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Silver Queen
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12 May 1987

Adolf A. Petancic, President
Houston Metals Corporation
910-800 West Pender Street
Vancouver, B.C. V6C 2V6
Canada

Dear Mr. Petancic,

Enclosed is my report on the economic geology of gallium and germanium that you requested. Please call me if you have any questions.

The reports that you sent on the Silver Queen Mine indicate that it is a volcanic-hosted polymetallic deposit similar to the Equity Silver deposit. It also appears similar to the Lepanto deposit (Philippines) and the Bor deposit (Yugoslavia), though with less copper. Both Lepanto and Bor contain fairly high Ge and moderate Ga concentrations. Such deposits tend to have high Ge grades associated with tennantite-tetrahedrite and other Cu or Ag sulfosalts, and with organic matter.

To develop an effective exploration and development strategy, and to design optimal extractive metallurgical processes, it is essential to understand the distribution of the metals in the ore. I could be of assistance to you in this task by doing petrologic and mineralogic analyses of ore samples, paying particular attention to locating the sites for Ge, In, Ag, and Ga. I have available to me a wide variety of analytic tools, including x-ray diffraction, scanning electron microscopy with energy dispersive x-ray elemental analysis, petrographic and ore microscopes, and others. I have several years experience in identifying Ge- and Ga-bearing phases and in studying a wide variety of ore deposits. My usual consulting rate is US$400. per day, plus incurred expenses, if any. Depending on the number and complexity of the samples analyzed, probably 5-12 days of work would be required. Representative ore samples should be sent, preferably with polished thin sections (though I can have these prepared).

As you certainly know, many mining ventures do not succeed due to poorly designed metallurgic processes that were based on incomplete or incorrect interpretations of the mineralogy of the ore; I try to help avoid these problems. I also keep in close touch with developments in the markets for Ge, Ga, and In, and I could keep you

5/12/87

informed on any major developments.

Best wishes on your success with the Silver Queen Mine!

Sincerely yours,

Lawrence R. Bernstein, Ph.D.
Geologist

GALLIUM AND GERMANIUM
EXPLORATION OPPORTUNITIES

Lawrence R. Bernstein, Ph.D.

Mineral Search
380 Willow Road, Menlo Park, CA 94025

May, 1987

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I. INTRODUCTION

History

Gallium and germanium were both discovered roughly 100 years ago, and for many years were considered exotic materials of no practical use. Gallium, atomic number 31, is a semi-metal with a melting point of 30°C, just above room temperature. Germanium, atomic number 32, is a semiconducting metalloid that has a gray color, metallic luster, and conchoidal fracture (see Appendix G for further data on Ge and Ga).

Germanium - The view of germanium changed dramatically in 1948, when the element was used to make the first transistor. Demand for germanium increased greatly in the 1950's and 1960's as solid-state components replaced bulky, high-power, and expensive vacuum tubes. In the late 1960's and 1970's, however, the vastly more abundant silicon gradually replaced germanium as the predominant semiconductor, and the demand for germanium decreased. Electronic uses of germanium have continued to decline, now accounting for less than 2% of the semiconductor market, though for certain high-frequency applications germanium is still required. It is also being increasingly used in gamma-ray and x-ray detectors.

In the early 1980's, demand for germanium again began a rapid increase, due primarily to its use in infrared optical components. Germanium, as well as some Ge alloys and glasses, is transparent to infrared radiation having wavelengths longer than 2 micrometers. This property allows it to be fashioned into lenses and windows in equipment for night-viewing, medical diagnosis, satellite mapping, and guidance and sighting systems for weapons and aircraft. The large military demand for such equipment caused Ge to be declared a U.S. strategic material in 1984. Other uses for Ge, including chemical catalysts, photovoltaics, medicines, and fiber optics, are now increasing, as will be discussed.

Gallium - In the late 1950's, the compound GaAs was found to have highly desirable electronic properties: it is 5 to 7 times "faster" electronically than Si or Ge, and can function at much higher radiation and temperature levels. It is also an excellent photovoltaic material. However, it has proven extremely difficult to grow large, high-quality single crystals of GaAs, as would be required for the mass-production of electronic components. Also, GaAs is extremely brittle and difficult to work with. As a result, the use of GaAs has been increasing very slowly and now represents less than 1% of the semiconductor market. Related compounds, such as

GaAlAs and GaP, have been used extensively in light emitting diodes (LEDs) and lasers. These lasers are becoming increasingly important in fiber-optic devices and compact disc players, among other uses. Although exact estimates of the amount of GaAs to be used in the future are very hard to make, there is no doubt that usage will increase at least several fold by the end of the century, as GaAs fabrication technology improves.

Economic Geology

The relatively low worldwide usage of Ga and Ge (roughly 55 tons Ga and 140 tons Ge in 1986) has allowed these elements to be produced at low levels, exclusively as byproducts. Gallium has traditionally been obtained as a byproduct of bauxite (50-80 ppm Ga), and to a lesser extent sphalerite (100-10,000 ppm Ga), refining. As the price of Ga has gradually declined from 1963 until 1984, most of the major aluminum companies (including all the U.S. producers) have suspended Ga recovery, waiting for higher prices. Prices have firmed in the last two years and demand may indeed soon exceed the supply.

Germanium has traditionally been produced from sphalerite (100-3000 ppm Ge). In the 1950's, some production was obtained from coal fly ash and some production also came until recently from the Cu-Pb-Zn mines at Tsumeb, Namibia and Kipushi, Zaire (both now exhausted of Ge ore). Continued production of Ge is now in some doubt, due to low Zn prices and the possible closure of large mines in Tennessee, Canada and Europe that contribute much of the world's Ge supply.

If, as generally predicted, demands for Ga and Ge continue to rise rapidly, the current sources will soon become insufficient. It should also be noted at this point that many uses, particularly for Ge, are awaiting larger, more consistent supplies and thus lower prices. The opportunities are now present to explore for new, higher-grade deposits of Ga and Ge that would help fulfill the rising demands and would also compete successfully with the traditional low-volume, high-cost sources. Based on my geochemical and geological research, I feel that such large high-grade deposits can be found in the U.S. and other countries.

2. GEOCHEMISTRY AND GEOLOGY

Germanium

Germanium, just below silicon in the periodic table, was long thought to behave identically to silicon in nature. The geochemist Victor Goldschmidt used Ge as an example of an element that would always be masked by a much more abundant and chemically similar element (Si). Subsequent studies have shown, however, that while much of the earth's Ge is dispersed in silicates in amounts of a few ppm, Ge behaves distinctly from Si in many environments. Germanium can be lithophile, chalcophile, siderophile, and organophile in different circumstances. Specifically, Ge is particularly enriched in the following geologic environments (its mean crustal abundance is about 1.5 ppm):

1. Native iron-nickel, both meteoritic and terrestrial (as much as 2000 ppm).
2. Sphalerite-rich sulfide deposits, particularly those formed at moderate to low temperatures in sedimentary rocks. Ge is concentrated in sphalerite (as much as 3000 ppm); 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, substituting for As, Sb, or Sn (as much as 1%).
4. Iron oxide deposits. Ge may be concentrated in hematite, goethite, or magnetite (as much as 100 ppm, possibly much more).
5. Oxidized zone of Ge-bearing sulfide deposits. Ge occurs in hydroxides, oxides, hydroxy-sulfates, and arsenates; it is particularly enriched in hematite and goethite (as much as 1%).
6. Pegmatites, greisens, and skarns. Ge is enriched primarily in topaz, garnets, and micas (as much as a few hundred ppm).
7. Coals and lignitized wood. Ge is bound to lignin-derivative organic compounds (as much as 2000 ppm).

The geochemistry of Ge is more thoroughly discussed in Appendix A.

The most favorable environments for large high-grade deposits are numbers 3 and 5 listed above, which will be described in more detail in the section on Exploration Targets (examples I, II, and III).

"Orange Bornite" - It is important to note that two germanium-rich minerals, germanite and particularly renierite, have long been overlooked or misidentified in sulfide ore samples. Both minerals are Cu-Ge-As-Fe sulfides, renierite containing 5-8% Ge and germanite 7-14% Ge. Both minerals closely resemble bornite in polished section, having similar color and relief. When bornite is present in the same section, renierite and germanite are seen to be more orange and slightly harder than bornite. Renierite is somewhat more orange than germanite, which has a pinker color. In distinguishing these minerals from bornite, it is also useful to note that they do not readily tarnish, while bornite quickly darkens in color. In hand samples, renierite resembles pyrrhotite in color, and is slightly magnetic, adding to the possible sources of confusion.

These facts are important, as there are many references to "orange bornite" in the literature. I have found that about 90% of these turn out to be renierite (sometimes with germanite), while most of the rest are mawsonite, a related mineral that contains tin instead of germanium. A large proportion of high-grade copper sulfide ores from around the world, particularly those with substantial As, are found to contain renierite and germanite. Further information on renierite and on some of the localities where it is found are given in Appendix B.

Gallium

Like Ge, Ga was long thought to be masked by a chemically similar element (Al), being dispersed in small quantities through the earth's crust. Gallium does, in fact, show somewhat less diverse geochemical behavior than germanium, though its behavior in many ways parallels that of Ge. In general, rocks containing high amounts of Al will also contain relatively high amounts of Ga. Thus, Ga is enriched in bauxite, clays, and aluminous igneous rocks. Gallium can also be chalcophile, siderophile, and organophile, though all to lesser degrees than Ge. The major environments where Ga is enriched are (the mean crustal abundance is about 17 ppm):

1. Native iron-nickel (as much as a few hundred ppm Ga).
2. Sphalerite-rich sulfide deposits, particularly those formed at low to moderate temperatures and in sedimentary host rocks (as much as 1% Ga).
3. Cu-rich sulfide deposits, particularly those in sedimentary rocks. Ga occurs in gallite, renierite, germanite, chalcopyrite, and other sulfides and sulfosalts, mainly substituting for Fe.
4. Oxidized zone of Ga-bearing sulfide deposits. Ga occurs mostly in jarosite-group minerals and limonite (as much as 0.7%).

5. Bauxite, particularly that derived from nepheline syenite and related alkalic rocks. Ga substitutes for Al (as much as 100 ppm).

6. Pegmatites, skarns, and greisens. Ga is most concentrated in micas and albite, substituting for Al (as much as 200 ppm).

7. Sodium-metasomatized granitic and syenitic rocks, associated with Zr, Ta, Nb, Be, and REE. Ga is most concentrated in albite (as much as 1500 ppm) and, to a lesser extent, in micas.

8. Phosphate-rich shales, such as the Phosphoria Formation (as much as 100 ppm). The reasons for the enrichment associated with phosphate are not understood, but may be related to the organic content.

The potential high-grade Ga deposits would be numbers 3 (certain zones) and 4, described later as exploration targets I, II, and III. Numbers 2, 5, and 8 represent extremely large, low-grade reserves that will ultimately become important if demand increases very greatly.

3. GERMANIUM AND GALLIUM EXPLORATION TARGETS

Introduction

Gallium has traditionally been produced as a byproduct from bauxite and sphalerite processing; germanium has been produced chiefly as a byproduct from sphalerite processing. As discussed, these sources are not expected to meet rising demands at current prices, and new primary sources are required. My research has found that large deposits containing relatively high grades of Ge and Ga occur in environments distinctly different than the traditional low-grade ores; these exploration targets (as well as the traditional ones) are summarized below. Major principles in locating large, new, higher-grade deposits include:

1. Association with high-grade Cu ore containing a high content of As.
2. Affinity of Ge for Sn and As.
3. Affinity of Ge for lignin-derivative organic materials.
4. Affinity of Ga for Al.
5. Affinity of Ge and Ga for Fe oxides and hydroxides, including supergene enrichment in such materials at moderate to high pH.

The most promising targets for large, new deposits that contain high grades of Ge and Ga are numbers III, I, and II below, in roughly that order.

I. Carbonate-hosted Cu-As±Pb±Zn±Sb sulfide deposits

Host rocks: Dolomite (diagenetic and hydrothermal), limestone, shale, siliceous dolomite, calcareous shale

Depositional environment: Intertidal marine, reducing environment, hypersaline

Tectonic settings: Intracontinental rift, passive margin shelf or rift

Deposit form: Lenses, breccia pipes, fractured fault zones; some replacement

Alteration: Dolomitization. Not usually distinctive or obvious

Metals concentrated: Cu, As, Pb, Zn, Ge, Ga, Sb, Co; lesser Ag, V, U, W, Bi, Ba

Characteristic ore minerals: pyrite, chalcopyrite, bornite, chalcocite, tennantite-tetrahedrite, renierite, germanite, sphalerite; commonly carrollite-linnaeite, enargite

Other features: Much pyrite appears to be early, possibly diagenetic. Hard, black organic material generally present within ore

Germanium-gallium distribution: Ge is usually concentrated in renierite, $Cu_{10}(Zn_{1-x}Cu_x)(Ge_{2-x}As_x)Fe_4S_{16}$ (5-8% Ge); germanite, $Cu_{11}Ge(Cu,Zn,Fe,Ge,W,Mo,As,V)_{4-6}S_{16}$ (7-14% Ge); and briartite, $Cu_2(Fe,Zn)GeS_4$ (18% Ge). Gallium is most concentrated in renierite and germanite (up to 1% Ga) and gallite, $CuGaS_2$ (34% Ga). These minerals can be locally concentrated in Ge-Ga-rich zones, as at Tsumeb, Namibia and Kipushi, Zaire, where thousands of tons of such high-grade Ge-Ga ore were found. More commonly, the minerals are disseminated in small, commonly microscopic, grains through Cu-rich sulfide ore. Renierite and germanite have often been mistakenly called "orange bornite", and have thus been overlooked in many deposits.

In these deposits, Ge also can be concentrated in enargite, tetrahedrite and other sulfosalts, and to a lesser extent in sphalerite (all up to 500 ppm). Gallium is sometimes concentrated in chalcopyrite (rarely up to 1%).

Ge-Ga grades: Up to 5-7% Ge and 0.5% Ga in high-grade zones; most ore is 50-500 ppm Ge and 10-200 ppm Ga.

Examples: Tsumeb, Namibia; Kipushi, Zaire; Ruby Creek, Alaska

Extractive metallurgy: Processing of complex polymetallic ores is difficult but is greatly facilitated by extensive flotation circuits. The Pb-Cu-Zn-As-Ge ore at Tsumeb, Namibia, provides an example of how processing has been done (see Figure 1). In summary, the ground ore was first treated chemically and floated to separate sphalerite from Pb-Cu-Ge ore. The Ge- and Ga-bearing minerals (germanite and renierite) were floated off using lime and sodium dichromate. Separation of renierite, which is magnetic, was also accomplished by use of Frantz ferro filters. Germanium recoveries were probably less than 50% at this stage, due to loss of Ge-minerals interlocked with other minerals, and the non-magnetism of germanite. At Tsumeb, the Ge concentrates were processed in five major steps: (1) a low temperature roast to remove arsenic and to oxidize the other metals; (2) sulfuric acid leaching; (3) evaporation of the solution to a sludge; (4) chlorination and distillation of the sludge to produce $GeCl_4$; and (5) hydrolysis of $GeCl_4$ to GeO_2. These processes were developed in the 1950's and early 1960's, and little research has been conducted subsequently. Modern methods, including solvent extraction using organic chemicals (discussed further under sphalerite deposits), could greatly increase recoveries of Ge and Ga at lower costs; it will, however, be necessary to set up research programs to adjust these techniques to particular ores.

Unfavorable points: Very few Ge and Ga analytical data are available from these ores. Although a few high-grade zones perhaps could be mined primarily for Ge and Ga, in general these ores would produce Ge and Ga only as byproducts.

Favorable points: As Ge and Ga usually have not been searched for in such deposits, the potential is great. Renierite and germanite, as mentioned, have often been misidentified and overlooked. The production of Ge and Ga could make a marginally economic copper mine highly profitable.

II. Polymetallic Igneous Hosted Deposits

This category comprises many types of deposits, including enargite-bearing porphyries and associated veins (as Butte), marine volcanogenic Cu-Zn-Pb deposits (Kuroko type), and polymetallic granitic-hosted deposits (as Freiberg, Germany and Jamestown, Colorado). Such deposits may or may not have high concentrations of Ge and Ga; the favorable indicators for Ge and Ga are given below.

Indicator elements: High Cu and As; generally high Ag, Sb, Au, Bi, V, Mo, Fe, Ba, Te, Sn, W; sometimes Au

Characteristic minerals: Chalcopyrite, bornite, tennantite-tetrahedrite, enargite, galena, sphalerite, complex Pb-Ag-Bi sulfosalts, renierite, germanite, argyrodite, fluorite, barite

Germanium-gallium distribution: Ge is generally concentrated in enargite and sulfosalts, up to roughly 5000 ppm. Renierite or argyrodite, Ag_8GeS_6 (6.5% Ge), commonly are present, generally as small disseminated grains. Ge is particularly concentrated in tin sulfosalts (commonly over 1% Ge), if any are present. Ga is mainly concentrated in renierite and germanite (up to 1%), sometimes chalcopyrite (up to 1%), enargite and sphalerite (few hundred ppm).

Ge-Ga grades: Most ore would average 50-500 ppm Ge and 10-100 ppm Ga; some much higher-grade zones may be present and would add to the attractiveness.

Extractive metallurgy: Similar to that for carbonate-hosted deposits, described above

Unfavorable and favorable points: Same as for carbonate-hosted deposits, described above

III. Oxidized Ge- and Ga-bearing Sulfide Deposits

These are oxidized versions of the carbonate-hosted and igneous-hosted deposits previously described. Only one economic deposit of this type of currently known - the Apex Mine in southwest Utah. The ore at this mine consists of goethite, limonite, hematite, jarosite, azurite, malachite, conichalcite, and several other metal oxides, carbonates, arsenates, and sulfates. It forms an irregular chimney-like body (or bodies) in breccia, gouge, and fissures associated with steeply dipping subparallel fault zones in limestone. The ore was derived from primary copper- and arsenic-rich sulfides, probably including renierite, germanite and gallite. The geology of this deposit is further discussed in Appendix C, and some statistics concerning the Apex Mine are given in Appendix F.

Supergene enrichment of Ge and Ga is, in general, expected (see Appendix H). Experimentally, Ge is 95% precipitated from water having a pH greater than 6 by ferric hydroxide; less Ge is precipitated at lower pH values. Ga apparently behaves similarly, and can also substitute for Al and Fe^{3+} in jarosite group minerals. The dependence of precipitation on pH suggests that more enrichment may occur in alkaline carbonate rocks than in most igneous rocks.

Chemical and geologic indicators for these deposits will be essentially the same as for the primary deposits that they are derived from (described above).

Indicator elements: High Cu and As; generally high Ag, Sb; lesser Ba, Bi, Co, Te, V, Mo, W, Au, Sn, Hg

Deposit form: Gossan; replacements of veins, lenses, breccia pipes

Germanium-gallium distribution: Ge is concentrated in hematite (up to 1%), goethite (up to 0.54%), and limonite (up to 0.5%). Ga is concentrated in limonite (up to 1%) and jarosite-group minerals (up to 0.7%). At Tsumeb, oxidized zones in the sulfide ore contain very rich Ge and Ga oxides, hydroxides, and hydroxysulfates.

Ge-Ga grades: Ore would be 0.05-0.5% each for Ge and Ga

Extractive metallurgy: A major advantage of these ores is the projected low expense for Ge and Ga recovery: perhaps only a few dollars per kilogram of each metal. At the Apex Mine, the process starts with a multi-stage sulfuric acid leach. Germanium is precipitated as GeS_2 by H_2S, and is later leached and oxidized to produce GeO_2, which is the marketable product. Gallium is precipitated by ammonia as $Ga(OH)_3$, which is ultimately refined to 99.9% Ga metal by a proprietary electrolysis method. A flow sheet for ore processing at the Apex Mine is shown in Figure 2. Recoveries from the ore are predicted to be at least 79% for Ga, 82% for Ge, 95% for Cu, 94% for Zn, and 91% for Ag. Carbonate gangue mixed with the ore neutralizes some of the sulfuric acid during leaching, and a flotation step may be added to separate out carbonate minerals. Lower than expected Ge recoveries will require modifications to the process, which have not yet been fully implemented.

Unfavorable points: Very little analytical data is available, and much preliminary analytical sampling work is required for exploration.

Favorable points: These are very favorable targets for several reasons: (1) Ge and Ga have not been looked for in most such deposits, which are common; (2) Fe-rich gossan material is generally discarded during mining operations, and millions of tons are present as surface tailings; (3) Ge and Ga concentrations can be very high and can make primary Ge and Ga extraction profitable; and (4) recovery of Ge and Ga from these ores should be inexpensive and efficient.

IV. Tin Deposits

All tin deposits are potential Ge producers, due to chemical similarities between Sn and Ge. Hypogene, coarsely-crystallized cassiterite generally contains 10-3000 ppm Ge, whereas hydroxyl and fibrous varieties ("varlamoffite" and "wood tin") commonly contain over 1% Ge. Tin sulfides and sulfosalts, such as those from some of the Bolivian mines, also commonly contain over 1% Ge. Considering the current tin crisis, Ge extraction could greatly increase the profitability of tin ores.

V. Bauxite Deposits

Bauxite will continue to be a large, important reserve for Ga. The Ga concentrations, substituting for Al, range from a few ppm to over 100 ppm, with higher values recorded from weathered alkalic rocks, such as nepheline syenite. Although Ga concentrations are relatively low, if Ga demand increases, the enormous volume of Al refining could make byproduct Ga extraction profitable. However, if significant new Ga sources come into production, the Ga price could be held too low for profitable extraction from bauxite.

Extractive metallurgy: In the Bayer process, bauxite is decomposed in a strong solution of sodium hydroxide, which puts sodium aluminate into solution. Gallium in the bauxite also goes into solution. The solution is partially evaporated, seeded with alumina trihydrate, and cooled, which precipitates out aluminum hydroxides and hydrates. Nearly all of the gallium remains in the spent solution, which is recycled with new ore. After several cycles, the gallium builds up to an equilibrium concentration of about 0.2 gram Ga per liter.

Several methods are available for recovering Ga from the spent Bayer liquor, which still contains considerable Al, Fe, V, and other elements. In Alcoa's Frary process (patented in 1952), most of the Al is first precipitated out, and all the remaining Ga and Al are finally precipitated by neutralizing the solution with acid. The precipitate is redissolved in a strong sodium hydroxide solution, and the Ga is extracted by electrolysis using stainless steel anodes and cathodes. In the de la Breteque process (used by Alusuisse, currently the world's chief Ga producer; originally patented in 1957), Ga is electrolyzed directly from the spent Bayer liquor using an agitated mercury cathode. The Ga must later be separated from the Hg by digestion and electrolysis. More recently (1976), a simpler and less expensive process was developed by Shalavina et al. (U.S. patent 3,988,150) whereby Ga is extracted from the spent Bayer liquor by cementation onto a liquid alloy consisting of about 99.5% Ga and 0.5% Al. A slight electric potential is maintained during the recovery, which separates the Al from the precipitated Ga. Recoveries of 99% were experimentally obtained, producing 99.99% Ga. Further research should produce still less expensive and more efficient processes.

VI. Iron Oxide Deposits

The known siderophile nature of Ge (and to a lesser extent Ga), plus the example of the Apex Mine, suggest that iron oxide deposits in general could be Ge–Ga exploration targets. Experimentally, there is a complete solid-solution between magnetite, $Fe^{2+}Fe^{3+}_2O_4$, and brunogeirite, $Ge^{4+}Fe^{2+}_2O_4$; this solid-solution may exist in nature. Hematite and goethite from the Apex Mine have up to 1% Ge, due to a similar solid-solution (Appendix H). Ga can substitute for Fe^{3+} in many minerals, particularly hydrothermal magnetite, though this substitution has been little studied.

Iron oxide deposits with the highest potential would probably be: (1) late-stage hydrothermal ores; and (2) sedimentary ores in an organic-rich environment, with high As and probably Cu, Ag, and V. These possibilities have received little if any consideration, though great potential is present for Ge and Ga byproduct production from many iron ores.

VII. Sphalerite Deposits

These have been traditional sources for both Ge and Ga, and are the best known by geologists. The most favorable indicators for high Ge and Ga are:

(1) Sedimentary environment, particularly carbonates
(2) Low- to moderate-temperature hydrothermal deposition
(3) Presence of organic material in the host rock and ore

In addition, reworked late-stage veins often have the highest Ge and Ga concentrations. Some recent research indicates that much of the Ge in high-Ge sphalerite ore is actually contained in associated oxides or Cu–Ge sulfides.

Extractive metallurgy: Sphalerite ores are first roasted to convert ZnS to ZnO. There are many techniques used to reduce ZnO to produce Zn, though the most common at present is electrolytic. In this process, the ZnO is dissolved in hot sulfuric acid. Impurities, including Ge and Ga, are extracted in stages from the solution by precipitation onto zinc dust, As_2O_3, or Sb_2O_3 (as well as by other proprietary techniques). These precipitates are then dissolved in hydrochloric acid. Most Ga is recovered by proprietary processes, though it is known that solvent extraction using tertiary aliphatic acids (and other organic chemicals) can precipitate Ga with extremely high efficiencies. Germanium concentrates will react to form $GeCl_4$, which can be separated by fractional distillation. The $GeCl_4$ can then be reacted with water to make GeO_2, which is filtered and dried. Metallurgie Hoboken-Overpelt, the world's chief Ge producer, has developed a technique (U.S. patent 3,883,634; 1975) to extract 99.97% of Ge from acid solutions by using organic compounds containing hydroxy-oxime. Through control of pH, Ge can be effectively separated from Cu, Zn, and other metals. The compound 19-hydroxyhexatriaconta-9,28-diene-18 oxime (LIX-63, General Mills) has been found to be particularly effective.

VIII. Coal, lignite, coal ash

Ge has long been known to concentrate in coals and particularly in coal ash. The highest concentrations are in lignite and lignitized logs (up to 0.2% Ge). In coal beds, the highest concentrations are at the margins and in partings. Field evidence and experimental work indicate that Ge is adsorbed and chelated from circulating water by lignin-derivative compounds during the early stages of coal formation. Though the Ge is organically bound, it remains in the ash (particularly fly ash), where it is highly concentrated (sometimes more than 1%). Ge has been profitably extracted from coal ash in other countries, and represents a large future reserve if the demand increases sufficiently. Ga is concentrated in coals to a lesser extent than Ge, and has not been studied in detail. Most fly ash contains 100-500 ppm Ge and 20-100 ppm Ga; the millions of tons of fly ash generated every year represent a valuable resource if economic recovery methods are developed.

Extractive metallurgy: Efficient extraction of Ge and Ga from coal and coal ash has been difficult and expensive to accomplish. The concentration of these metals in the fly ash during the burning of coal makes fly ash (a waste product of very low commercial value) the only sensible feedstock for extraction. Many processes have been used, particularly in England, to recover Ge and Ga, including leaching, electrostatic separation of particles, and vaporization techniques. The U.S. Bureau of

Mines (Report of Investigations 6940, 1967) tested several methods, and found the most efficient to be: (1) heating the ash pelleted with CaS_x to vaporize Ge as sulfides, followed by (2) heating the resulting material with finely mixed alkaline chloride to vaporize $GaCl_3$. Recoveries of Ge and Ga are probably no more than 70%. More modern techniques of leaching, solvent extraction with organic chemicals, and electrolysis, could possibly reduce costs to a level of profitability, though considerable research would be required.

IX. Thor Lake type deposits

Gallium is enriched in aluminous igneous rocks, such as syenite and nepheline syenite. Many of the most Ga-rich bauxite deposits, such as those in Arkansas, are themselves derived from such igneous rocks. Recently, part of the Precambrian Blachford Lake igneous complex at Thor Lake, in the Northwest Territories of Canada, has attracted attention due to its high Ga content.

Relatively little is currently known about the gallium distribution at Thor Lake. The ore consists of sodium-metasomatized granitic and syenitic rocks that contain high concentrations of Zr, Ta, Nb, REE, Be, and Ga. Some albite-rich rocks in the "T-zone" contain 0.15% Ga, and large quantities of ore contain 0.05% Ga. Highwood Resources, Ltd. estimates reserves of at least 1,000,000 to 2,000,000 kg of contained Ga just in the wall-zone of the "T-zone", with amounts up to 4 times this being likely. Profitable extraction technology does not yet exist to recover the Ga, but work is in progress to develop new techniques. When this resource is developed, or if similar deposits are found, the world supply of Ga could be dramatically increased. The geology of this deposit is further described in Appendix D.

Extractive metallurgy: Laboratory methods using high-temperature alkaline leaching have not recovered more than 10% of the contained Ga. Experiments at high pressures are now planned. Profitable extraction technology is many years away, and will be much more expensive than for Apex-type deposits, and probably more than for bauxite. The tremendous amount of Ga available, however, will be an incentive for considerable research on the subject, and could lead to new methods.

4. MARKET ANALYSIS AND OUTLOOK

Introduction

Accurate market analyses for Ge and Ga are difficult to produce; "reliable" supply and demand estimates vary by over an order of magnitude. The difficulty results from (1) a relatively small market at present, controlled by a few companies; and, more importantly, (2) from the secretive nature of most companies in the electronics and defense industries regarding new technologies. Excellent indications of the market conditions are the commodity prices; even these, however, are difficult to obtain, as the actual prices are frequently very different from the official, published prices (Figure 3). The discussion below provides a summary of the best information available to the author. Detailed numerical analyses of the markets (provided at very high prices by some analysts) are probably of little value, due to technological advances that are being made almost weekly. For the same reason, projecting past trends into the future is also of little value. It is probably most important to evaluate recent technological developments, and project how these will affect Ga and Ge usage.

While production of gallium and germanium is currently meeting worldwide usage, rising demands in the next few years could result in tight supplies and even temporary shortages of these elements. In addition, the United States currently must import nearly all of the gallium and germanium used for domestic consumption. The federal government, in view of the military uses of both elements, considers this situation undesirable. It has declared germanium a strategic material and recommends that first priority in government-related purchases be given to U.S. producers. The conditions thus appear highly favorable for domestic gallium and germanium exploration and production.

Gallium

Current supply-demand situation - The market for Ga has been soft and fairly volatile for the last ten years. The price for 7N Ga (99.99999% Ga - electronic grade) peaked in 1981 at $630/kg, and declined to $525/kg in 1983, which remains the quoted price. Firming of the price (lack of discounting) has occurred since October, 1985, due in part to delays in the expected output from the Apex Mine in Utah.

In the 1980's, there has been very little U.S. primary production of Ga. Until 1982, Alcoa produced Ga as a byproduct of bauxite processing at Bauxite, Arkansas, but has not recovered any in recent years. Eagle-Picher Industries Inc., Quapaw, OK, recovers byproduct Ga from zinc concentrates and slag at a variable rate of 0-3,000

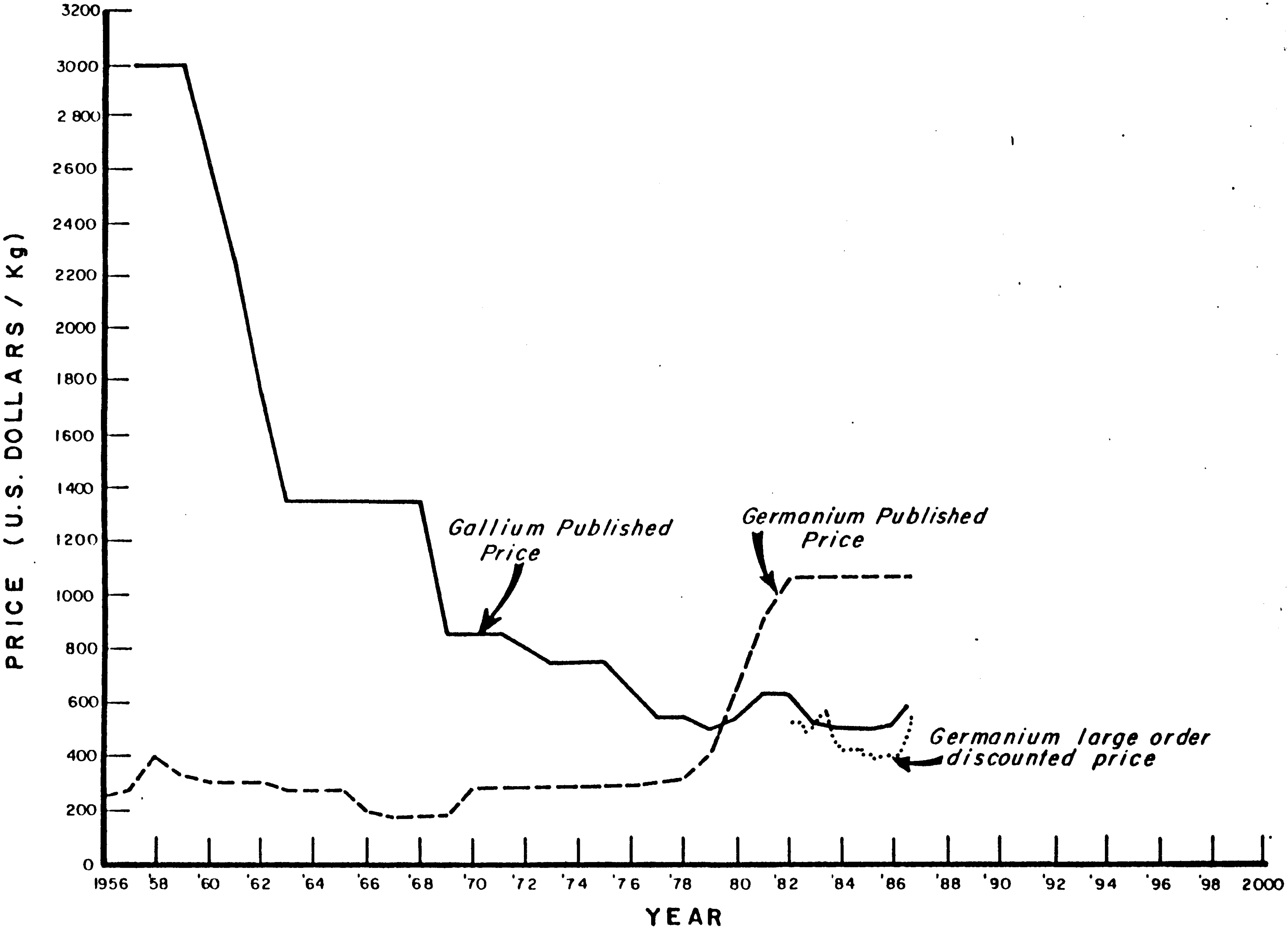

Figure 3. Gallium and germanium prices, 1956-1986.

kg per year. Small amounts of Ga are also produced under license from Monsanto Company at Rock Springs, Idaho, as a byproduct of phosphate production. For the large aluminum and zinc producing companies, Ga production represents a minor activity, and higher prices are required to attract them back into the market. The Apex Mine (Canadian owned) should enter full production in mid-1987, and will supply 8-10,000 kg per year.

In other countries the situation is quite different. Japan has, for several years, been greatly expanding its production of Ga, in anticipation of greatly increased demand for GaAs. Sumitomo Chemical Co. in 1983 opened a plant with a capacity to produce 10,000 kg of Ga per year (mostly from bauxite) while Sumitomo Electric Industries Ltd. has built a plant to produce 10,000 kg per year of GaAs. Dowa Mining Co. Ltd., Rasa Industries, and several other Japanese firms are also moving rapidly to greatly increase production of Ga from bauxite and sphalerite ores. Japan is also engaged in worldwide exploration for new Ga resources. Hungary (Ajka division of Hungalu Hungarian Aluminum Corp.) plans to double its gallium production to 8,000 kg/year by 1988, extracted from 1.3 million mt of bauxite. Switzerland (Alusuisse), West Germany, France, China, England, and Canada (Cominco) are also producing increasing amounts of Ga from bauxite and sphalerite. Recently the Norwegian chemical company Elkem announced plans to build a plant to produce 10,000 kg/yr of Ga from undisclosed byproducts of Al refining. Rhone-Poulenc of France announced that it plans to build a plant in Western Australia that could produce over 50 tons Ga per year (!) using material from Alcoa's alumina operations. A large alkalic rare metal deposit near Halls Creek in Western Australia is reported to contain 50 million tonnes grading 150 ppm Ga; an Australian-American joint venture of Union Oil and West Coast Holdings plans to start mining this deposit as early as late 1988. Extraction of Ga from this ore may prove difficult, however.

Primary production of Ga as estimated by the U.S. Bureau of Mines was 16,200 kg in 1983 (See Table 1 and Appendix E) and was about 30,000 kg in 1986 (phone conversation). These figures are much lower than those of industry analysts and of specialists at producing companies. These estimates are about 35,000 kg in 1983 and about 50-70,000 kg for 1986. Projections for future years vary even more, as shown in Tables 2 and 3. Industry analysts assume that GaAs will account for about 10% of the semiconductor market by 1995, giving a figure of about 800,000 kg/yr; some analysts project twice this much. It is clear that current and projected capacity (Table 2) could not begin to meet this demand, and the price would rise several fold. This would bring the bauxite industry into the picture in a major way, as well as new sources such as clays, phosphate rock, coal ash, and others.

Table 1. Primary Gallium Production in 1983

Country	Ga Production (kg)
U.S.	0
Canada	2,000
Germany (FRG)	3,000
France	2,500
Japan	3,000
Suriname	500
Guyana	500
Hungary	500
Guinea	300
China	2,000
Other	1,900
Total	16,200

Estimates are those of the U.S. Bureau of Mines, 1985; also see Appendix E. These figures are generally considered low by industry analysts, who calculate that about 36,000 kg of Ga was produced in 1983.

Uses, technological developments, and other demand considerations

1. Gallium is used primarily as gallium arsenide (GaAs), gallium phosphide (GaP), and related semiconducting compounds for the manufacture of electronic components. The largest current use is in light emitting diodes (LEDs) and laser diodes (such as those used in compact disc players and in fiber optics telecommunications systems). These markets are currently expanding rapidly. One recent development is the decision by the major automobile companies to use LEDs for the rear red lights on cars. This will use a considerable amount of gallium in coming years.

2. GaAs is 5-7 times faster electronically than silicon, and can function as a semiconductor at higher temperatures and radiation levels than can silicon. For these reasons, GaAs is preferred for the new generations of ultra-high speed computers, and for military and space applications that involve adverse environmental conditions.

3. Many gallium compounds can convert electrical energy to light, and vice versa. There is currently very intensive research to create optoelectronic circuits that use these properties, with the goal of producing computers that operate primarily on light instead of electricity. In this way, data processing can be performed at the maximum speed, that of light. By using many light wavelengths simultaneously, the effective speed of data processing can be further increased through the use of parallel processing rather than serial processing. Commercial products using this technology are still at least several years in the future.

4. Another photoelectric use for gallium compounds is photovoltaic power generation, where light is converted directly to electricity. This use should increase in the next decade as photovoltaic materials become more efficient and the cost per kilowatt hour becomes competitive with fossil fuels. In the long term (10 or more years), this could become a major use for gallium compounds.

5. Several gallium compounds, particularly GaAs, can both detect and produce radar and microwave radiation. The military is very interested in developing compact, solid state radar devices using GaAs, and this usage is expected to increase over the next several years. The rapid processing of radar data will probably also require the increasing use of GaAs integrated circuits.

6. Technical problems in producing suitably pure and perfect GaAs single crystals have significantly hampered the development of GaAs devices, and these problems have not yet been entirely solved. One promising new technology (epitaxy) has developed that uses thin layers of gallium compounds on silicon, germanium, or GaAs substrates. This technique avoids the problems of producing large single

crystals. Commercial devices using this technology should appear in the next few years.

7. In the last few years research has indicated that gallium nitrate, $Ga(NO_3)_3$, may be an effective low-toxicity anti-cancer agent. Animal trials and a few human trials have been encouraging, but it is still too early to project whether this will lead to a new gallium market.

8. Large quantities of gallium metal or $GaCl_3$ may be used in the next few years for studies of solar neutrinos reaching the earth. From 60 to 120 tonnes of Ga may be required for facilities in the U.S., Italy, the U.S.S.R., and possibly elsewhere. As this is a one time use, and the Ga may eventually be recycled, it is not included in Table 3. The sudden demand could, however, create a spike in prices.

9. The lack of domestic gallium production is of concern to the U.S. government, due to gallium's military and high-technology applications. Government programs to stimulate production and to stockpile gallium are being considered.

10. Gallium imports into the U.S. jumped from 8,000 kg in all of 1985 to 10,000 kg in the first six months of 1986. Prices have been gradually rising from $525. to about $600. per kg for some electronic grade gallium over the past two years, reflecting increased demand.

Outlook - It is evident that making quantitative estimates for future Ga demand is dependent upon many uncertain variables. It is clear, however, that the unique electronic and electro-optical properties of some Ga compounds will certainly lead to much higher demands in the next few years. The most conservative forecast, of the U.S. Bureau of Mines, predicts a five-fold increase in demand by 2000, while industry and independent analysts predict a 20-30 fold increase. The actual figure is probably between these extremes, with a 20-25% growth rate per year. The major factors influencing demand are: (1) the highly desirable properties of Ga compounds, which are increasingly required for new high-technology equipment, and (2) new processes to produce Ga-bearing electronic components that minimize Ga usage, for economic and technical reasons. If new, large, less expensive sources of Ga become available, the economic incentives to lower Ga usage would greatly diminish.

Germanium

Current supply-demand situation - Following a strong market in the mid-1970's through the early 1980's, when the price of Ge went from $293/kg in 1976 to $1060/kg in 1982, the market softened until 1986. Though the published price has remained constant at $1060/kg, there has been discounting (due partly to the high value of the

Table 4. Germanium Production in 1983

Country	Ge Production (kg)
U.S.	20,000
Belgium	20,000
France & Italy	20,000
Germany (FRG)	10,000
China	5,000
USSR & East Europe	10,000
Total	85,000

Estimates are those of the U.S. Bureau of Mines, 1985; also see Appendix E. Figures include refinery production from both domestic and imported feedstocks. Most ore was produced in the U.S. and France.

Table 6. Estimated Germanium Demand by Use, 1986-1996
(Metric Tons)

	1986	1991	1996 LOW	1996 PROBABLE	1996 HIGH
Infrared Optics	55	50	35	45	70
Catalysts	45	80	85	100	200
Fiber Optics	25	30	35	45	100
Electronics	5	7	5	10	40
Medicine	5	17	5	40	150
Optical Storage	0	30	30	100	200
Other	5	6	5	10	70
TOTAL	140	220	200	355	830

dollar). The spot price has been firming recently, and is currently $600-650. Germanium dioxide is sold at $660/kg (discounted on large orders to about $400-450).

In recent years, germanium has been recovered almost exclusively as a byproduct of sphalerite processing. Ore is produced primarily from the Elmwood and Gordonsville Mines in Tennessee, and the Saint-Salvy deposit in southern France. Other zinc mines around the world, including Pine Point, Canada, produce varying amounts of germanium-bearing concentrates. Concentrates from the Tennessee ores are shipped to Metallurgie Hoboken-Overpelt SA (MHO) in Belgium, the leading refiner of Ge (20,000 kg/yr). Societe Miniere et Metallurgique de Penarroya in France refines most of the Saint-Salvy ore. Eagle-Picher Industries Inc., Quapaw, OK produces Ge from a variety of domestic and imported concentrates (about 20,000 kg/yr), while Societa Mineraria e Metallurgica di Pertusola S.A. in Italy, Preussag Metall AG in West Germany (about 10,000 kg/yr), and Bleiberger Bergwerks Union AG in Austria are other major producers. China, Japan, and the U.S.S.R. also produce considerable amounts of Ge. Japan is rapidly increasing its Ge production capacity, and is apparently using some Kuroko-type ores as feedstock. Current world production and demand is about 140,000 kg/yr of Ge; estimates of production in 1983 are given in Table 3 and Appendix E.

Due to the softening of the market in 1983-1985, and the expected production of the Apex Mine (about 14-18,000 kg/yr), interest in finding new germanium resources has generally declined. There are several recent and potential developments that could quickly change the supply-demand situation, however: (1) low zinc prices have made the Tennessee mines unprofitable, and they may be closed; (2) the Pine Point Mine is scheduled to close in 1987; (3) the U.S. military has become concerned about Ge supplies, and had Ge made a strategic material in 1984; 30,000 kg were originally requested for the stockpile, and this was raised to 147,000 kg in 1985 (2000 kg were purchased from Eagle-Picher in April, 1987); and (4) new high-volume uses for Ge are being developed, as discussed below. The Ge market is much more diverse than that for Ga, and includes more high-volume uses than does the Ga market (microelectronics). In addition, many potential uses are awaiting lower Ge prices.

Uses, technological developments, and other demand considerations - The major uses for Ge can be classed as: (1) electronic components; (2) infrared optics; (3) fiber optics; (4) catalysts; (5) medicines; and (6) alloys. In the future, optical storage devices could become the major, high volume use of germanium. These uses are considered separately below, together with some emerging markets, particularly optical storage. In 1984, the estimated world-wide uses in percents were:

Use	Percent
Infrared Optics	48
Catalysts	20
Fiber Optics	18
Electronics	5
Medicines	4
Other	5

Electronics: After being the predominant semiconductor in the 1950's and 1960's, Ge now represents less than 2% of this market. The current usage represents applications where Ge is considered far superior to other materials, such as some ultra-high frequency devices and solid-state x-ray, gamma-ray, and infrared detectors. It is also a preferred substrate for LEDs. Many of the highest efficiency photovoltaic materials also use considerable amounts of Ge, as well as Ga and Si. All of these markets, except LEDs, are expected to gradually increase through the rest of the century.

Infrared optics: This is currently the major use for Ge, accounting for about half the Ge market. Germanium metal, as well as some Ge alloys and glasses, is transparent to infrared radiation having wavelengths longer than 2 micrometers. It can thus be used in the same way that optical glass is used for visible light: to make lenses and windows to transmit and focus infrared radiation onto film or electronic detectors. The major applications are: (1) military: for night-viewing scopes on airplanes, tanks, guns, etc.; also for guidance systems on missiles, airplanes, and various vehicles; (2) night-viewing equipment (also for fog and smoke) for police, firemen, researchers, and others; (3) satellite mapping equipment; (4) medical diagnostic equipment (increasingly used for detecting tumors in the early stages); (5) heat-loss monitoring for buildings and industrial equipment; and (6) monitoring devices for fire alarms. These uses have all been increasing, and will remain strong through at least the rest of the decade. Since most of the military equipment is stockpiled or is destroyed, little Ge will become available for recycling.

Fiber optics: This industry is experiencing considerable growth, and much more is expected through the end of the century. In most modern fibers, up to several percent Ge is added to the cores to increase transmissivity. The major volume use for fiber optics is as cables to replace conventional wire telecommunications systems. Major advantages of fiber optics over wire are: (1) compact size (as little as one-fifth the space of Cu cables), so that systems can enlarge their capacities without having to create new, expensive underground conduits; (2) no danger of short circuits; (3) no problems with distortions caused by changes in the electromagnetic field; and (4) they cannot be tapped by any known technology. Many companies around the world are getting into this field; in 1986, Corning Glass Works and Siecor Optical Cable Plant are expected to open plants that will each produce over 1 million km of fiber per year, and many other plants are also opening. All the major telecommunications companies, including AT&T, GTE and MCI, are now installing fiber optics cables. For fiber optics applications, $GeCl_4$ and GeO_2 are used rather than Ge metal, at lower costs.

Catalysts: Germanium compounds (mainly GeO_2) have long been known as excellent catalysts for petroleum cracking and some plastics manufacturing, though the high price and uncertain supply of Ge have discouraged many users. The Japanese, however, are moving ahead rapidly in this field. They now use Ge as a major catalyst in the production of polyester fiber and polyethylene terephalate (PET), a common commercial material for plastic bottles. Other countries are now following this lead, and this will probably become the major use for Ge in the next year. Even a small increase in Ge supplies and decrease in prices could increase this market by several fold.

Medicines: Germanium and many of its compounds have very low toxicities for humans and higher animals, but are toxic to most plants and micro-organisms. In the past few years, several organic germanium compounds have proven to be pharmacologically active against a variety of serious diseases, including cancer, malaria, and arthritis. Clinical, animal, and in-vitro trials are now being conducted in the United States, Japan, Europe, and elsewhere to establish levels of effectiveness and proper dosages.

The first compound tested (and still the most studied) is called spirogermanium. In vitro and animal studies showed that this compound is very effective against many forms of cancer. Early results of human clinical trials (sponsored in part by NIH and the National Cancer Institute) are mixed, with some positive and some negative results. Spirogermanium appears to accentuate the effects of other anti-cancer drugs, so that lower (and less toxic) doses are required. Spirogermanium itself has low toxicity, with transient neurotoxicity at very high doses.

Recent research shows that spirogermanium has several other important medicinal properties. Researchers at several universities in the United States, France, and elsewhere found that it is very effective in killing malaria parasites in vitro, including strains that are highly resistant to other drugs. Early results of human clinical and field trials are also encouraging for the injected form of the drug, and work has begun on oral administration. Spirogermanium is also effective against other parasitic diseases, based on early experimental results.

In addition, spirogermanium has beneficial effects on the immune system and against autoimmune diseases such as arthritis and possibly multiple sclerosis. The Smith, Kline and Beckman Company reports that spirogermanium may be the most effective drug tested against arthritis, acting on the causes of the disease and not simply on the resultant inflammation.

Other germanium drugs are being developed primarily by the Japanese. The compound called Ge-132 was found to stimulate the production of interferon in mice, and generally appears to be effective against cancer and viruses, and in stimulating the immune system. It also appears to relieve pain and to slow the progress of osteoporosis. Further trials of this compound are just beginning. Several other compounds are also under investigation as potential anti-cancer agents, the most promising being called PCAGeS. This compound is effective against several forms of cancer in mice, and also stimulates the immune system.

Several germanium compounds, particularly Ge-132, are currently sold in Japan in small quantities, mainly by the Koei International Co. in Osaka. This company has recently started selling Ge-132 (obtained from a cultivated herb) in the United States as a "food" product, as its use as a drug has not been approved by theFDA.Themajor outlet is currently Nutri-Cology, Inc. of San Leandro, CA. This market will probably remain very small, consisting mainly of health-food faddists.

The exclusive rights to spirogermanium are held by Unimed, Inc. of Somerville, NJ. Unimed is funding some of the current research, together with NIH, NCI, and the World Health Organization (WHO; mainly for malarial research), and some European and Japanese organizations. The spirogermanium is produced under contract by Norac of Azusa, CA. They have used as much as a few hundred kg per year of 99% GeO_2 in their operations. Spirogermanium is now very expensive ($20,000/kg), though the price will decrease as production increases.

Doses of spirogermanium are about 400 mg/day per patient, containing 72 mg Ge. About 250 million people now have malaria, and many millions more have other parasitic diseases, arthritis, and cancer. The potential for veterinary usage is also great. If 100 million doses are given in a year, about 7 tonnes of Ge (10 tonnes GeO_2) would be required; 1 billion doses would require 70 tonnes of Ge (100 tonnes GeO_2). If Ge-132 proves effective and safe in clinical trials and becomes an accepted drug, this could further increase the germanium demand: spirogermanium contains about 18 wt. percent Ge, whereas Ge-132 contains about 43 wt. percent Ge.

Alloys: Small amounts of Ge are used as hardening agents for some Cu, Al, and Mg alloys; this use has been limited by high Ge prices. Germanium is also used to make precision-casting gold alloys for dental and jewelry use. Specialty alloys, such as non-tarnishing yellow Cu-Ge alloys as gold substitutes in jewelry, have remained little used due to high Ge prices.

Optical storage: Through the present time, magnetic tapes and discs have been the predominate means of storing information for computers, as well as for many audio and video systems. Magnetic storage has several disadvantages, including: (1) deterioration with age and use; (2) susceptibility to erasure through exposure to changing electric and magnetic fields; and (3) relatively low information packing density. To overcome these difficulties, particularly the last one, it has become essential to develop new data storage devices. The most promising technology is optical storage, in which data is encoded and read by lasers on discs. These discs, several inches in diameter, can easily hold hundreds of megabytes of information (compared to a few megabytes for similar size magnetic discs). In addition, the discs can be constructed in protective transparent sheaths that protect them from deterioration with age and use, and they would be difficult to sabotage or accidentally destroy. At present, read-only compact laser discs are commercially available, made primarily of high density polymers.

Research to develop erasable and re-recordable discs is currently very intense. The most promising materials developed for such devices are germanium alloys, particularly germanium-tellurium alloys. The basic principles of these phase-change optical storage devices are: (1) the disc is coated with a layer of polycrystalline Ge alloy; (2) to encode data, very brief laser pulses hit the disc, and convert tiny spots of the crystalline alloy to a metallic glass; (3) the metallic glass has different optical properties than the crystalline alloy, and the data can be read by a low-intensity laser; and (4) the data can be erased and the disc made ready to accept new data by using longer laser pulses to anneal the metallic glass back to a crystalline alloy. As can be imagined, exceedingly few compounds have the necessary properties to meet the many constraints of this system. Since GaAs lasers are used, the light wavelengths are such that it is almost certain that Ge alloys must be used on the discs. According to people at IBM, this technology should become commercially available in 1987, and ultimately it will largely replace current magnetic storage materials. If, as now predicted, germanium is used in these devices, the demand for Ge will rapidly rise and will remain high for many years.

In 1985, roughly 2 billion magnetic tapes and discs were sold in the U.S., as well as about 400 million phonograph records. For the world, the figures are about four times as high, and are increasing by several percent each year. Assuming that re-recordable optical discs are about 5¼ inches in diameter and have Ge-alloy thicknesses of 0.1 to 1.0 micrometers, approximately 5 to 50 metric tons (mt) of Ge would be used for each billion discs. To cover the magnetic storage demand in 1985, roughly 10 to 100 mt of Ge would be required in the U.S., and 40 to 400 mt for the world. In 1991, when optical storage technology should be firmly established, the demand could be much greater. These figures are preliminary and very rough estimates, but they do indicate that demand for Ge could rise substantially in the next few years due to the use of Ge alloys in optical storage discs.

At the moment, IBM and Xerox appear to be the leading U.S. companies developing optical storage materials, though many smaller companies are also involved and could produce breakthroughs. All of the Japanese electronics companies are also involved in intense research, and there are reliable reports that working prototype devices have been produced.

Other uses: Germanium compounds are also used as phosphors in many fluorescent bulbs. Many experimental superconductors also use Ge; if practical superconductors using Ge are developed, this would become a very high volume use. Germanium is increasingly being used as an additive in optical glass, to increase the refractive index; this use is fairly price sensitive. In addition, some barium-germanium compounds are increasingly used in medical diagnostic techniques.

Outlook - Nearly all the uses mentioned above are expected to keep increasing through the rest of the century. Germanium demand for catalysts, fiber optics, medicines, and optical storage devices could increase substantially in the next few years. Importantly, any increase in supplies and decrease in prices could greatly expand all of these markets. If advances are made in Ge-based superconductors, this could provide a large market in the long term (10 to 20 years). The current lack of exploration activity for Ge, combined with uncertain byproduct production from zinc deposits, provides an excellent opportunity to find large new deposits that would compete successfully against other suppliers.

5. SUMMARY

1. Gallium and germanium are produced almost exclusively as minor byproducts of bauxite (Ga) and of sphalerite (Ge and Ga) processing. These commodities are of relatively low interest to the major Al and Zn companies that produce them, which results in uncertain supplies and high prices.

2. Demands for gallium and germanium are rising rapidly; even the most conservative estimates predict several-fold increases by the end of the century. Gallium will be required for new generations of electronic equipment and photovoltaic devices and possibly in medicines. Germanium will be needed for infrared optics, catalysts, fiber optics, and perhaps optical storage, medicines, and alloys. Major increases in these germanium markets could result from increases in supplies and decreases in prices.

3. Large, relatively high-grade deposits of Ge and Ga can be found using the models described here. New concepts in Ge and Ga exploration include: (1) association of Ge and Ga with high-grade Cu ore containing a high content of As; (2) affinity of Ge for Sn and As; (3) affinity of Ge for some organic compounds; and (4) affinity of Ge and Ga for iron oxides and hydroxides, including supergene enrichment within these materials.

4. If large, relatively high-grade Ge-Ga deposits are found, they would produce large amounts of Ge and Ga at low costs, and would thus compete successfully against the high-cost, byproduct producers that have little stake in Ga and Ge production.