples were found to contain 96–270 ppm Ge, while other samples were found to contain <1.5–27 ppm Ge by emission spectroscopy. These results suggest that moderate enrichment of Ge can be expected in Zn-rich Kuroko-type and other submarine-hydrothermal derived massive sulfide deposits.

Oxidized sulfide ore deposits. At the Apex mine, Washington County, Utah, germanium and gallium are extracted from highly oxidized Cu-Pb-Zn-Ag sulfide veins in dolomite. The sulfides have been entirely altered to limonite, goethite, hematite, and azurite, with lesser malachite, conicalchalcite, plumbian jarosite, and other oxides, carbonates, arsenates, and sulfates. Germanium is enriched predominately in goethite (up to 5310 ppm Ge) and hematite (up to 7000 ppm), while Ga is enriched predominately in plumbian jarosite (up to 7000 ppm) and limonite (up to about 2 percent) (DUTRIZAC *et al.*, 1985; BERNSTEIN, 1985a). Germanium was not detected by Dutrizac *et al.* in the jarosite or soft "limonite" (<300 ppm), but does occur in "amorphous Zn-Pb-arsenates" (300–400 ppm) admixed with goethite.

At Tsumeb, a fracture zone extending from the surface intersects the sulfide ore at a depth of about 900 m (SÖHNGE, 1964). This fracture zone has allowed meteoric water to create a lower oxidized zone in the sulfide ore. Within this zone

Table 2. Minerals containing essential germanium.

Mineral	Formula	Crystal Structure	Occurrence	References
Sulfides				
Argyrodite	Ag_8GeS_6	Ortho., s.d.*	Freiberg; Bolivia; and elsewhere	1,2,3
Briartite	$Cu_2(Fe,Zn)GeS_4$	Tetrag., s.d.	Tsumeb, Namibia; Kipushi, Zaire	5
Germanite	$Cu_{11}Ge(Cu,Zn,Fe,Ge,W,Mo,As,V)_{4-6}S_{16}$	Isometric, s.d.	Tsumeb; Kipushi; Ruby Creek, AK; & elsewhere	4,6,7
Renierite	$Cu_{10}(Zn_{1-x}Cu_x)Ge_{2-x}As_xFe_4S_{16}$	Tetrag., s.d.	Tsumeb; Kipushi; Ruby Creek; and elsewhere	4
unnamed	GeS_2	Ortho. (?)	Forestville, PA (deposited by burning coal)	8
Germanates/oxides				
Argutite	GeO_2	Tetrag., rutile	Pyrenees sphalerite deposits, France	9
Bartelkeite	$PbFe^{2+}Ge_3O_8$	Monocl., benitoite(?)	Tsumeb - lower oxidized zone	10
Brunogeierite	Fe_2GeO_4	Isometric, spinel	Tsumeb; Pyrenees sphalerite deposits, France	9,11
Carboirite	$FeAl_2GeO_5(OH)_2$	Tricl., chloritoid	Pyrenees sphalerite deposits, France	9
Ge-lepidomelane	$(K,Na,H_3O)_2Fe_6(Ge_5Al_3)O_{20}(Cl_2(OH)_2)$	Monocl. (?)	Pyrenees sphalerite deposits, France	9
Otjissimeite	$PbGe_4O_9$	Tricl., benitoite(?)	Tsumeb - lower oxidized zone	12
Hydroxides				
Mangan-stottite	$Mn^{2+}Ge(OH)_6$	Tetrag.	Tsumeb - lower oxidized zone	13
Stottite	$Fe^{2+}Ge(OH)_6$	Tetrag.	Tsumeb - lower oxidized zone	13,14
Sulfates				
Itoite	$Pb_3Ge(SO_4)_2O_7(OH)_2$	Ortho.	Tsumeb - lower oxidized zone	15
Fleischerite	$Pb_3Ge(OH)_4(SO_4)_2 \cdot 3H_2O$	Hexag.	Tsumeb - lower oxidized zone	15
Schaurteite	$Ca_3Ge(OH)_6(SO_4)_2 \cdot 3H_2O$	Hexag.	Tsumeb - lower oxidized zone	13

*s.d. = sphalerite derivative structure

References: 1. Hillier, 1940; 2. Perichaud *et al.*, 1966; 3. Nhan, 1970; 4. Bernstein, 1985b; 5. Geier and Ottemann, 1972; 6. Geier and Ottemann, 1970; 7. Yushkin *et al.*, 1975; 8. Lapham *et al.*, 1980; 9. Johan *et al.*, 1983; 10. Keller *et al.*, 1981a; 11. Ottemann and Nuber, 1972; 12. Keller *et al.*, 1981b; 13. Geier, 1974; 14. Strunz *et al.*, 1958; 15. Frondel and Strunz, 1960.

Table 3. Abundance of germanium in silicates.

		Environment or locality	Mean (ppm Ge)	Range (ppm Ge)	Number of samples	References
Nesosilicates						
Garnet	skarns		34.0	0.9 - 180	271	1,2,3
	metamorphic		2.7	1.5 - 6.0	7	4,5
Olivine			1.8	0.4 - 3.4	9	4,5,6,7
Topaz			116.	5 - 700	84	8,9,10
Willemite	Franklin, NJ		<10.	all <10	3	11
	New Mexico		164.	47 - 350	6	11
Sorosilicates						
Epidote	skarns		4.7	1.1 - 10	21	1,3
Inosilicates						
Amphibole	skarns		8.6	1.2 - 50	48	1,3
	other		2.9	1.5 - 9	14	4,5,6,9
Clinopyroxene	skarns		14.7	1.1 - 80	67	1,2,3
	pegmatites		11.4	10.4 , 12.3	2	4
	other		1.9	0.6 - 4.4	13	4,5,6,7,9
Spodumene	pegmatite		27.8	27.8	1	4
Orthopyroxene			1.6	0.3 - 2.9	4	4,7,9
Phyllosilicates						
Biotite	igneous		3.9	1.2 - 8.5	26	4,5,9
	metamorphic		2.7	1.8 - 4.0	16	5
Muscovite	granitic rocks		2.6	1.1 - 6.5	13	4,5,9
	pegmatites		33.5	16.5 - 62.7	4	4
Tektosilicates						
Microcline	pegmatites (perthitic)		17.6	7.8 - 29.2	4	4,9
Plagioclase	granitic, intermediate		2.3	1.3 - 3.6	6	4,5,9
	mafic		0.8	0.05 - 1.3	3	4,9
	pegmatites		8.3	7.0 , 9.5	2	4,9
Orthoclase	granitic		2.1	0.95 - 3.8	10	4,5,9
Quartz	macrocryst.	igneous	1.5	0.8 - 3.3	16	5,12
		metamorphic	3.0	0.8 - 8.0	21	5,12
	pegmatites, greisens	3.0	0.85 - 7.1	9	5,12	
	sedimentary	2.5	0.8 - 6.3	9	12	
	chalcedony	basalt	3.8	1.1 - 8.5	16	13
	rhyolite	9.1	3.2 - 22.0	11	13	

Silicate inclusions in sphalerite, central Pyrenees sphalerite deposits, France:

	wt. percent	wt. percent		
Titanite (nesosilicate)	19.08	19.08	1	14
Allanite (sorosilicate)	10.63	10.63	1	14
Zoisite (sorosilicate)	6.01	5.59 , 6.42	2	14
Chlorite (phyllosilicate)	1.26	0.10 - 2.45	13	14
Quartz (tektosilicate)	0.61	0.26 - 0.87	5	14

References: 1. Ando, 1964; 2. Miroshnichenko et al., 1971; 3. Bekmukhametov et al., 1973; 4. Hörmann, 1963; 5. Schrön, 1968; 6. El Wardani, 1957; 7. Harris, 1954; 8. Seim and Schweder, 1969; 9. Burton et al., 1959; 10. Oftedal, 1963; 11. Sheffer, 1966; 12. Balitskiy et al., 1969; 13. Blankenburg and Schrön, 1982; 14. Johan et al., 1983

several Ge oxides, hydroxides, and hydroxy-sulfates occur as alteration products of primary germanite and renierite. These minerals are discussed in more detail below.

LYALIKOVA and KULIKOVA (1969) found *Thiobacillus* bacteria that are able to accelerate the breakdown of sulfides and put Ge into solution, precipitating sulfates.

CRYSTAL CHEMISTRY AND MINERALOGY

Valency and bonding

Germanium has the outer-electron configuration $3d^{10}4s^24p^2$ and generally occurs in the quadrivalent state. The tendency towards quadrivalency in crystals is very strong: divalent Ge compounds such as GeO and GeS can be synthesized in the laboratory only with difficulty, and are generally not stable under atmospheric conditions or at temperatures much above 25°C (YABUMOTO, 1958; COTTON and WILKINSON, 1966; ROCHOW and ABEL, 1975).

The relatively high electronegativity of Ge (2.02; COTTON and WILKINSON, 1966) leads to the formation

of predominately covalent bonds with many ligands. For example, Ge-O bonds have roughly 31% ionic character and Ge-S bonds have only 7%. For sulfides in particular, the geometric configuration of the orbitals contributing to covalent bonding must be taken into account.

Germanium, like silicon, usually occurs in tetrahedral coordination. This coordination, combined with fairly similar ionic radii (Ge: 0.39 Å, Si: 0.26 Å) (SHANNON, 1976) and covalent radii (Ge: 1.22 Å; Si: 1.17 Å) (COTTON and WILKINSON, 1966), leads to the observed isomorphous substitution of Ge for Si in silicates. Germanium analogs for a multitude of silicates (germanates) have been synthesized in the laboratory, including analogs of quartz, feldspars, olivines, pyroxenes, garnets, and micas. A systematic classification of the known synthetic germanates, together with an extensive bibliography, is given by WITTMAN (1966).

As with SiO₂, a dense high-pressure tetragonal form of GeO₂ (argutite) having the rutile structure exists, with Ge in octahedral coordination. Due to the larger

size of Ge, this phase is stable at a much lower pressure than tetragonal SiO_2 (stishovite); in fact, argutite is stable at atmospheric pressure. In general, germanates undergo analogous phase transformations at lower pressures than analogous silicates. This facilitates experimental phase-stability studies that would, if silicates were used, require prohibitively high pressures. It is possible that unlike Si, Ge may be able to substitute in small quantities in the octahedral sites of silicates, particularly at moderate to high pressures.

Germanium is found to occur in octahedral coordination with highly electronegative OH^- ions in the mineral stottite, $\text{FeGe}(\text{OH})_6$ (STRUNZ and GIGLIO, 1961). Similarly, Ge sometimes has octahedral coordination with the highly electronegative ion F^- , as in the synthetic compounds K_2GeF_6 and Cs_2GeF_6 (GLOCKLING, 1969). This is due to the predominately ionic nature of the bonding in these compounds, and the radius ratio of approximately 0.3, which is on the boundary for octahedral *versus* tetrahedral coordination. The complex structure of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ is found to have Ge in both tetrahedral and octahedral coordination with O (GLOCKLING, 1969).

In the known quadrivalent Ge-bearing sulfides, germanium occurs in tetrahedral coordination. This is expected due to the highly covalent nature of the Ge-S bond: Ge forms tetrahedrally directed sp^3 hybrid bonds to the sulfur atoms. It is conceivable that in an extremely sulfur-rich environment, hexavalent Ge might occur with octahedral d^2sp^3 bonding, though this has not been observed. One other possibility would be for divalent Ge to occur in triangular-pyramidal coordination. This is similar to tetrahedral coordination, also using sp^3 bonds, though one of the tetrahedral sulfur apices is replaced by a "lone pair" of electrons. This configuration occurs in some divalent tin sulfides, such as herzenbergite, SnS , and teallite, PbSnS_2 . Tin, directly below Ge in the periodic table, is chemically similar to Ge; the major differences are its larger atomic size and its much greater tendency to occur in the divalent state.

Mineralogy

Germanium in the earth's crust occurs primarily as trace quantities dispersed in silicate minerals, though notable concentrations occur in some oxides, hydroxides, hydroxy-sulfates, and sulfides. The known mineralogical distribution of Ge will be reviewed in this section, with emphasis on those minerals containing substantial concentrations of Ge. Minerals containing essential Ge are listed in Table 2, and data on minerals containing minor to trace quantities of Ge are given in Tables 3, 4, and 5. For consistency in the quality of trace element data, only quantitative data obtained since 1954 are included in Tables 3, 4, and 5.

Silicates and germanates. WICKMAN (1943) noted that there may be a tendency for Ge to concentrate in silicates having no or few links between silicate tetrahedra in preference to

silicates that are highly polymerized. HARRIS (1954) tested this hypothesis by analyzing coexisting phases in partly glassy rocks from various localities. He found that Ge is indeed concentrated in olivine and pyroxene and depleted in quartz and feldspar within these rocks. Subsequent studies (e.g. BURTON *et al.*, 1959; HÖRMANN, 1963; SCHRÖN, 1968) have confirmed that within a particular sample of igneous or metamorphic rock there is a tendency for Ge to be enriched in the nesosilicates, inosilicates, and phyllosilicates, and to be depleted in the tectosilicates. As can be seen from Table 3, however, the variation of Ge content with geologic environment is generally of greater significance. There is a strong tendency for Ge to be concentrated in late magmatic differentiates and in other rocks that crystallize in the presence of a high volatile concentration, such as pegmatites, greisens, and skarns. The silicate minerals generally reported to have the highest Ge contents (with the exception of those from the French Pyrenees sphalerite deposits) are topaz, garnet, and mica from these rocks.

Except for the highly germanian quartz from the sphalerite deposits of the French Pyrenees (up to 0.87 wt. percent Ge; Table 3), little variation in the Ge content of macrocrystalline quartz from various environments has been noted. BLANKENBURG and SCHRÖN (1982) found that Ge appears to be concentrated in cryptocrystalline quartz nodules (agate), particularly in those from rhyolites as opposed to those from basalts (see Table 3). They found that the Ge content of agate is consistently higher than that of macrocrystalline quartz in the same nodule.

Chlorite from the French Pyrenees sphalerite deposits can contain up to 2.45 wt. percent Ge, and germanate equivalents of chloritoid and lepidomelane also occur as microscopic inclusions within sphalerite (JOHAN *et al.*, 1983). There is apparently complete Ge-Si solid solution between chloritoid and its germanate equivalent carboirite. As can be seen in the lower part of Table 3, Ge is dramatically enriched in those silicate inclusions having less polymerized silicate tetrahedra.

Sulfides. Germanium occurs as an essential component of several sulfide minerals (Table 2), as well as occurring as a significant trace element in several more (Table 4). The highest trace concentrations are found in sphalerite, enargite, stannite, canfieldite, and colusite. All of these minerals have sphalerite- or wurtzite-derivative structures, with quadrivalent Ge in tetrahedral sites.

The minerals renierite, $\text{Cu}_{10}(\text{Zn}_{1-x}\text{Cu}_x)\text{Ge}_{2-x}\text{As}_x\text{Fe}_4\text{S}_{16}$, and germanite, $\text{Cu}_{11}\text{Ge}(\text{Cu,Zn,Fe,Ge,W,Mo,As,V})_4\text{S}_{16}$ are of sufficient local abundance at Tsumeb, Namibia and Kipushi, Zaire to constitute the richest known ores of Ge. Smaller amounts of these minerals, particularly renierite, are found in numerous other localities worldwide. They occur primarily in copper-rich portions of dolomite-hosted Cu-Pb-Zn sulfide ores, though they are also found in other epigenetic Cu-rich sulfide ores (BERNSTEIN, 1985b). Associated minerals include chalcopyrite, bornite, galena, pyrite, tennantite-tetrahedrite, chalcocite, digenite, and sphalerite. Renierite comprises a solid-solution series between the endmembers $\text{Cu}_{10}\text{ZnGe}_2\text{Fe}_4\text{S}_{16}$ and $\text{Cu}_{11}\text{GeAsFe}_4\text{S}_{16}$, through the coupled substitution $\text{Ge}(\text{IV}) + \text{Zn}(\text{II}) \leftrightarrow \text{As}(\text{V}) + \text{Cu}(\text{I})$ (BERNSTEIN, 1985b). Arsenian renierite has been found at the Ruby Creek Cu-Zn-Pb deposit in Alaska, and in the Jamestown district, Colorado. Germanite is of highly variable composition, and actually may consist of more than one mineral. Varieties containing several percent of V, W, and As have been reported from several localities (GEIER and OTTEMAN, 1970; YUSHKIN *et al.*, 1975). Briartite is another related Ge-bearing Cu sulfide mineral found at Tsumeb and Kipushi, occurring mainly as microscopic inclusions within tennantite. It is the Ge equivalent of the tin mineral stannite-kesterite, $\text{CuSn}(\text{Fe,Zn})\text{S}_4$.

Argyrodite, Ag_8GeS_6 , is the mineral in which the element germanium was discovered by WINKLER (1886). The mineral was first found in the complex Cu-Pb-Ag veins near Freiberg, Germany, together with galena, pyrite, and numerous other sulfides and sulfosalts. It has since been identified in some of

Table 4. Abundance of germanium in sulfides.

Mineral	Environment or Locality	Mean (ppm Ge)	Range (ppm Ge)	Number of samples	Ref.
Arsenopyrite		<3	1.6 - 5	11	1,2
Bornite		4.5	0.05 - 8	10	1,2
Canfieldite		>10000	>10000	1	3
Chalcopyrite	Kuroko-type deposits, Japan	9.8	<3 - 100	86	1
	veins and skarns, Japan	<3	<3 - 25	53*	1
	Devon, England	0.5	0.5	1	2
Colusite		413	90 - 790	3	3
Covellite	Japan	70	40 - 100	4	1
Cylindrite	Bolivia	7	<10 - 15	4	3
Enargite	Japan	287	40 - 500	7	1
Franckeite	Bolivia	277	90 - 480	6	3
Galena	Japan	<3	all <3	146	1
	Magmont mine, Viburnum Trend	18.3	(9 - 20)*	86	4
	other	<3	all <3	85	2,5
Herzenbergite	Bolivia	100	90 - 110	2	3
Marcasite	Toroku Mine, Japan	65.5	20 - 100	20	1
	other	0.8	0.8	1	2
Molybdenite	Tyrnyauz deposit, USSR	17.0	1.2 - 32	10	6
	other	1.4	1.1 - 1.6	3	2
Montesite	Bolivia	128	70 - 280	4	3
Pyrite	Japan	<3	<3 - 20	533	1
	other	0.6	0.4 - 0.7	3	2
Pyrrhotite		3	0.5 - 30	109	1,2
Sphalerite	Mississippi Valley MO,KY,IL,TN	235	0 - 1000	61	7,8
	Magmont mine, Viburnum trend	120	(41 - 130)*	24	4
	England	286	250 - 670	9	11
	Japan - Kuroko-type deposits	66.1	<3 - 370	132	1
	Japan - veins	<3	<3 - 60	624	1
	Japan - skarns	<3	<3 - 40	180	1
	St. Salvy, France - stratiform	576	300 - 700	17	9,10
	St. Salvy, France - veins	1475	300 - 3000	16	9,10
	St. Salvy, France - skarn	2.5	0 - 5	2	10
	Argentina - low temperature	310	7 - 2000	6	12
	Argentina - med. temperature	14	<7 - <70	3	12
	Argentina - high temperature	22	<7 - <70	4	12
	epigenetic, low temperature	177	5 - 500	46	5
	epigenetic, high temperature	<3	<3 - 10	13	5
	syngenetic	5.3	<3 - 20	9	5
Stannite	Bolivia	280	<10 - 2830	32	3
	Cornwall	6.1	6.1	1	2
Tellurite	Bolivia	388	110 - 690	4	3

*Figures in parentheses are the range of average values from different parts of the mine.

References: 1. Ando, 1964; 2. Burton *et al.*, 1959; 3. Moh, 1976; 4. Bhatia and Hagni, 1980; 5. El Shazly *et al.*, 1957; 6. Lyakhovich and Sandomirskiy, 1974; 7. Hall and Heyl, 1968; 8. Jolly and Heyl, 1968; 9. Barbanson and Geldron, 1983; 10. Geldron, 1981; 11. Brewer *et al.*, 1955; 12. Angelleli *et al.*, 1973.

the Sn-Ag deposits of Bolivia, and in Ag-bearing sulfide deposits of Poland (NHAN, 1970), France (PERICHAUD *et al.*, 1966), and New Zealand (RAMSAY and KOBE, 1974). The related sphalerite-derivative compounds Cu_8GeS_6 and Cu_2GeS_3 have been synthesized and studied (*e.g.* RIVET, 1965; KHANAFER *et al.*, 1974), though they have not yet been found in nature.

The unnamed mineral GeS_2 is known only as delicate dendritic crystals formed around a gas vent in a burning coal pile at Forestville, Pennsylvania (LAPHAM *et al.*, 1980). It was found associated with ottemanite, Sn_2S_3 , and amorphous sulfur.

Of the minerals containing high trace quantities of Ge, sphalerite is the most studied and the most important economically. It is currently the major source of Ge, with most commercial ore averaging several hundred ppm Ge. Numerous investigations (*e.g.* BREWER *et al.*, 1955; EL SHAZLY *et al.*, 1957; JOLLY and HEYL, 1968; ANGELELLI *et al.*, 1973) have found Ge to be most concentrated (up to 3000 ppm) in sphalerite from low-temperature epigenetic deposits, particularly those in sedimentary rocks. Sphalerite from higher-temperature vein deposits and from low-temperature syngenetic deposits usually contains only a few ppm Ge. There appears little general correlation between Ge and Fe contents in sphalerite, with a positive correlation occurring at some deposits and a negative correlation at others.

BARBANSON and GELDRON (1983) found Ge to be concentrated in some late sphalerite veins relative to adjacent stratiform sphalerite at the Saint-Salvy deposit in southeastern France. They interpret this to mean that Ge was remobilized

from the stratiform sphalerite and country rock, and re-deposited in the late sphalerite veins.

The mechanism of Ge substitution in sphalerite is not well understood. The possibilities include: (1) substitution of Ge(II) for Zn(II); (2) substitution of Ge(IV) for Zn(II) coupled with some form of charge compensation; and (3) substitution of Ge atoms for equal numbers of Zn and S atoms, either scattered or in clumps. The first possibility is highly unlikely, as Ge(II) is not likely to go into tetrahedral coordination in a covalently bonded crystal (COTTON and WILKINSON, 1966; VAUGHN and CRAIG, 1978). Synthetic GeS forms orthorhombic crystals having micaceous cleavage, with Ge in highly distorted octahedral coordination to S (WILEY *et al.*, 1980). If Ge(II) were actually able to substitute for Zn(II) in tetrahedral sites, more substitution would be expected than is observed, due to the similarity in ionic radii. The second possibility may occur, with coupled substitution of either Ge(IV) plus a vacancy for two Zn(II), or Ge(IV) plus two monovalent atoms (such as Cu(I) or Ag(I)) for three Zn(II). Correlation of the concentration of monovalent atoms with Ge content has not been observed in published analyses, though the data are too scarce to rule it out. The third possibility also may exist, though it is difficult to test analytically.

MALEVSKIY (1966) performed some simple experiments to study the substitution of Ge in sphalerite. He found that when ZnS and GeS , or ZnS and GeS_2 , were melted and recrystallized in various proportions, the resulting ZnS always contained less than 100 ppm Ge. Similar results were obtained when Zn and Ge metals and S were heated together in the proportions necessary to form mixtures of these sulfide compounds.

Table 5. Abundance of germanium in oxides, hydroxides, halides, and oxyalts.

Environment or locality		Mean (ppm Ge)	Range (ppm Ge)	Number of samples	Ref.
Oxides and hydroxides					
Cassiterite	Cornwall	95	0 - 315	5	1,9
	Bollvis other	244 118	70 - 470 0 - 3000	5 92	9 9
"wood tin"		5070	980- 10000	5	9
"varlamoffite"		>5650	0->10000	5	9
Corundum	Franklin, N. Carolina	0.8	0.8	1	1
Goethite	Apex mine, Utah	2770	800 - 5310	14	8
	other	0.3	0.3	1	1
Hematite	Apex mine, Utah	7000	7000	1	10
	other	26.7	1.3 - 83	5	1,2
Ilmenite		1.5	0.8 - 2.7	3	1,2
Magnetite	skarns	2.5	0 - 26	328	3,4
	"sedimentary-volcanic"	10.3	3 - 30	32	3
	other	5.1	0.6 - 20	45	1,3,5
Rutile		0.5	0.3 , 0.7	2	1,6
Halides					
Fluorite		6.4	0.4 - 28	54	1,7
Halite		0.04	0.00 - 0.09	3	1
Carbonates					
Aragonite	Andros Island, Bahamas	0.04	0.04	1	1
Calcite		0.07	0.05 - 0.08	4	1
Cerussite	Mold, N. Wales	0.26	0.26	1	1
Dolomite	Galloway, Scotland	0.17	0.17	1	1
Siderite		0.29	0.12 , 0.45	2	1
Strontianite		0.50	0.44 - 0.58	3	1
Phosphates					
Monazite	Travancore, India	0.44	0.44	1	1
Sulfates					
Barite		0.73	0.28 - 1.47	5	1
Celestite		0.47	0.31 - 1.08	4	1
Gypsum		0.34	0.13 - 0.60	5	1
Tungstates					
Scheelite	Cumberland, England	1.20	1.20	1	1
Wolframite	Spain	0.59	0.59	1	1

References: 1. Burton *et al.*, 1959; 2. El Wardani, 1957; 3. Vakhrushev and Semenov, 1969; 4. Ando, 1964; 5. Harris, 1954; 6. Schröb, 1968; 7. Puzanov *et al.*, 1973; 8. Dutrizac *et al.*, 1985; 9. Moh, 1977; 10. Bernstein, 1985a.

When ZnS was heated with excess Ge metal, however, up to 3.8 wt. percent Ge could be incorporated. Malevskiy found that the measured unit cell parameter of Ge-sphalerite is exactly equal to the calculated unit cell for a ZnS-Ge solid solution, and proposed that Ge substitutes for both Zn and S. This proposal is reasonable, as sphalerite and Ge metal have the same lattice-type (diamond), while both GeS and GeS₂ have very different structures.

The large amounts of Ge sometimes found substituting for quadrivalent, tetrahedrally coordinated Sn in sulfides is not surprising, due to the chemical similarity of these elements. The greatest substitution is in canfieldite, which can contain over one weight percent Ge (MOH, 1976). Up to 2830 ppm Ge has been reported from stannite, and at least 7950 ppm Ge has been found in colusite (MOH, 1976). Interestingly, considerable Ge has been reported in several sulfosalts containing divalent, trigonal-pyramidal Sn (such as teallite, PbSnS₂, with up to 690 ppm Ge reported by MOH (1976)). This may represent the only known occurrence of divalent Ge in sulfides; however, it is more likely that quadrivalent Ge is substituting, coupled with a compensating substitution elsewhere in the structure.

High concentrations of Ge often reported from enargite, Cu₃AsS₄, are probably due to the substitution of Ge(IV) for As(V), possibly coupled with the substitution of Zn(II) for Cu(I) as in renierite. Similar substitutions in other sulfosalts may also lead to high Ge concentrations, and should be looked for. For example, FRONDEL and ITO (1957) reported a sample of tennantite from Tsumeb to contain roughly 500-5000 ppm Ge.

FLEISCHER and HARDER (1946) reported that some unpublished spectrographic analyses by the U.S. Geological Sur-

vey showed the presence of Ge in "many samples of cinnabar and metacinnabar in amounts up to tenths of a percent". Metacinnabar is isostructural with sphalerite, whereas the highly distorted Hg site in cinnabar may allow the substitution of Ge(II). It is also possible that much of the analyzed "cinnabar" is, in fact, metacinnabar.

The relatively high concentration of Ge reported in marcasite from the Toroku mine, Japan (Table 4; ANDO, 1964) is unusual, as samples of marcasite and other disulfides generally contain little Ge. The Toroku mine is in a coal-rich province, which could have increased the Ge content of the ore-forming fluids. It is also possible that the Ge is actually contained in secondary iron oxides and hydroxides, not in the marcasite itself.

Iron-nickel (terrestrial). Due to the enrichment of Ge in iron meteorites, data were sought on the Ge abundance of terrestrial iron-nickel. The only available data were obtained from EUGENE JAROSEWICH (pers. commun., 1985), on the iron-nickel from the basalts of Disco Island, Greenland. He found up to 650 ppm Ge in the iron-nickel, with only up to 5.5 ppm Ge in the silicates (probably high due to contamination). This extends the reported siderophile tendency of Ge to a natural terrestrial material.

Oxides and hydroxides. Several Ge oxides and hydroxides are known from the lower oxidized zone at Tsumeb (see Table 2), where they occur with concentrations of tennantite, brunogeierite, and renierite. The hydroxides stottite, FeGe(OH)₆, and mangan-stottite, MnGe(OH)₆, contain Ge in octahedral coordination with OH. Stottite forms octahedral, transparent red crystals up to at least 1 cm across in cavities. A zinc bearing variety, FeZnGe₂(OH)₁₂, may also be a distinct species (GEIER, 1974).

Argutite, GeO_2 , occurring as inclusions in sphalerite at the French Pyrenees sphalerite deposits, has a rutile structure with Ge in octahedral coordination. Interestingly, argutite has not been found to contain any Si, though Zn, Fe, and Mn are present in amounts up to 4.32, 2.16, and 0.32 weight percent respectively (JOHAN *et al.*, 1983).

Brunogeierite, Fe_2GeO_4 , which has a spinel structure, has been found at the Pyrenees sphalerite deposits and at Tsumeb. The synthetic equivalent of brunogeierite is found to be a normal spinel with Ge^{4+} in tetrahedral coordination and Fe^{2+} in octahedral coordination (DURIF-VARAMBON *et al.*, 1956; ROSSITER, 1966). OTTEMANN and NUBER (1972) found what they interpret to be considerable solid solution between magnetite and brunogeierite; this could be represented by $(\text{Ge}^{4+}_x\text{Fe}^{3+}_x)(\text{Fe}^{2+}_{2-x}\text{Fe}^{3+}_x)\text{O}_4$. Magnetite, particularly that from skarns, is often found to be enriched in Ge (Table 5), though only up to 30 ppm Ge has been reported. HARRIS (1954) found Ge to be enriched in magnetite from partly glassy volcanic rocks.

Considerable substitution of Ge for Sn can occur in cassiterite: up to at least 3000 ppm in epigenetic coarsely crystalline varieties, and up to more than one weight percent in fibrous and hydroxyl varieties ("wood tin" and "varlamoffite") (MOH, 1977). Cassiterite, like argutite, has the rutile structure.

Goethite and hematite also have large capacities for incorporating Ge, particularly in the oxidized zones of Ge-bearing sulfide deposits. At the Apex mine in southwest Utah, goethite is the chief Ge ore mineral, containing up to 5310 ppm Ge (DUTRIZAC *et al.*, 1985), with hematite containing up to at least 7000 ppm Ge (BERNSTEIN, 1985a).

The minerals bartelkeite, $\text{PbFeGe}_3\text{O}_8$, and otjismeite, PbGe_4O_9 , could be classed as germanates (viewed as containing GeO_4 tetrahedral groups). KELLER *et al.* (1981b) suggest that these minerals have structures closely analogous to that of benitoite, $\text{BaTiSi}_3\text{O}_9$, as does synthetic hexagonal PbGe_4O_9 . This compound has three Ge^{4+} ions in 4-coordination making up Ge_3O_9 rings, and one Ge^{4+} ion in 6-coordination.

Sulfates. The hydroxy-sulfate minerals itoite, fleischerite, and schaurteite are known from the lower oxidized zone at Tsumeb. There they occur in small cavities as alteration products of primary Ge minerals.

Only a few analyses of Ge in anhydrous sulfates have been published (see Table 3); in these, it appears that Ge is depleted compared to the crustal average. FRONDEL and ITO (1957) report a semiquantitative analysis of anglesite from Tsumeb, however, to show at least 500 ppm Ge.

Halides. PUZANOV *et al.* (1973) found enrichment of Ge (up to 28 ppm) in many samples of fluorite from localities in the U.S.S.R. They observed generally higher Ge concentrations in early-formed fluorite (220–140°C) than in later generations (130–70°C). Data for halite are scarce, but show Ge contents of much less than 1 ppm.

Carbonates. The limited data for carbonate minerals, as for carbonate rocks, show a high depletion of Ge relative to the crustal average (Tables 1, 3). An exception may be some of the carbonates from the Tsumeb ore deposit. FRONDEL and ITO (1957), using semiquantitative spectrographic analysis, found at least 5 ppm Ge in calcite, aragonite, azurite, rosasite, and otavite from Tsumeb, and at least 50 ppm Ge in two samples of cerussite. They proposed that Ge^{2+} was substituting for the metals in these minerals. While this is a possibility, the known instability of divalent Ge compounds makes it somewhat unlikely. Other possibilities include substitution of Ge^{4+} in metal or interstitial lattice sites; adsorption of Ge or Ge compounds; or admixture of Ge minerals (such as the hydroxy-sulfates or hydroxides).

Arsenates, vanadates, phosphates, molybdates, and tungstates. Few data on the Ge contents of these minerals are available. Due to the similarity in ionic radii, it is reasonable to expect some substitution of Ge(IV) (0.39 Å) for As(V) (0.34 Å) in minerals containing tetrahedral AsO_4 groups. FRONDEL and ITO (1957) did in fact observe at least 500 ppm Ge in the arsenates bayldonite, olivenite, and duffite from Tsumeb, and

at least 50 ppm in mimetite and 5 ppm in adamite. DUTRIZAC *et al.* (1985) report 300–400 ppm Ge in "amorphous Zn-Pb-arsenates" from the Apex mine, Utah. Similarly, Ge(IV) may be expected to substitute for V(V) (0.34 Å) and P(V) (0.31 Å) in vanadates and phosphates. FRONDEL and ITO (1957) reported at least 50 ppm Ge in the phosphate pyromorphite, at least 5 ppm in the phosphate tsumebite, and 0.5–5 ppm Ge in the vanadates mottramite and vanadinite from Tsumeb.

A number of synthetic germanates and germanate-phosphates having the apatite structure (common to many arsenates, phosphates, and vanadates) are known, such as $\text{Ca}_2\text{Ce}_3(\text{GeO}_4)_3\text{Cl}$ and $\text{Ca}_3\text{Ce}_2(\text{GeO}_4)_2(\text{PO}_4)\text{Cl}$ (STRUNZ *et al.*, 1960). In these, coupled substitutions occur in the large octahedral metal sites to maintain charge balance. It is reasonable to assume that similar coupled substitutions may occur in natural arsenates, phosphates, and vanadates, so that considerable Ge could potentially be found in these minerals. Lesser substitutions would be expected in molybdates and tungstates, due to the much larger sizes of these ions.

AQUEOUS AND ORGANIC CHEMISTRY

Aqueous chemistry

In dilute (<0.005 m), nearly neutral aqueous solutions, INGRI (1963) found Ge to exist primarily as $\text{Ge}(\text{OH})_4$. In dilute basic solutions, he reported an increase in the proportions of the ions $\text{GeO}(\text{OH})_3^-$, $\text{GeO}_2(\text{OH})_2^{2-}$, and $(\text{OH})_3(\text{Ge}(\text{OH})_4)_3^{3-}$; GAYER and ZAJICEK (1964), however, report mostly H_2GeO_3 and HGeO_3^- in such solutions. In dilute acidic solutions, Ge is presumably present mostly as H_2GeO_3 . DE ZOUBOV *et al.* (1963) give Eh-pH diagrams for the Ge- H_2O system, showing fields for the major aqueous species H_2GeO_3 , HGeO_3^- , and GeO_3^{2-} (found in highly basic solutions) as well as Ge^{2+} , GeH_4 , HGeO_2^- , GeO_2^{2-} (?), and $\text{Ge}_2\text{O}_7^{2-}$ (?). If sulfate or phosphate are present at pH 7–9.5 the ions $\text{GeO}_2(\text{SO}_4)^{2-}$ or $\text{HGeO}_2(\text{PO}_4)^{2-}$ will form; the species H_2GeF_6 and H_2GeCl_6 are also reported from aqueous solutions (GLOCKLING, 1969).

The only available experimental data on various inorganic Ge species in natural waters are given by GOLEVA and VOROB'YEVA (1967). They examined groundwaters from several sulfide ore deposits in the U.S.S.R. that have pH values ranging from 5.9 to 8.3. They found H_2GeO_3 to be the predominate Ge species (always over 80%), with smaller amounts of HGeO_3^- and traces of GeO_3^{2-} (less than $10^{-3}\%$); the mode of analysis was not described. Both HGeO_3^- and GeO_3^{2-} were found to be most abundant in the more basic waters, with HGeO_3^- being particularly abundant (up to nearly 20%) in some waters containing SO_4^{2-} . The Ge contents of waters from various types of ore deposits were found to range from 0.001 to 0.100 ppm, with the highest concentrations occurring at high and low pH values. A similar result was noted by KOGA (1967) and UZUMASA and SEO (1959) at hot springs in New Zealand and Japan. No consistent correlation of Ge with other trace or minor elements was found, including with fluorine.

KRAYNOV (1967) obtained rather different analytical results on some thermal carbonate waters from the U.S.S.R. He found Ge concentrations of 0.012 to 0.200 ppm, with the higher values roughly correlating with higher temperatures. He also found a rough negative correlation with Ca content, and positive correlations with F content in crystalline rocks, and with methane content. Kraynov concluded that Ge will be most concentrated in hot alkaline- and halogen-rich waters that pass through thermally metamorphosed organic-bearing sedimentary rocks.

In the ocean, the concentration of Ge is only about 60 parts per trillion (Table 1), though this represents a substantial enrichment relative to the lithosphere when compared to Si. The Ge to Si ratio (by weight) in the ocean is about 1:43,000, while it is about 1:198,000 for the lithosphere (Si data from MASON and MOORE, 1982). FROELICH and ANDREAE (1981) found the vertical profile of Ge in the ocean to closely follow that of Si, being highly depleted near the surface. The concentrations range from nearly zero picomoles per liter (pM) at the surface to 100–115 pM at depth, varying little with geographic location. This vertical distribution is thought to result from the uptake of Si (and accidentally Ge) by siliceous organisms living near the surface, whose remains sink to form siliceous ooze. Limited data indicate that fresh water contains considerably less Ge than does the ocean, suggesting that the Ge content of marine siliceous sedimentary beds could reflect the varying input of rivers, and thus climatic change, over geologic time (FROELICH and ANDREAE, 1981).

In addition to dissolved inorganic Ge in the ocean, LEWIS *et al.* (1985) report the presence of methylated Ge species that do not vary in concentration with depth. These species are thus apparently not involved in biological activity within a particular oceanic zone, or are so stable in solution that complete mixing takes place. The species monomethylgermanium and dimethylgermanium are found in average concentrations of 326 and 97 pM, respectively, varying little with location in the open ocean. River and rainwater are found to contain no more than a few pM of these compounds. The origin and geochemical behavior of these species remain unknown.

Organic geochemistry

Literature on the organic chemistry of germanium is extensive (a review is given by GLOCKLING, 1969), though very little of it is concerned with natural processes. The frequent concentration of Ge in coal has, however, prompted several studies.

Plants apparently absorb and concentrate Ge both from the air and the soil (KABATA-PENDIAS and PENDIAS, 1984). Even low concentrations, however, are found to be highly toxic, at least to higher plants (SANKHLA and SANKHLA, 1967). This implies that the high Ge content of coal did not arise from the activities of living plants. The distribution of Ge in coal, being higher near the top and bottom of beds, and being particularly high in isolated lignitized logs, also indicates that Ge was introduced sometime after burial of the plant material.

As mentioned, many studies have shown Ge to be concentrated in the organic matter of coal rather than in admixed minerals. In particular, Ge is concentrated in the vitrain fraction and in lignite. These are materials generally thought to be derived from the woody parts of plants. Vitrain is one of the least sorptive fractions of coal, indicating that Ge concentration occurs during the peat or lignite stages of coal formation, before vitrain has formed (MANSKAYA and DROZDOVA, 1968). RATYNSKIY *et al.* (1966) showed that hard coals, containing large amounts of vitrain, indeed absorbed far less Ge from aqueous solutions than did lignites.

Experimental studies have found Ge to be absorbed by peat and to form stable organic compounds, particularly with the humic acids abundant in peat (MANSKAYA *et al.*, 1961, 1972). MANSKAYA and DROZDOVA (1968) found 77.5–83.9% of the Ge in lignite samples to be tightly bound, with the rest weakly adsorbed, probably on reactive groups; in bituminous coal samples, 97.8–100% of the Ge was found to be tightly bound. Subsequent experiments (MANSKAYA *et al.*, 1972) showed that Ge is absorbed by humic acids in peat and then forms stable complexes with lignin-derivative compounds containing orthodiphenol and orthohydroxyquinoid groups. In lignites, Ge will also be absorbed, forming chelates with similar lignin-derivatives. During coalification, highly condensed aromatic

organogermanium compounds will form; these will have increased stability due to a greater number of Ge-C bonds.

DISCUSSION, INCLUDING THERMODYNAMIC AND EXPERIMENTAL CONSTRAINTS, AND CONCLUSIONS

Germanium is observed to be enriched in the following geological environments:

1. Native iron-nickel, both meteoritic and terrestrial.
2. Sphalerite-rich sulfide deposits, particularly those in sedimentary rocks. Ge is concentrated in sphalerite; it rarely occurs as germanate inclusions within sphalerite (metamorphosed deposits).
3. Copper-rich sulfide deposits, particularly those in sedimentary rocks. Ge forms its own sulfide minerals or is concentrated in sulfosalts.
4. Iron oxide deposits. Ge may be concentrated in hematite, goethite, or magnetite.
5. Oxidized zone of Ge-bearing sulfide deposits. Ge occurs in hydroxides, oxides, hydroxy-sulfates, and arsenates.
6. Pegmatites, greisens, and skarns. Ge is enriched primarily in topaz, garnets, and micas.
7. Coals and lignitized wood. Ge is bound to the organic compounds.

In addition, Ge is noted to be substantially depleted in carbonate rocks, to be enriched in some hot springs, and to have nearly the same abundance in silicic and mafic igneous rocks.

This observed pattern of distribution potentially could be explained by using (1) thermodynamic and kinetic data, (2) experimental phase equilibria studies, and (3) crystal and fluid chemical information. Thermodynamic data are scarce, though values for the free energy of formation have been published for two geologically relevant Ge compounds: GeS_2 and GeO_2 . Data for GeS have also been published, though as mentioned, this compound appears to be metastable under observed conditions. Phase diagrams using these data are shown in Fig. 2.

A few experimental studies have investigated the behavior of Ge in melts. These studies have found Ge to be highly siderophile both in the iron-olivine system and in the Fe-FeS system (both at 900°C, 500 bars) (WAI *et al.*, 1968; WAI, 1974). Iron metal can apparently contain up to 20 atomic percent Ge (VIAENE, 1972). These results are in accord with the observed enrichment of Ge in iron meteorites and in the Disco Island native iron. Disco Island provides a natural high-temperature experiment, displaying the partitioning of Ge into metallic iron in a cooling basaltic melt. Some of the Ge at this locality may have been derived from coal incorporated into the basaltic melt, which acted to reduce the iron. Terrestrial iron not associated with coal, such as josephinite, should be analyzed for Ge to see if it is also Ge-enriched. Reasons for the highly variable Ge content observed in iron meteorites are not clear; WAI (1974) proposed that some low-Ge iron

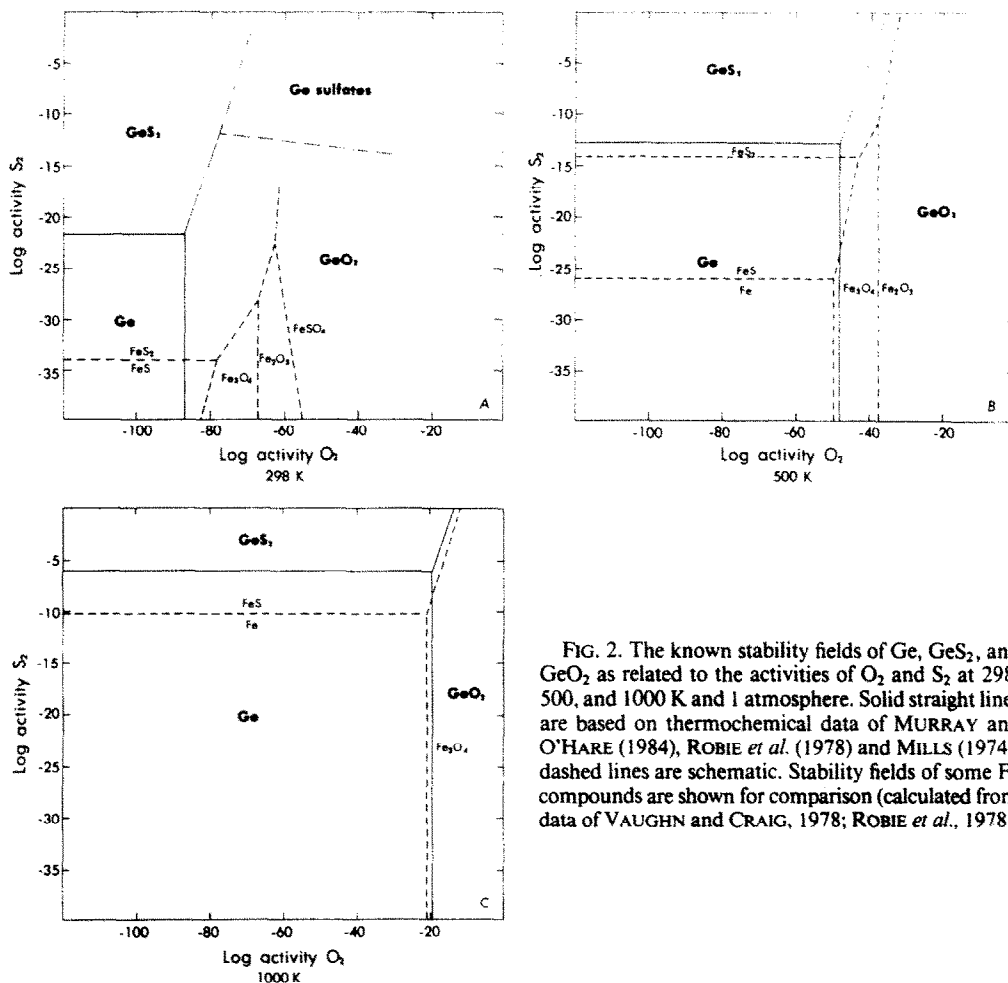


FIG. 2. The known stability fields of Ge, GeS₂, and GeO₂ as related to the activities of O₂ and S₂ at 298, 500, and 1000 K and 1 atmosphere. Solid straight lines are based on thermochemical data of MURRAY and O'HARE (1984), ROBIE *et al.* (1978) and MILLS (1974); dashed lines are schematic. Stability fields of some Fe compounds are shown for comparison (calculated from data of VAUGHN and CRAIG, 1978; ROBIE *et al.*, 1978).

meteorites may have resulted from the reduction of troilite, which generally has a low Ge content.

CAPOBIANCO and WATSON (1982) found Ge to closely follow the behavior of Si in synthetic basaltic melts: Ge is selectively partitioned into the melt during crystallization of forsterite, to the same degree as Si at one atmosphere pressure. Thus, Ge enrichment will occur in magmas crystallizing olivine, though at low pressures Ge/Si remains nearly constant in the melt. This pattern was observed by ARGOLLO and SCHILLING (1978) in a suite of volcanic rocks from Hawaii: late fractionates are enriched in Ge and Si, though Ge/Si remains nearly constant in all the rocks. At high pressures Si goes into forsterite more readily than does Ge (CAPOBIANCO and WATSON, 1982), due to the smaller size of the Si atoms.

It is remembered, however, that Ge is generally observed to be enriched in olivine and pyroxene relative to quartz and feldspar. Thus, early-formed mafic rocks crystallize from relatively low-Ge magmas, though the crystallizing minerals will have relatively high Ge partition coefficients; in later granitic differentiates the reverse situation prevails. This will result in the bulk Ge

content of mafic and granitic rocks being roughly equal, as is observed. Fractional crystallization will tend to concentrate Ge in late hydrothermal fluids, accounting for the enrichment of Ge in pegmatites, greisens, skarns, and hydrothermal sulfide ore deposits.

Though little information is currently available on the aqueous chemistry of Ge (previously discussed), some features seem probable in natural hydrothermal systems. The enrichment of Ge in topaz and to a lesser extent in fluorite, micas, and F-bearing hot springs suggests the presence of aqueous F-bearing Ge species, perhaps H₂GeF₆ or related molecules. The compound GeF₄, for example, is known to be highly volatile (ROCHOW and ABEL, 1975). The enrichment of Ge in hydrothermal sulfide deposits suggests the possibility that S-bearing Ge species may also form in some hydrothermal fluids. This is substantiated by the Ge-enrichment of some S-rich hot springs, such as Sulfur Bank, California, where up to 0.2 ppm Ge was found in the water (WHITE and ROBERSON, 1962).

The distribution of Ge in unmetamorphosed sulfide ore deposits can be divided into two major categories: (1) those where Ge is concentrated in amounts up to

3000 ppm in sphalerite, and (2) those where Ge forms its own sulfide minerals (such as renierite and germanite), or substitutes for metal atoms in sulfosalts such as enargite or for tin in tin sulfides and sulfosalts. As discussed previously, limited experimental data indicate that Ge enters ZnS only in low to moderate sulfur activity environments, with Ge possibly substituting for both Zn and S (MALEVSKIY, 1966). Where sulfur is more abundant, Ge will not readily substitute in ZnS but will form its own sulfides if the Ge concentration is sufficient. At lower Ge concentrations it will substitute in tetrahedral metal sites in sulfosalts. This substitution apparently occurs most readily for arsenic and tin. The behavior of Ge also appears dependent on the activities of Cu and Ag, elements essential in forming the predominant Ge-sulfide minerals (Table 2). Thus, Ge will tend to be concentrated in sphalerite in relatively low- to moderate-sulfur environments, while forming its own sulfide minerals or entering sulfosalts in higher-sulfur environments (or in high Cu or Ag environments).

Germanium in hydrothermal fluids is probably derived from two major sources. First, as mentioned, Ge may be concentrated through fractional crystallization, remaining in the residual igneous fluids. The other possibility is that Ge is picked up from the country rocks, particularly from those containing organic material, by migrating fluids. The frequent association of Ge-bearing sulfide deposits with organic-bearing sedimentary host rocks (e.g. Mississippi Valley, Ruby Creek, Kipushi, Tsumeb, St. Salvy) may be due in part to this mechanism.

The chalcophile properties of Ge are probably limited to sulfur-rich hydrothermal systems. WAI (1974), for example, found Ge to be highly lithophile in the pyrrhotite-olivine system. As pyrrhotite has only octahedral metal sites, however, this is not a good test for the behavior of Ge in silicate melts where sulfides having tetrahedral metal coordination are present. A better indication of the lithophile nature of Ge in oxygen-rich melts and solutions is that the Gibbs free energy of reaction is strongly negative at all temperatures for the equation $\text{GeS}_2 + \text{O}_2 = \text{GeO}_2 + \text{S}_2$: -372.9 kJ/mol at 298 K, -337.5 kJ/mol at 500 K, and -257.0 kJ/mol at 1000 K (calculated from data of MILLS, 1974 and ROBIE *et al.*, 1978). Evidence is also provided by relations in the Pyrenees sphalerite deposits (JOHAN *et al.*, 1983). In these deposits, sphalerite was regionally metamorphosed, presumably at a lower activity of S_2 and higher activities of O_2 and SiO_2 than when it originally formed. The Ge in this case apparently left the sphalerite and went into oxides and silicates, even forming germanate equivalents of silicates.

The enrichment of Ge that is sometimes observed in sedimentary iron deposits and in the oxidized zones of iron-bearing sulfide deposits is probably related to the ability of iron hydroxides to incorporate Ge as they are precipitated from aqueous solutions. BURTON *et al.* (1959) found 95% of dissolved Ge to be precipitated

from sea water by $\text{Fe}(\text{OH})_3$, and PAZENKOVA (1967) found 93% of dissolved Ge to be precipitated by $\text{Fe}(\text{OH})_3$ in waters having a pH greater than about 6; less Ge was incorporated in more acidic waters. The frequent enrichment of Ge in magnetite from a variety of environments probably reflects the solid solution between magnetite and the closely related mineral brunogeierite, Fe_2GeO_4 .

In the oxidation of Ge-bearing sulfide ore deposits, Ge is found to go into oxides, hydroxides, and hydroxy-sulfates, sometimes forming its own minerals. Germanium becomes particularly enriched in iron hydroxides and oxides such as goethite, hematite, and stottite.

A schematic interpretation of the distribution of germanium in various geologic environments, as related to the activities of S_2 and O_2 , is shown in Fig. 3. This diagram should be compared with the limited available quantitative data shown in Fig. 2. The qualitative relationships shown in Fig. 3 require additional observational testing, which should lead to further understanding of germanium geochemistry.

The data and conclusions presented above suggest several geological and mineralogical indicators that could be useful in the exploration for new germanium deposits. Germanium is most likely to be highly concentrated in Cu-rich portions of hydrothermal sulfide deposits in sedimentary carbonates, particularly in those containing coal or coal-like organic material. The presence of high concentrations of As, Sb, Sn, or possibly V in such ores also increases the probability of Ge being present. Renierite, germanite (both of which are often mistaken for bornite or "orange bornite"),

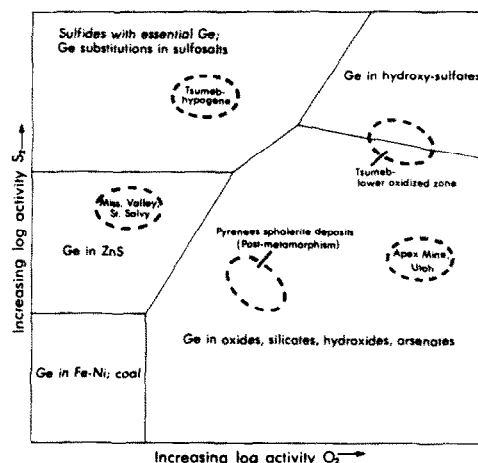


FIG. 3. Schematic diagram showing the proposed behavior of germanium in various geologic environments as related to the activities of O_2 and S_2 (at approximately 300 to 600 K and 1 atmosphere). It is noted that a high activity of Cu or Ag will tend to promote the formation of Ge-bearing Cu or Ag sulfides even at low to moderate S_2 activities. This diagram is based on experimental data discussed in the text, thermochemical data as presented in Fig. 2, and on the observed natural distribution of Ge.

brriartite, argyrodite, enargite, and tin sulfides and sulfosalts are the chief hosts for Ge in these ores. Germanium should also be looked for in epigenetic low-temperature sphalerite deposits in carbonate or shale host rocks, particularly in those containing organic material. The Ge in Zn and Pb-Zn deposits could, in some cases, make marginally non-economic deposits feasible to mine.

Germanium is sometimes enriched during supergene processes, becoming particularly concentrated in iron oxides and hydroxides, and more rarely in arsenates and hydroxy-sulfates. Due to this supergene enrichment, the limonite and related material of oxidized Ge-bearing Cu-Fe sulfide deposits, which is generally considered as waste, may actually contain high concentrations of Ge that could greatly increase the economic value of such deposits.

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