CANADA CENTRE FOR INLAND WATERS UNPUBLISHED MATERS

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### BERYLLIUM

ITS PRODUCTION AND USE IN CANADA

- A Background Paper -

D. B. Lymburner

H. Knoll

Social Sciences Research

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## OCCURRENCE OF BERYLLIUM

Beryllium occurs in the earth's crust to an extent of 0.001%.

The recent use of a berylometer, a field instrument which can detect beryllium-bearing minerals by nuclear reaction, could likely result in greater degrees of detection, and produce higher estimates ().

Beryllium is contained in 55 minerals, but in only one, beryl, has beryllium been found in sufficient quantity to constitute a commercial ore.

Beryl is a beryllium aluminum silicate; emerald and aquamarine are almost pure forms of this mineral.

The beryl ore usually contains feldspar, quartz, and mica, and although widely distributed, the concentration is seldom such to permit mining for beryl alone. Therefore most beryllium is produced as a coor by-product of a number of minerals.

Other commonly known beryllium minerals include bertrandite, phenacite, barylite, and chrysoberyl. (See Appendix )

#### PRODUCTION OF BERYLLIUM

Little is known about the extent of the world reserves of beryl because its occurrence is scattered and unpredictable. The resources: of hand-cobbed beryl, are rapidly being depleted. Although the world supply, at the moment, still exceeds the demand of major beryllium-consuming countries.

Increasing market demand and improved concentration technology may encourage the finding and development of new deposits.

One estimate places the cobbable beryl reserves in 25 countries at 300,000 tons of beryl which would render about 12,000 tons of beryllium metal ( ).

Beryl deposits have been discovered in Labrador and Mexico. The Canadian deposit in the Salt Lake area of Labrador was found by Rio Tinto Ltd. of Toronto some ten years ago. But Canada has no beryllium production yet. The reserve is not being developed because of the unfavorable location of the find, the present market demand, and the technical difficulties in concentrating berylllium.

The Labrador deposit reportedly has 3 million tons of barylite ore containing 0.5% beryllium oxide. This could yield 5,400 tons of beryllium.

World production of beryl has in recent years been in the hands of 12 to 15 countries; foremost among these are Argentina, Brazil, countries in southern Africa, and the U.S.S.R.

#### Table

#### Production of Beryl

	1957-61	1962	1963	1964	1965	1966
World	11,080	11,000	7,700	5,200	4,900	3,600

As Table ( ) indicates, the beryl production has not been very large. At that, it takes 25 tons of beryl to make 1 ton of beryllium:

The world beryllium production in 1968 was about 200 tons.

Prices for beryl are generally negotiated because no established prices exist. In early 1968 the average price of imported beryl, containing approximately 11% of beryllium oxide, was \$365 a ton in the United States. By late 1968 the price had risen to \$500 - \$600 a ton. This price increase reflects a supply shortage of the mineral. 97% pure beryllium itself fetched \$124,000 a ton on the 1969 market.

The high cost of beryllium is to an extent the result of the scarcity of economically mined resources, the complexity of extracting the metal from its minerals, and the intricate fabrication of beryllium.

Beryllium is used in nuclear, military, and electronic equipment. In these applications beryllium has no substitute. Therefore the growth rates for worldwide beryllium demand is expected to range from 3% to 7% a year ( ), the electronics industry being that of greatest expending demand.

New uses and probable demand by expanding economies in developing countries are among the reasons substantiating the prospects for rapid growth of the beryllium market.

Canadian consumption of beryllium is likely to increase, especially in nuclear applications as nuclear technology, compelled by shortages and high costs of other fuels, advances.

#### CANADIAN IMPORTS OF BERYLLIUM

With Canada having no beryllium production of its own, all beryllium must be imported. Canada buys copper-beryllium alloys, and! extracts the required beryllium from that.

How much beryllium-copper enters Canada cannot be accurately assessed because the Statistics Canada import classification does not distinguish between copper alloys and beryllium-copper. Consequently, the statement of the total quantity of copper alloys imported involves the import of beryllium-copper.

Table ( ) shows the quantity and value of imports in 1970 of possible beryllium-containing copper alloys.

#### Table

Imports of Possible Beryllium Containing Copper

The United States is Canada's major supplier of copper alloys. Minor amounts of these alloys Canada buys from Britain, West Germany, and Switzerland.

Closer insight into Canadian beryllium imports may be gained by examination of information compiled in the U.S.

#### Figure

U.S. Beryllium Exports to Canada

TABLE

# IMPORTS OF POSSIBLE BERYLLIUM CONTAINING COPPER ALLOYS CUMULATIVE TOTALS 1970

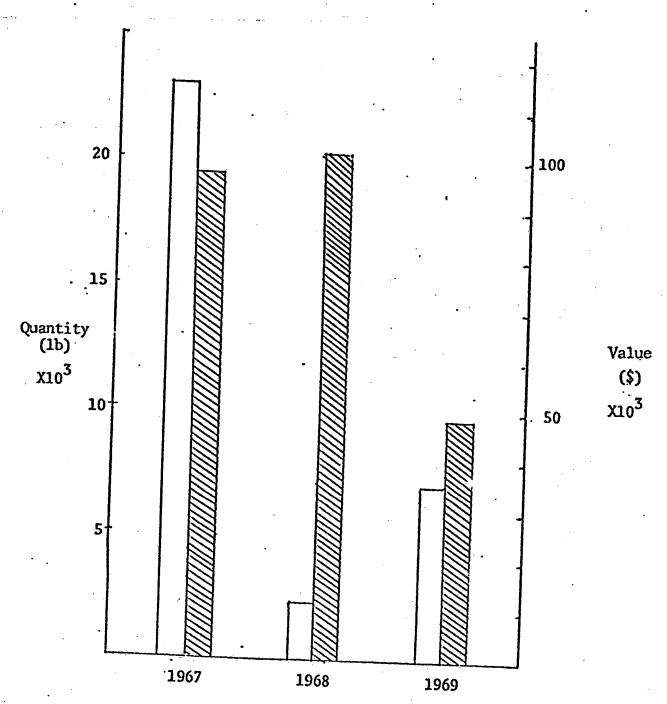
	COMULATIVE TOTALS 1970	•		
COMMODITY	DBS CLASSIFICATION	. QUANTITY (POUNDS)	991.0 am 4	
Copper Alloy Castings			VALUE (DOLLARS	
Copper Alloy Pipe and Tubing	Class 452-90	673,800	732,737	
Copper Alloy Plates Share	Class 452-85	2,367,300		
Strip and Flat Products N.E.S.	Class 452-78	890,100	2,517,174	
Copper Alloy Power, Electrolytic		070,200	1,304,653	
rabilicated Materials NES	Class 452-99	1,901,100	1.815,647	
Copper Alloy Refinery Shapes, Bars Rods and Sections			,,,,,	
•	Class 452-75	10,959,000	44	
Copper Alloy Wire and Cable			6,954,083	
except insulated	Class 452-88	588,200	850,284	
Copper Alloy Scrap	Class 253-99	* · · · · · · · · · · · · · · · · · · ·		
	• • • • • • • • • • • • • • • • • • • •	7,542,200	3,093,197	
	TOTAL	24,921,700	·	
OURCE: Dominion Bureau of Statistics (c		,	17,267,775	

SOURCE: Dominion Bureau of Statistics (Statistics Canada (Cat. 65-203)

NOTE: Beryllium copper is a copper alloy; If it contains more than 50 per cent copper, it is listed by D.B.S. as a copper alloy, and no account of actual beryllium content can be made.

U.S Dol

U.S. export of Be to Canada Dollar value of Be Export



Source: U.S. Bureau of Mines, Minerals Yearbook, Vol. I, III Metals, Minerals and Fuels, 1969.

Note: Beryllium alloys wrought or unwrought, and waste and scrap, consisting of beryllium, lumps, single crystals and powder, and beryllium rods, sheets and wire.

#### CANADIAN EXPORTS OF BERYLLIUM COMMODITIES

The Export Commodity Classification published by Statistics
Canada lists two classes of Beryllium export:

- 1. beryllium-copper/refinery shapes
- 2. beryllium oxide.

But again, as with the import data, the listings include wider classifications, thereby making it impossible to determine the accurate exportations of beryllium.

Table ( ) shows the totals for the commodity classes compiled by Statistics Canada.

#### Table

Exports of Beryllium Alloys and Compounds

In 1970, 73% by weight of these commodities were exported to the United States; the remainder went mainly to markets in Japan and the United Kingdom.

#### TABLE

# EXPORTS OF BERYLLIUM ALLOYS AND COMPOUNDS CUMULATIVE TOTALS 1970

Commodity	D. B. S. Classification	y	Quantity (Pounds)	Value(Dollars)
Beryllium Copper . Refinery Shapes	Class 452-79, Copper Alloy Shapes and Section	s.	28,868,000	19,641,000
			•	
Beryllium Oxide	Class 402-99, inorganic Bases and Metallic Oxides N.E.S.	S	142,209,700	13,480,000
•				
	TOTAL	•••••	171,077,700	33,121,000

Source: Dominion Bureau of Statistics (Statistics Canada) Cat. 65-004

Note: Available data do not permit an account of actual Beryllium content in each D.B.S. classification.

N.E.S. - Not elsewhere specified

#### USES OF BERYLLIUM

#### Beryllium Metal

#### Suitability

For nuclear applications: Be-9, the naturally occurring isotope of beryllium, is stable, but emits neutrons when it is bombarded with nuclear particles. Its small atomic mass and its non-acceptance of slow neutrons, make beryllium a better moderator in atomic energy devices than graphite.

As rocket fuel additive: Beryllium is light in weight. When it combines with oxygen, large amounts of energy are released which yield a high specific thrust.

Metallic beryllium finds rare applications outside of aerospace and nuclear technology.

Powdered beryllium metal is added to rocket fuels to improve the performance of the fuel.

The Atomic Energy Control Board at the nuclear-powered generating station at Chalk River, Ontario uses anywhere from a few to several hundred pounds of beryllium.

In nuclear plants the beryllium metal is used for experimental work where it is employed as a canning material for the uranium-fuel elements. Or, it is machined into moderators and reflectors in compact high-flux nuclear generators.

Beryllium metal may also serve in the generation of neutrons.

#### Beryllium Alloys

Beryllium-Aluminum

Suitability:

Metallic beryllium added to aluminum or other metals, forms an effective self-generating oxidation-resistent surface film on the melt. This happens even if beryllium is present in very minute quantities. As a low-percentage component of an alloy, beryllium acts as a precipitation hardener. In precipitation hardening the alloys are heated almost to their melting points, and then quickly cooled in water. After cold-shaping, the alloy is reheated to 250° - 500°C.

In Canada the use of beryllium-aluminum alloys for items which require a fine grain, a non-oxidizing surface, and good thermal and electrical conductivity, such as cookware, is still only experimental, according to the metallurgy department at Reynold Aluminum Company of Canada Ltd. Industrially, titanium is used for grain refining, and boron for improving the conductivity of aluminum.

#### Beryllium Alloys

Beryllium-Copper

Suitability:

2-4% of beryllium added to copper gives greater strength to copper. The degree of strength varies directly with the beryllium content; but the electrical thermal conductivity, also affected, varies inversely with the beryllium content. This alloy is also of unusual hardness.

More than half of all the beryllium used in the United States is used in the form of a beryllium-copper alloy. Data are not available to assess the Canadian total consumption of beryllium-copper, but one may assume that it is similar in proportion to the United States.

Beryllium-copper alloys are used in the electrical industry for instruments and devices where high electrical and thermal conductivity, and hardness is of advantage; for example, current-carrying springs, fuse clips, and contacts.

The use of beryllium-copper in any primary manufacturing processes seems very limited in Canada. Wherever equipment involving this alloy is needed, it is imported, usually from the United States

Atlas Alloys of Toronto is a Canadian supplier of beryllium-copper. The company estimates that 75% of this all this alloy is used for making plastic moulds; the remaining 25% are used mainly by the electronics industry.

Husky Manufacture & Tool Company in Toronto uses 1000 - 1500 lbs. of beryllium-copper a year for casting plastic moulds; Johnson, Mathey, and Mallory used 3000 lbs. of this alloy last year for its precision-castings and diaphragm pumps.

### SUMMARY OF PRODOMINANT USES OF

### BERYLLIUM COMPOUNDS

<del></del>	•							• •					· · · · · · · · · · · · · · · · · · ·
Uses	ceramic	glass	muclear reactor fuel	nuclear reactor moderator	catalyst .	electronics	mantle	radar .	welding material	plating	rocket fuel	plating	laboratory
Beryllium -					<del></del>	·	<del>-,</del> -	····			<u> </u>	<u></u>	
- oxide	x	x	x	x	x		Y	Y	•			•	
- acetate - carbonate								•	•		,		x prep. of pure
- halides													x Beryllium salts
- nitrate		X	X	X			٠.,				•••		
- sod. fluoride	x.	x x		•						,			
- nitride	^	^							X				
- sulphate													x (prep. of C-14)
- hydride					٠.			•					x prep. of
- pot. sulphate												x	x Beryllium oxide

#### BERYLLIUM IN THE ENVIRONMENT

Considerable quantities of airborne beryllium may emanate from the extracting, refining, and machining of substances containing beryllium.

Crushing, grinding, and cutting beryllium yields dusts of this metal.

Melting, pouring, and welding with beryllium-containing alloys gives rise to fumes. Both dust and fumes of beryllium oxide come off the alloying and reducing processes to refine scrap alloys, above all, beryllium-copper. Wet-grinding and polishing beryllium alloys produces mists of soluable beryllium compounds.

Beryllium pollution occurs wherever finely divided beryllium metal, its oxide, or its compounds are processed.

Coals, depending on where they are mined, may contain 1.5 - 2.5 ppm of beryllium by weight. Despite these low concentrations, the amount of beryllium added to the atmosphere by burning coal may be significant considering that ten million tons of coal are consumed in Canada every year. However, the form of beryllium in coal may be beryl ore, and therefore quite harmless.

The major known sources of beryllium pollution are machineshops and foundries handling beryllium or beryllium alloys, ceramic plants using beryllium in their glazes, and incinerators burning beryllium-containing wastes.

Because of the value of beryllium for hardening the substances to which it is added, its presence is common and likely to increase, which is to indicate that beryllium will be more and more in contact with the general public.

#### TOXICITY OF BERYLLIUM

Intense research in 1949, following an outbreak of beryllosis in the U.S., established the toxicity of the physical and chemical forms of beryllium. In fact, beryllium ranks as one of the most dangerous non-radioactive substances in industrial use. The current limits of exposure substantiate this:

2 ug/m<sup>3</sup> air averaged over an eight-hour work period, 25 ug/m<sup>3</sup> air for a short-term exposure, 0.01 ug/m<sup>3</sup> air averaged over 30 days for people living in the neighbourhood of plants using beryllium.

Beryllium is harmful especially to those in close or constant contact with it. Beryllium is so inherently dangerous, particularly when breathed into the lungs - it is not taken up significantly by the digestive tract - that it needs to be watched more carefully than other materials. Fumes and dusts arising from some of the industrial processes involving beryllium may cause bronchitis, trachitis, or pneumonia. Chronic beryllium disease (beryllosis) has a long latent period, making it difficult to calculate retrospectively the length and degree of prior exposure.

Once in the body, beryllium remains there indefinitely, because the body has no mechanism whereby it can rid itself of this toxic substance.

At the histo-chemical level beryllium seems to cause marked hypergammaglobulinemia along with increased IgG levels (). This may imply that some medical complications of beryllium-poisoning result from immunological reactions due to beryllium(). The blood of

persons who have professional contact with almost insoluble beryllium compounds shows a tendency toward the activation of the anti-coagulating system; those working with soluble beryllium compounds have blood which shows a tendency toward the inhibition of the anti-coagulating system. The explanations for these findings are still hypothetical ( ).

Rats, dogs, cows, fish and other aquatic life experimentally or naturally subjected to the ingestion of beryllium compounds showed no ill effects at all. One experiment, in which the toxicity of beryllium salts was tested toward fathead minnows and bluegills in hard and soft waters, demonstrated that beryllium is much more toxic in soft than in hard water ( ).

For plant life, beryllium, when in aqueous solution at low pH values, is very toxic. Although at high pH levels beryllium proved beneficial to plants, especially to plants deficient of magnesium.

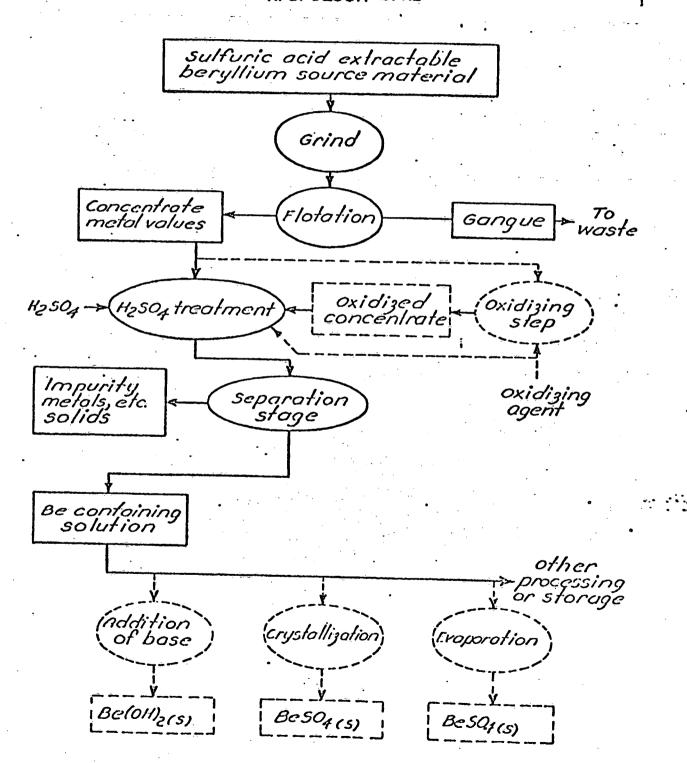
#### RECOVERY OF BERYLLIUM

There is no recovery of beryllium made from end-use products in Canada. This may be so because of the specialized applications of this element, and the small amounts required by any single use.

But considering the potential hazard the waste disposal of beryllium can create, one can recommend the employment of a relatively simple method, patented in the U.S. in June 1972, of recovering beryllium. In this process an aqueous slurry of beryllium and other metal values is heated to a certain temperature under controlled conditions. The pH of this slurry is kept at 2 N, which assures the solubilization of all beryllium values, and the rejection of all oxides and materials which tend to form such salts, i.e. iron, aluminum, thorium, and rare earth metals. The metal impurities are rejected in that they remain undissolved or precipitate as hydrolysis products.

Solid beryllium values, in high purity, can be recovered from the acidic solution.

#### R. S. OLSON ET AL



BERYLLIUM DEPOSITS

S OF DEPOSITS	BERYLLIUM M MAIN	INERALS MINOR	EXAMPLES OF FOREIGN DEPOSITS	INDUSTRIAL IMPORTANCE ABROAD
colitic, streaky(syngenetic) ite pegmatites.	Beryl.	Phenacite	Brazil (Minas-Geraes) etc.	Precious stones
ck and fully differentiated tite-microcline granite matites.	Gadolinite or beryl.	<del>-</del>	U.S.A.Texas(Baringer Hill)South Torway(Iveland, Setersdalen, etc.)	Very rare sub-type; can be use as a source of yttrium and rar earths of its group.
ak and fully differentiated covite-microcline granite matites.	Beryl.	Phenacite, chrysobery, bertrandite, herderite, beryllonite	North-east Brazil (Rio Grande do l,Norte, Paraiba) India(Rajputana,etc. e, Argentina, Madagascar, etc.	Widespread sub-type. ) Commercially important.
laced muscovite-albite gran- pegmatites.	ium) & sodi	-Bertrandite umberyllonite - herderite,	, Australia(Wodgina)China, U.S.A.Conne e, - etc.) northeast Brazil, etc. etc.	
laced spodumenealbite and idolite-albite granite peg-	2.Helvite Beryl (rosterite) and(vorobye vite)	bertrandit	U.S.A. (New Mexico-Harding deposit- e, etc.) South-West Africa.	Rare type. Important commercial type, exped for the rare elements.
cite pegmatites of the cross line(mico-plagioclase veins	- Beryl.	Emerald, phenacite, chrysobery, bavenite.	Africa (Transvaal-Somerset mine de- posit-etc.,)Australia (Poona etc.)	Fairly rare valuable commerciatype.
laced hackmanite-natrolite, ite-natrolite and ussing-pegmatites of nepheline nites.	Epididymite	Eudidymite chkalovite	, Greenland	No commercial value

(APPENDIX EC - A cont	वा	Г
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ES OF DEP TS	BERYLLIUM MI	INERALS MINOR	EXAMPLES OF FOREIGN DEPOSITS	INDUSTRIAL PAPORTANCE ABROAD
rtz-muscovite,quartz- az,quartz-beryl greisens.	Beryl, helvite	Bertrandite, phenacite bavenite.	U.S.A. (Nevada, South Dakota)	Are studied in connection with on the development of methods for the beneficiation of disseminate beryl.
dspar-quartz,quartz,mica- rtz, and other veins.	Beryl.	Bertrandite, phenacite, helvite.	U.S.A. (New Mexico, Luna Co.,; Colorado, Chaffee Co., etc.) Argentina (San Louis province) etc.	Are studied in connection with a on the development of methods for beneficiation of disseminated be
rtz,quartz-hematite	Helvite, danalite.	Beryl, bertrandite, phenacite.		None as yet.
prite pneumatolytes and rothermalites in lime-	Phenacite, chrysoberyl.	Euclase.	U.S.A. (Alaska, Seward peninsula, Cape Mountain and Lost River deposits.)	None as yot.
ens(fluorite-mica- netite).	Helvite,dana- lite,chryso- beryl.	Phenacite, beryl.	'U.S.A. (New Mexico, Iron Mountain and other deposits) ·	Are studiff in connection with to development of the technological flowsheet:
onate veins.	Beryl, (emerald helvite.	-	Columbia (Muso district)	No information.
inc veins.	1	Phenacite, milarite bavenite.	Switzerland, Germany.	None.

SOURCE: A.A. Beus, Geochemistry of Beryllium, (San Francisco: W.H.Freeman and Company, 1966).

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TABLE

IMPORTS OF POSSIBLE BERYLLIUM CONTAINING COPPER ALLOYS

CUMULATIVE TOTALS 1970

COMMODITY	DBS CLASSIFICATION	QUANTITY (POUNDS)	VALUE (DOLLARS)
Copper Alloy Castings	Class 452-90	673,800	732,737
Copper Alloy Pipe and Tubing	Class 452-85	2,567,300	2,517,174
Copper Alloy Plates, Sheets, Strip and Flat Products N.E.S.	Class 452-78	890,100	1.304,653
Copper Alloy Power, Electrolytic and Alloy Fabricated Materials NES	Class 452-99	1,901,100	1.815,647
Copper Alloy Refinery Shapes, Bars Rods and Sections	Class 452-75	10,959,000	6;954,083
Copper Alloy Wire and Cable except insulated	Class 452-88	588,200	850,284
Copper Alloy Scrap	Class 253-99	7,542,200	3,093,197
	TOTAL	24,921,700	17,267,775

SOURCE: Dominion Bureau of Statistics (Statistics Canada (Cat. 65-203)

NOTE: Beryllium copper is a copper alloy; If it contains more than 50 per cent copper, it is listed by D.B.S. as a copper alloy, and no account of actual beryllium content can be made.

#### TABLE

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·		Class 450 05		732,737
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S.		Class 452-78	890,100	1,304,653
tic s NES		Class 452-99	1,901,100	1,815,647
Bars	· .	•		
•		Class 452-75	10,959,000	6;954,083
	•	Class 452-88	588,200	850,284
	. •.	Class 25399	• • • • • • • • • • • • • • • • • • • •	
			7,342,200	3,093,197
•.	•	TOTAL	24,921,700	17,267,775
	S. Viic Is NES Bars	S. Vtic Ls NES	Class 452-90 Class 452-85 Class 452-78  Class 452-99  Bars Class 452-75  Class 452-88  Class 253-99	Class 452-90 673,800  Class 452-85 2,367,300  Class 452-78 890,100  Class 452-99 1,901,100  Bars  Class 452-75 10,959,000  Class 452-88 588,200  Class 253-99 7,542,200

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OTE: Beryllium copper is a copper allow	v: TE.		

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