TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

BULLETIN N° 65 MARCH 1991 FIRST QUARTER

T.I.C. meetings in 1991

APRIL 23rd

An informal meeting will be held at 40 rue Washington, 1050 Brussels, on the morning of April 23rd 1991 when delegates will have the opportunity to meet each other and to hear a report on the meeting of the Executive Committee due to take place on April 22nd. Lunch will be served at the close of the discussions.

Invitations will be sent out in March to all member company voting delegates, and member companies may invite guests. Others who would like to attend, but who have not yet told the secretariat of their interest, should contact the T.I.C. at 40 rue Washington, 1050 Brussels, telephone (02) 649 51 58, telex 65080, fax (02) 649 32 69.

OCTOBER 23rd-25th

The next General Assembly, the Thirty-second, will be held on October 24th 1991 in Philadelphia. In the general pattern which is becoming a tradition of our association, the meeting will open on Wednesday October 23rd with registration of participants and a cocktail party. On Thursday a programme of technical presentations will succeed the formal Assembly, and dinner will be hosted by the meeting's sponsors, Cabot Corporation and Showa Cabot Supermetals. A plant tour of Cabot's tantalum processing facilities at Boyertown will be offered on Friday October 25th. Social events will be held at the Sheraton Society Hill Hotel, where rooms have been reserved for the delegates, and sightseeing trips in and around Philadelphia will be arranged for people accompanying the participants.

More details of the conference programme will appear in the June Bulletin, and, again, invitations will be sent to the voting representatives of member companies in due course.

President's Letter

As in previous years, the T.I.C.'s Executive Committee will be meeting in Brussels in April. This proved last year to be a good opportunity for an informal gathering and exchange of views, and I hope that the opportunity will again be taken by our members to get together on April 23rd.

Many changes have taken place in the world over the past year, including to the shape and structure of our industries. Our quarterly Bulletin can do much to keep us all abreast of developments, however it would certainly help the process if individual members would contact our staff in Brussels by phone, fax, telex or mail with any information which they feel could be of general interest.

Peter Adams
President
7th February 1991

New applications of tantalum and niobium

Recent literature references of interest to our industry include the following :

1. The performance of cobalt based magnets (containing 22-28 % rare earth elements, 10-25 % iron, 1-10 % copper, 0.2-5 % zirconium plus hafnium) is much improved, especially in the second quadrant, by the addition of 0.05-0.5 % tantalum plus vanadium plus titanium.

   Hitachi Metals Ltd.
   Japanese Patent 02 098 101 (10 April 90)

   [Note : A similar claim is made in J.P. 02 098 103 for a 0.05-0.5 % niobium addition.]

2. A moisture sensitive element, made by sintering at 1250-1400 °C a titania/silica mixture with the addition of 0.1-10 mol percent barium carbonate and 0.01 to 2 mol percent of tantalum oxide can be used in the assembly of a humidity sensor. It will function over a wide range (5 % - 95 % R.H.) with reduced aging and temperature dependency.

   Nippon Oil and Fats Co. Ltd.
   Japanese Patent 02 100 301 (12 April 90)

3. An oxide metal film resistor, with a particular temperature coefficient, can be formulated by varying the addition to tin oxide of titanium oxide (between 0.1 and 0.70 mol percent) and tantalum oxide (0.005 - 0.025 mol percent).

   Taiyo Yuden Co. Ltd.
   Japanese Patent 02 062 001 (1 March 90)

   [Note : A similar effect is claimed by the above company in the succeeding patent for antimony and niobium oxide addition to $SnO_2.TiO_2$ systems.]

4. Niobium titanium alloy is sandwiched with copper strip in the preparation of superconducting magnets, but as a result some deleterious reactions can occur (e.g. the formation of copper titanium alloys). A barrier is provided by winding either niobium or tantalum metal foil around the NbTi elements.

   Nippon Steel Corp.
   Japanese Patent 02 094 498 (5 April 90)

5. Lithium dry cells can be constructed with a niobium sulphide or selenide positive electrode. This can be formed by spraying a niobium powder slurry on to a substrate and then drying it to leave a niobium layer 0.1 mm thick. This is then reacted with selenium (or sulphur vapour) at up to 780 °C.

   American Telephone and Telegraph Co.
   European Patent 0 368 448 (16 May 90)

6. The linear motor car is a train supported by a magnetic field, produced by a superconducting magnet. It is being tested in Japan and the first model, unmanned, reached 517 km/hour. The second, carrying passengers, ran at 407 km/hour, and a practical system is expected to be developed by the end of this decade. The magnet is made from niobium titanium wires cooled by liquid helium.

   Y. Kyotani
   Titanium Zirconium Japan 37 (4) 1-7 (October 1989).

7. Compounds of niobium and aluminium (Nb_3Al melting at 1960 °C, Nb_2Al at 1870 °C) are of interest as high temperature structural materials. The ceramic reinforcement, however, must not react with the alloy, and tests show that this restricts usage to oxides, of which zirconia, stabilized by yttrium oxide, is the most probable. Such a composite would be attractive for application above 1400 °C.

   A.K. Misra
   Journal of Materials Research 5(7) 1561-1566 (July 1990).

8. Certain elements, which include niobium and tantalum, suppress pitting and wet corrosion when added to the magnetic elements of information recording material.

   Hitachi Ltd.
   Japanese Patent 01 292 646 (24 November 89)

9. Titanium-base alloys containing one or more of tantalum, chromium or rhenium show excellent corrosion resistance in acid environments.

   Teijin Ltd.
   Japanese Patent 02 077 538 (16 March 90)

10. Tantalum foil may be produced by hydrogen reduction of tantalum chlorides, and the deposition of the resulting fine powder on a substrate in a turnace at 700-1100 °C. A foil having an effective surface area two or more times the projective area, and consisting of continuous fine grains of tantalum, is claimed.

    Showa Denk K.K.
    Japanese Patent 01 222 027 (5 September 89)

T.I.C. statistics

TANTALUM

PRIMARY PRODUCTION

(quoted in lb Ta_2O_5 contained)

	4th quarter 1990
Tin slag (2 % Ta_2O_5 and over)	217 778
Tantalite (all grades), other	208 106
Total	425 884

Note :

17 companies were asked to report, all 17 replied. The companies which reported included the following, whose reports are essential before the data may be released :

Datuk Keramat Smelting
Greenbushes
Malaysia Smelting
Mamoré Mineração e Metalurgia
Metallurg group
Pan West Tantalum (Wodgina Mine production)
Tantalum Mining Corporation of Canada
Thailand Smelting and Refining

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

LMB quotation :	*US \$ 30*	*US \$ 40*	*US \$ 50*
1st quarter 1991	271 800	367 100	392 500
2nd quarter 1991	271 800	367 100	392 500
3rd quarter 1991	276 800	373 100	398 500
4th quarter 1991	276 800	373 100	398 500
1st quarter 1992	276 800	373 100	398 500

Note :

The quarterly production estimates are based on information available, and do not necessarily reflect total world production.

PROCESSORS' RECEIPTS

(quoted in lb Ta contained)

	4th quarter 1990
Primary raw materials (e.g. tantalite, columbite, struverite, tin slag, synthetic concentrates)	586 015
Secondary materials (e.g. Ta_2O_5, K_2TaF_7, scrap)	118 851
Total	704 866

Note :
14 companies were asked to report for the fourth quarter, 13 replied.

PROCESSORS' SHIPMENTS

(quoted in lb Ta contained)

Product category	*4th quarter 1990*
Ta_2O_5, K_2TaF_7	25 865
Carbides	139 524
Powder/anodes	245 398
Mill products	73 964
Ingot, unworked metal, other, scrap, alloy additive	40 857
Total	525 608

equivalent to 709 571 lb Ta_2O_5.

Notes :

14 companies were asked to report, and all 14 replied. For both receipts and shipments by processors, reports by the following companies are essential before the data may be released :

Cabot Corporation, Electronic Materials
  and Refractory Metals
W.C. Heraeus
Kennametal
Metallurg Group
Mitsui Mining and Smelting
NRC Inc.
Showa Cabot Supermetals
Hermann C. Starck Berlin
Treibacher Chemische Werke
Vacuum Metallurgical Company
V Tech

NIOBIUM

PRIMARY PRODUCTION

(quoted in lb Nb_2O_5 contained)

	3rd quarter 1990	*4th quarter 1990*
Concentrates : columbite, pyrochlore	13 662 168	10 510 966
Occurring with tantalum : tin slag (over 2 % Ta_2O_5), tantalite, other	780 241	207 710
Total	14 442 409	10 718 676

Note :

For both the third and fourth quarters 18 companies were asked to report, 17 replied. The companies which reported included the following, whose reports are essential before the data may be released :

Cambior
Mineração Catalao de Goiás
Niobium Products Co. (CBMM)

PROCESSORS' SHIPMENTS (1)

(quoted in lb Nb contained)

Product category	*3rd quarter 1990*	*4th quarter 1990*
Compounds and alloy additive : chemical and unwrought forms (e.g. $NbCl_5$, Nb_2O_5, NiNb, FeNb [excluding HSLA grades])	1 125 605	1 142 598
Metal and alloys : mill products, powder, ingot, scrap	123 368	133 600
HSLA grade FeNb	5 508 288	6.317 902
Total	6 757 261	7 594 100

(1) Provisional : may be revised.

Note :

Fifteen companies were asked to report, 13 replied for the third quarter and 15 for the fourth quarter. Reports by the following companies are essential before the data may be released :

Cabot Corporation, Electronic Materials
  and Refractory Metals
Greenbushes
W.C. Heraeus
Kennametal
Metallurg Group
Mitsui Mining and Smelting
Niobium Products Co. (CBMM)
NRC Inc.
Hermann C. Starck Berlin
Teledyne Wah Chang Albany
Treibacher Chemische Werke
Vacuum Metallurgical Company

Capacitor statistics

U.S. TANTALUM CAPACITOR SALES

(thousands of units)

3rd quarter 1990

Foil	158
Metal-cased	21 146
Moulded	73 099
Dipped	91 683
Chips	119 917
Wet slug	1 858
Total	307 861

(Data from EIA)

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

3rd quarter 1990 165 239

(Data from ECTSP)

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

3rd quarter 1990

Production	1 105 326
of which exports	269 807

Tantalum : a raw materials update

By Mr L.S. O'Rourke, a presentation made to the T.I.C. meeting in Perth, November 1990.

At the Kobe symposium in 1986, the overhang of 11 million pounds Ta_2O_5 was reviewed in some detail. A six year period was projected for supply/demand equilibrium to be restored. Continuing reviews, notably at the T.I.C. meetings at Orlando and Frankfurt, have tracked the trend. Inventories now have reached the levels shown in Exhibit I below.

		1982	*1988*	*1989*	*1990*	*1995*
Processor	Demand	2 115	3 322	2 772	2 925	3 300
	Receipts	1 930	1 317	2 400	2 565	3 300
	Inventory	11 000			2 000	2 000
Production	Potential	3 000	3 200	3 300	3 075	3 520
	% Utilized	64	41	73	83	94

Tantalum Materials Balance
1995 Projection

The exhibit confirms that the goal of the processors in reaching a 6-9 months inventory level by 1990 has been achieved. Further, lower adjustments can be anticipated : for the reasons presented at the Frankfurt assembly, processors will not again exceed these levels. One of the principal management responsibilities in that processing sector has been liquidation of the massive overhang. Emphasis now is being placed on the sourcing and cost control of replacement inventory, a topic to be discussed here.

Note in this exhibit that the production potential of active sources is at 83 % utilization. This has allowed important new production to enter the market. While nominal capacity has been relatively flat throughout the 1982-1990 period, at 3.0 to 3.3 million pounds Ta_2O_5, there are significant changes in the types of raw materials delivered.

Further changes in sourcing will be seen in the next five years, as shown in Exhibit II below.

	1990	*1995*
Columbite	100	100
Scrap	435	400
Synthetics	775	775
HG Slag	530	580
Tantalite	1 085	1 515
Struverite (Conv.)	150	150
	3 075	3 520 *

* Additional indicated potential : 775

Tantalum Materials Origin
Thousands of Pounds Oxide

Most notable is the reduction in high grade slag deliveries which dominated 1975-1982 supply. Reduced tin production, and the reservation of material as working capital for industrial development within Thailand, understandably led to this scenario.

While some increase in high grade slag availability may be foreseen, this source will not again reach its one time level of 800-900 thousand pounds annually. The strong advance will be in tantalite, chiefly within Australia, from the advance of Greenbushes into the hard rock stratum, the realization of Pan West, and the emergence of Goldrim.

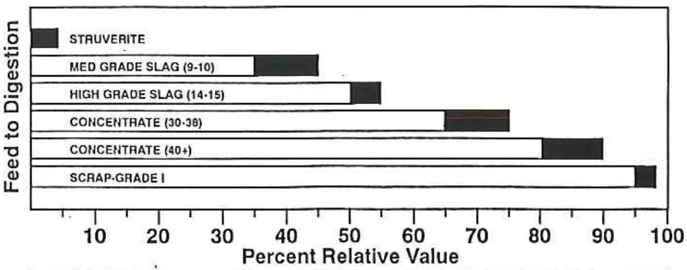
Further extension of supply stems from struverite as a bona fide source, by way of intermediate upgrading processes in China, which only recently have matured.

The four forces in the 1991-1995 supply pattern will be tantalite, synthetics produced from low grade slags, medium to high grade slags such as Iscor and Thailand, and converted struverite.

Division of the projections into these four categories is not incidental to this presentation. Considerations other than Ta_2O_5 content define these categories, a factor which will be emphasized in the balance of this review.

For decades, tantalum pricing has been tied in fact and in perception to reported price indexes, as in Metals Week and the London Metal Bulletin. Despite the 1979-1983 abuse of these devices, some deliveries continue to relate to such immaterial, frequently distorted indexes. The London Metal Bulletin itself at one time editorialized "let the user beware", in defense of its continuing publication in spite of extensive, critical review. However, inertia allowed continued use of indexes in key negotiations for future delivery and to support argumentation on all pricing from columbite to electronic grade powders. "Reported pricing" indexes continue to promote misunderstanding and even distrust, detracting from the proper considerations of true and fair value.

The breadth of the supply pattern in Exhibit II emphasizes the limited value of "30 % concentrate" references, even if accurate. It is due time that each feedstock group be understood, analyzed, discussed, and priced on the concept of relative value. Consider Exhibit III.



Key Factors		
	● Yield	● Niobium Values
	● Waste Disposal	● Inventory Expense
	● HF, Energy, Supplies	● Exchange Rates

Tantalum Raw Materials
Relative Value Ranges
Digestion Thru K-Salt

Here a range of relative values for six feedstocks is developed. Each material varies (A) in value to a given processor due to his location or infrastructure, and his plant design, (B) within each category, e.g. a given tantalite may exhibit higher solubility or lower columbium content than another.

Professional price negotiations should include these key factors as they relate to the participants. This procedure is routinely used in the sale of tantalum end products. Less routinely, the largest consumer of tantalum powder once purchased its entire year's supply not on a dollar per pound basis but on the more rational basis of dollar per microcoulomb. As a direct result, each powder producer (there were then five) was stimulated to intensive development toward improved product performance.

Sellers and buyers should be expected to function on a technical basis in a $ 100 million annual materials market. To abdicate to an artificially indexed price, or to purchase on such generalized and unrealistic bases as are used in GSA transactions, is not responsible. Mutual exchange on the technical questions of processing can only aid both supplier and processor in improving their positions. Were this not the case, arsenic and antimony would still deter certain markets, solubility would still be law for others, and Thaisarco would still be at 8 %-9 % grade.

There is a solution then to the constantly voiced question of coping with the traps inherent in "reported pricing" indexes, namely to abandon their application in contracts, and to employ only technical cooperation. There is no forum more suitable than the T.I.C. to promote such cooperation and serve all of its constituents by raising the understanding of feedstock to an open, technically suitable level.

Research in Britain on tantalum and niobium

The following research programmes are currently under way in British universities and technical institutions :

1. University of Aberdeen :
   New titanate and tantalate ferroelectric materials; by Dr. A.R. West and others
2. Queen Mary College :
   (i) Niobium and molybdenum : deformation of single crystals,
   (ii) The effect of oxidation resistant coatings on the mechanical properties of niobium alloys; by Dr. F. Guin
3. University of Manchester :
   The production of niobium alumina cermet materials by CVD reactions; by Dr. F.R. Sale
4. University of Oxford :
   Niobium single crystals containing dispersed zirconia : alloys of niobium and zirconium; by Prof. J.W. Christian and others
5. British Museum, Dept. of Mineralogy :
   Rare earth- and uranium-bearing oxides of niobium and tantalum; by Dr. A.M. Clark

Applications of high-purity tantalum and market trends for niobium in Japan

Presented by Mr Yoshiharu Nozawa, Executive Director, Vacuum Metallurgical Co., Ltd., at the T.I.C. meeting in Perth, November 1990.

In 1988, Mr Yoichiro Takekuro, President of our company, made a detailed report on the tantalum market in Japan, with trends in demand

and an analysis of the market structure, which was published in the T.I.C. quarterly Bulletin no. 59 (September 1989). He also reported on market trends in 1990 in an article in Bulletin no. 63 (September 1990). Since there is nothing to be added to the above, this paper covers high-purity tantalum applications for electronic devices, and the niobium market, including niobium applications.

TANTALUM

High-purity tantalum

During the nearly 30 years that VMC has been dealing with high-purity tantalum it has developed several markets for the product. The following sections describe high-purity tantalum applications in the electronics parts industry, and the production of high-purity tantalum.

Electronics applications

Table 1 shows electronics industry applications of high-purity tantalum. 6N purity tantalum, the purest, is required for semiconductor applications, 5N to 4N for liquid crystal displays, and 4N for thermal printer heads.

APPLICATIONS	USES	PROCESSES	MATERIALS	PURITY
Semiconductor	Dielectric Thin Film	CVD Sputtering	Ta_2O_5	6N
Display	Gate Electrode	CVD Sputtering	Ta Ta-Mo	5N 4N
Thermal Printing Head	Resistive and Wear Resistant Film	Sputtering	Ta-Si Ta_2O_5	4N

Table 1 - High-purity tantalum applications

An important role for semiconductors is in computer technology. Previous 4Mb and 16Mb DRAMs used silicon, but the high performance dielectric and insulator characteristics of Ta_2O_5, long put to use in capacitor insulating films, were needed for 64Mb DRAMs. Either the CVD (Chemical Vapor Deposition) or target sputtering technique is used to deposit a film under 8nm thick.

Producing high-purity tantalum

VMC improved existing purification processes to meet the need for 6N purity tantalum, the purest, in semiconductor applications.

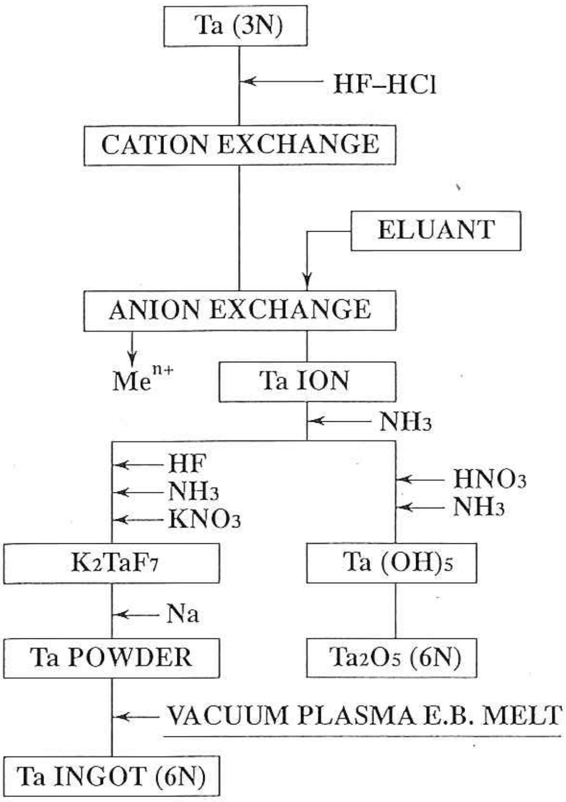


Figure 1 - The production of high-purity tantalum

As Figure 1 shows, both chemical and physical purification processes are used. Purification begins by using cation exchange on 3N or 4N powder, then tantalum ions are trapped through anion exchange; the anion exchange resin is cleaned with eluent - HF, HCl, and HNO_3 to elute metallic ions other than tantalum ions. Next, NH_3 is added to the high-purity tantalum eluate to precipitate tantalum oxyfluoride. Since the base phase still contains tantalum, the eluate is further processed by adding HNO_3 and NH_3 to precipitate $Ta(OH)_5$ which is then thermally treated to obtain 6N purity Ta_2O_5.

Meanwhile, the tantalum oxyfluoride is exposed to HF, NH_3 and KNO_3, and the resulting K_2TaF_7 is reduced with Na to attain high-purity tantalum powder. The powder is then melted into a high-purity ingot by using the VPEB (Vacuum Plasma Electron Beam) technique.

In the CVD technique, Ta_2O_5 thin film is deposited through the reaction of $Ta(OC_2H_5)_5$ with O_2 or that of $TaCl_5$ with CO_2 and H_2.

In the sputtering technique, tantalum film is deposited by sputtering a tantalum target in an argon atmosphere, and then the film is oxidized to form Ta_2O_5. Alternatively, sputtering in a mixed $Ar + O_2$ atmosphere can be used to form a Ta_2O_5 film. For 64Mb DRAMs, 6N purity tantalum will yield the required highly-insulating, high-dielectric film.

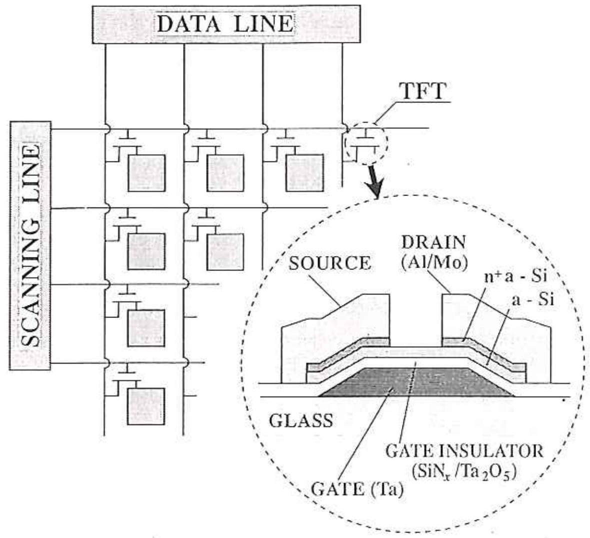


Figure 2 - Cross sectional structure of TFT-LCD

Figure 2 shows high-purity tantalum used in an active drive device of a liquid crystal display. Active matrix system LCDs which use a separate switching device for each pixel have superior display characteristics, and an enlarged cross sectional view of such a switch for a 14" LCD panel is shown in the figure. The manufacturing process is identical to that for tantalum semiconductor devices. The tantalum gate electrode has a Ta_2O_5 insulating film formed through anodic surface oxidation after sputtering deposition.

Another electronics application of tantalum is a binary alloy composed of Ta and Si which is employed as a resistive thin film for thermal printing heads.

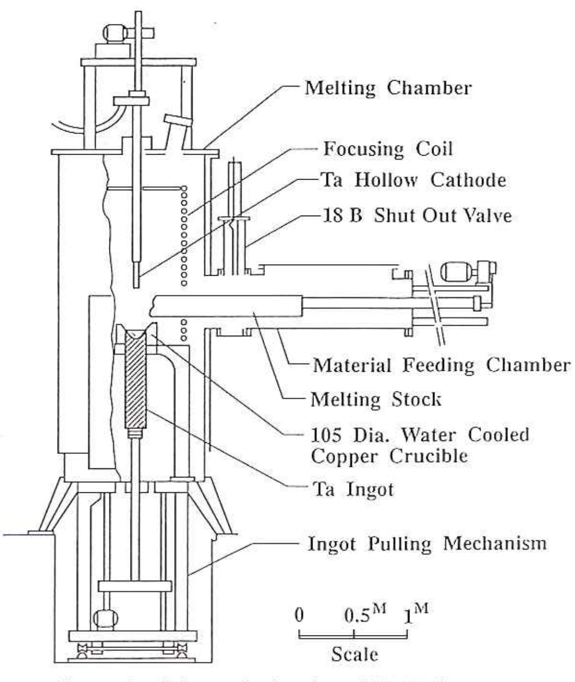


Figure 3 - Schematic drawing of VPEB furnace

Figure 3 shows a schematic drawing of the VPEB equipment. A Ta hollow cathode is used as a heater. An inert gas, such as Ar or He, generates plasma in the cathode, from which thermoelectrons are emitted and accelerated toward the Ta source material which then melts.

The 10^{-3} torr vacuum around the Ta source material makes VPEB equipment suitable for both purification and alloying. Figure 3 shows a pull-down type ingot, as an example. There are several types available.

ELEMENT	TYPICAL VALUE(ppm)
Fe	0.004
Ni	0.07
Cr	0.004
Al	0.02
Cu	0.02
Na	<0.05
K	<0.05
U	<0.0004
Th	<0.0004

Table 2 - Analysis of tantalum ingot (6N)

Table 2 gives an analysis of the tantalum produced by the above process. Transition metal elements such as Fe, Ni, Cr and Cu, and aluminium are under 0.1 ppm. Impurity elements which migrate through films, such as Na and K, are under 0.05 ppm, and radioactive elements such as U and Th, which can cause soft errors in semiconductor memories, are less than 0.0004 ppm.

NIOBIUM

Global and domestic market structure

Official data on the domestic niobium market come from two sources : the Ministry of International Trade and Industry's report of production statistics for steel, which includes domestic ferro-niobium production, and the Ministry of Finance's report of import customs clearance statistics, which includes ferro-niobium imports. Since there are no official data on niobium metal, high-purity niobium oxide or niobium carbide, all data shown in Table 3 are our estimates.

CBMM's analysis of the world-wide demand for niobium reports that 75 % is alloyed with steel, 12 % is used in stainless and special steel, 10 % goes into "superalloys", and the remaining 3 % is used as niobium metal or niobium oxide. The overall structure of the Japanese market demand is similar, with 96 % of all niobium added to steel, special steel or stainless steel, and 4 % used for niobium metal or high-purity compounds.

However, niobium demand for "superalloy" use is 10 % worldwide, but only 0.3 % in Japan due to the small size of the domestic aerospace industry, a situation that will not be changed easily.

Japanese niobium market trends

Excluding niobium used in steel, the estimated 1989 domestic consumption was between 103 and 115 metric tons, as shown in Table 3. About 15 % of this niobium went into superconducting materials, 9 % into anti-corrosion and heat-resistant materials, 57 % into optical glass, 10 % into SAW (surface acoustic wave) devices and ceramic capacitors, and 9 % into cemented carbide.

Domestic demand for niobium has grown slowly and unremarkably, and this trend will probably continue unchanged.

The niobium metal market

Domestically, niobium metal is used as a superconducting magnet material, but its industrial applications are limited at present. Demand usually fluctuates according to government project use. An eight-year long project to establish practical mag-lev railway techniques begins in 1990, with the test route to be constructed in the first 5 years and test runs performed in the remaining 3 years. However, this project will create only three to five mag-lev train cars, not enough to expand the metallic niobium market.

MRI (Magnetic Resonance Imaging), another niobium metal application, is not as common in medical treatment in Japan as it is in Europe and America. Niobium magnets are becoming more popular, but have difficulty in competing, on a cost basis, against ordinary electromagnets and permanent magnets. This competition is especially severe in Japan; magnet development is intensive here because Japan produces more rare earth magnets than any other country in the world.

Recently, a compact superconducting accelerator was developed for possible use in next-generation LSI lithography. Such devices could generate some demand for niobium, but this is not expected at present.

The superalloy market is as mentioned above, and demand for sodium lamps has been flat for the past few years.

The niobium compounds market

Demand for niobium from the optical glass market is based on good sales of popular cameras and the growing production of video cameras. Video camera production grew only 4 % in 1989, but in the first half of 1990 3.69 million video cameras were produced, 16 % more than during the same period in 1989.

For 1995, the projected production of LN ($LiNbO_3$) for SAW devices is double the projection for LT ($LiTaO_3$). LN production in Japan is already exceeding the expected growth rate. The general expectation in the Japanese LN market is that LN will be used in all SAW products except those exposed to very wide temperature variations, resulting in a very high LN SAW market share. This will produce a strong future demand for high-purity (5N) niobium pentoxide for LN.

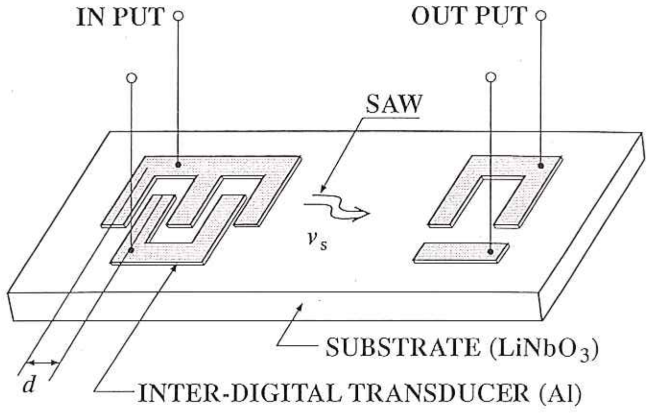
Ceramic capacitor production has equalled or exceeded tantalum capacitor production for several years now due to improved ceramic capacitor performance, the advantages of ceramic chip capacitors, and skyrocketing tantalum prices.

Although interest in cemented niobium carbide grew when tantalum prices shot up, production has not grown a great deal because of the superior characteristics of tantalum carbide and stabilized tantalum prices.

Niobium applications in SAW devices

The overall Japanese niobium market has been outlined in the preceding sections. This section focuses on the SAW device application of LN, in which interest has been growing.

TVs, video decks, audio equipment, mobile telephones and many other electronic products use the outstanding frequency filtering capabilities of SAW (Surface Acoustic Wave) devices to improve image and sound quality. They have become indispensable devices in many electronics markets, and $LiNbO_3$ is widely used as a substrate for SAW devices. About 70 % of all SAW devices are used for frequency filters, and the balance for resonators, delay lines, etc.



$$f_0 = v_s / 2d$$

f_0 ; Central Frequency
d ; Electrode Distance
v_s ; SAW Velocity

Figure 4 - SAW device structure

Figure 4 shows an example of SAW device internal structure, which uses the surface wave which propagates along the surface of a substrate.

A thin-film aluminium interdigital transducer is deposited on a $LiNbO_3$ substrate. When radio frequency signal is applied to the input, a piezoelectric effect generates a surface wave. The centre frequency of the filter is "$f_o = V_s/2d$", where "V_s" is surface wave velocity, determined by the substrate material, and "d" is the distance shown in the figure. Signals input at the frequency "f_o" pass through to the output, but signals away from f_o are filtered out. There are three basic types of substrates for SAW devices : single crystal, thin film, and ceramic. They have different properties and, consequently, are used for different purposes. $LiNbO_3$ and $LiTaO_3$ are both single crystal substrates and are used for similar purposes. However, since $LiNbO_3$ has the advantages of an order of magnitude higher signal conversion efficiency and low cost, it has replaced $LiTaO_3$ in some applications, in spite of $LiTaO_3$'s higher thermal stability.

$LiNbO_3$ substrates for SAW devices are manufactured by, first, mixing high-purity Li_2CO_3 and high-purity Nb_2O_5, calcining the mixture, and then growing a single crystal. Then, in an process called poling, the crystal is heated to the Curie point or higher and a DC voltage applied, to align the crystal's polarity so that it will have the desired piezoelectric characteristics. Finally, the single crystal is sliced into $LiNbO_3$ substrates for LN SAW devices.

In the above process, we use the Czochralski method to grow single crystals of $LiNbO_3$. We have improved the Czochralski method and developed travelling solvent Czochralski equipment so that we can manufacture large and homogeneous, high-quality single crystals of $LiNbO_3$.

Wafers cut from single crystals of $LiNbO_3$, 101.6 mm (4") in diameter and approximately 100 mm long, are used as substrates for SAW devices. The demand for this type of substrate has been rapidly growing, and is expected to grow even further in the future.

Moreover, LN may find another application as a waveguide in optical circuits, due to its low propagation loss at optical frequencies. This use of LN could lead to even more market growth than is already expected.

APPLICATIONS		VOLUME
Super Conductor	($NbTi$, Nb_3Sn)	16 ~ 18
Anti-Corrosion	($FeNb$, $NiNb$)	9 ~ 10
Sodium Lamp	($NbZr$)	0.3 ~ 0.5
TOTAL NIOBIUM METAL		25 ~ 28
Optical Glass	(Nb_2O_5)	60 ~ 65
SAW, Capacitor	($LiNbO_3$) (Nb_2O_5)	10 ~ 12
Cemented Carbides	(NbC)	8 ~ 10
TOTAL NIOBIUM COMPOUND		78 ~ 87
TOTAL NIOBIUM METAL and COMPOUND		103 ~ 115
Iron, Steel, Stainless (Ferroniobium)		2480
GRAND TOTAL		2583 ~ 2595

Table 3 - Demand for niobium in Japan in 1989, estimated by VMC based on data from product makers and others. (Unit : Tons of niobium contained)

Tantalum, niobium and rare earth resources of the Mount Weld carbonatite, Western Australia

This paper was prepared by Mr R.K. Duncan, Consultant Geologist, and presented at the T.I.C. meeting in Perth by Mr D.J. Kingsnorth, of Carr Boyd Minerals.

INTRODUCTION

The Mt Weld carbonatite is a circular volcanic neck or plug, approximately 3 km in diameter, lying buried beneath alluvium and Tertiary lake sediments 35 km south of Laverton in the Eastern Goldfields of Western Australia (Fig. 1).

Since the time of intrusion 2 billion years ago, erosion has stripped away more than 4 vertical kilometres of the plug and surrounding greenstone country rocks, most of this vast volume of material being transported eastwards to the Officer Basin.

Because the carbonatite consists dominantly of calcite and other soluble carbonates, it has been further eroded by groundwater solution to form a basin somewhat lower than the surrounding country. The process of solution and internal collapse has resulted in concentration of less soluble phosphate, oxide and silicate minerals, particularly apatite, magnetite and vermiculite, into a residual layer some 10-70 m thick overlying deeper unweathered carbonatite. This zone of residual mineral concentration hosts the major apatite phosphate deposits at Mt Weld (Fig. 2).

The upper parts of the residual mineral deposits were in turn subjected to deep weathering and alteration, producing a suite of sediments and soils with complex secondary mineralogy. This section of the weathered carbonatite profile has been termed the supergene zone, and is the host to the most significant deposits of tantalum, niobium and rare earths. The combination of residual zone and supergene materials derived from the carbonatite are termed the carbonatite regolith.

Approximately 70 million years ago, the carbonatite and overlying deposits were buried and preserved by a layer of lake sediments from 0-70 m thick, and following drying up of the lake system, alluvial stream deposits built up a 20 m thick layer which completely obscured all surface expression of the carbonatite.

DISCOVERY AND EXPLORATION

Discovery of the carbonatite (Duncan, 1988) followed from a regional airborne survey carried out by the Australian Bureau of Mineral Resources in 1966. A pronounced magnetic anomaly indicated the

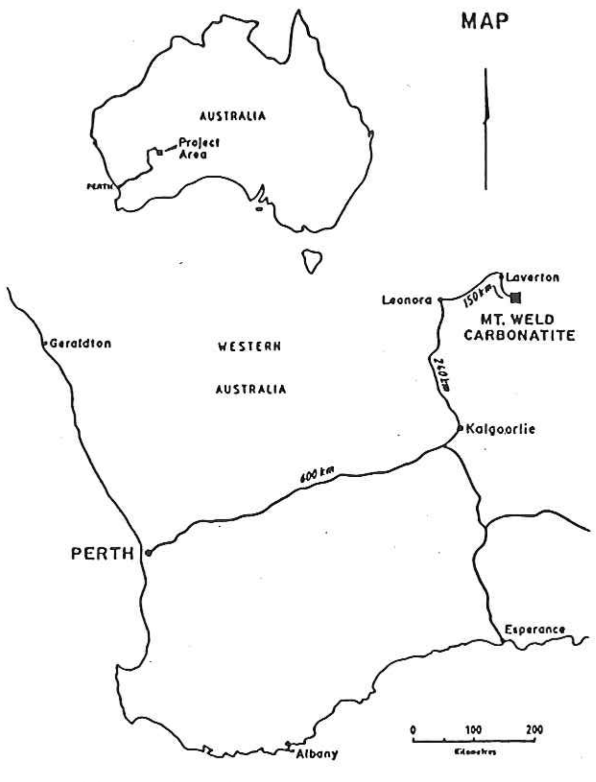


Figure 1 Location of the Mt Weld carbonatite.

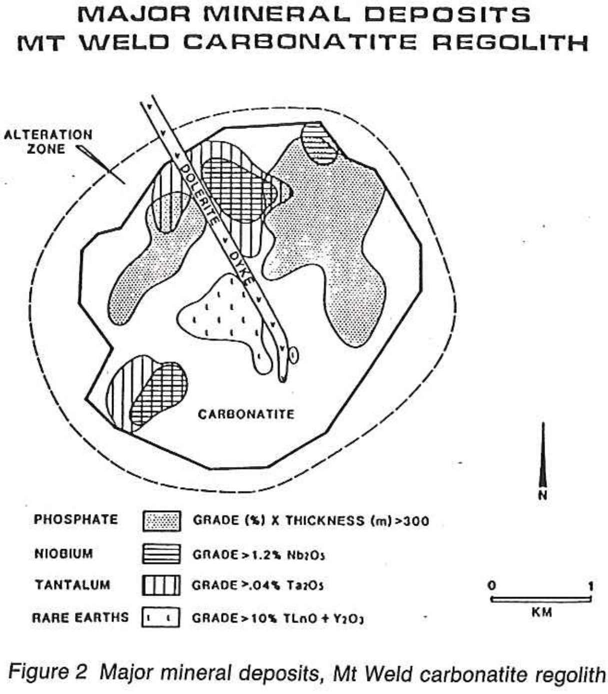


Figure 2 Major mineral deposits, Mt Weld carbonatite regolith.

presence of a large circular feature beneath the alluvial plain. Utah Development Company pegged the area in 1967 and later confirmed the presence of the carbonatite by diamond core drilling. The drilling was primarily aimed at niobium mineralisation in the unoxidized carbonatite but was largely unsuccessful. Exploration of the carbonatite was minimal until drilling and sampling by Union Oil Development Corporation during 1981-84 outlined the major resources of the carbonatite regolith and overlying sediments (Willett et al. 1987).

High groundwater flows in the karst-like regolith and the fine grained nature of much of the mineralisation required the development of sophisticated drilling and sampling techniques, particularly the Wallis Air Core reverse circulation drilling system and a custom built hydrocyclone dewatering plant for optimum sample capture.

A total of 29 000 m of reverse circulation exploration drilling in approximately 420 vertical holes and 1740 m of diamond drilling have provided the primary data for the economic evaluation of the various deposits of the carbonatite regolith.

The apatite phosphate deposits have been assessed and exploitation studies carried out to prefeasibility levels by CSBP & Farmers, the Western Australian fertiliser manufacturing company which owns the rights to fertiliser feedstock minerals. Further development is being delayed until more favourable economic circumstances apply, particularly in regard to development capital and transport costs.

Most recently, Carr Boyd Minerals (now controlled by Ashton Mining) purchased the rights to all non-fertiliser feedstock commodities at Mt Weld and is currently in the process of a full feasibility study of rare earth extraction and marketing from secondary monazite deposits over the central zone of the carbonatite.

GEOLOGY AND MINERALOGY

The highest grade tantalum and niobium intercepts consistently occur in pale grey highly phosphatic fine grained clayey sediments. These sediments are probably partly old soils complete with preserved plant roots, worm burrows and possibly termite excavations. They also show features of deposition in shallow lakes or clay pans. They consist of highly weathered residual minerals from the carbonatite as well as some exotic rounded quartz grains presumably washed in from surrounding areas. The majority of the material appears to be derived from residual apatite, magnetite and vermiculite, probably as a result of considerable leaching of calcium, potassium and phosphate.

In the primary or unweathered carbonatite, niobium and tantalum occur together in the calcium niobate mineral, pyrochlore, which is heterogeneously distributed through the carbonatite and varies widely in its composition. Mineralogical investigation has shown that reddish and dark amber varieties probably contain up to 10 % each of Ta_2O_5 and U_3O_8 (Mariano 1981). The distribution of the pyrochlores reflects variations in primary carbonatite intrusive phases.

With solution and weathering of the carbonatite, pyrochlore was concentrated together with the major residual minerals apatite, magnetite, and vermiculite. It is normally observed as tiny grey to pale brown octahedra in the heavy mineral fraction of the residual zone, commonly showing large variations in abundance, but rarely producing grades higher than 1 % Nb_2O_5 or 200 ppm Ta_2O_5.

Within the supergene zone, where weathering has destroyed apatite, magnetite and most primary minerals, pyrochlore is totally altered to soft, white, friable crandallite consisting dominantly of calcium, aluminium and phosphate with highly variable levels of rare earths, barium and strontium. Detailed scanning electron microscope studies have shown that some of the niobium and tantalum has been leached from the crandallite and dispersed into secondary iron, manganese, and titanium oxides.

The large high grade rare earth deposits, currently the subject of feasibility studies by Carr Boyd Minerals, are composed largely of thorium-deficient secondary monazite (Lottermoser, 1987a) accompanied in part by the yttrium-rich phosphate, churchite (Lottermoser 1987b). The rare earth deposits have grades of combined lanthanide oxides up to 45 % and are probably derived from supergene destruction of residual apatite which in the primary carbonatite contain up to 1 % lanthanide oxides. Concentrations of yttrium (up to 3400 ppm Y_2O_3) and lanthanides (up to 6.5 % TLnO) are also hosted by crandallite in the niobium and tantalum ore deposits, but these may only be significant if they can be produced as by-products of niobium and tantalum extraction.

Figure 2 demonstrates the plan relationships of the various deposits in the Mt Weld regolith while Figure 3 shows the vertical distribution of deposits, particularly the relationship between the residual zone apatite phosphate concentrations and the supergene zone tantalum and niobium deposits. While parts of the niobium and tantalum deposits overlie potentially economic apatite mineralisation, the rare earth deposits are spatially separate.

LANTHANIDE AND YTTRIUM RESOURCES

The data base defining the high grade lanthanide and yttrium mineralisation at Mt Weld consists of approximately 176 drill holes with 1920 intervals analysed for 20 elements. Substantial work has been carried out on analytical verification, estimation of sampling errors, geological control of mineralisation, and determination of density and other geotechnical parameters involved in resource/reserve calculations.

Reserve evaluation has been carried out with drill holes at 40 m centres in the areas of highest grade lanthanide development and 100 m in surrounding areas. Good ore continuity has been confirmed in sub-horizontal mineralogical horizons consisting of soft friable *siltstone* with variable manganese and iron oxide cemented zones.

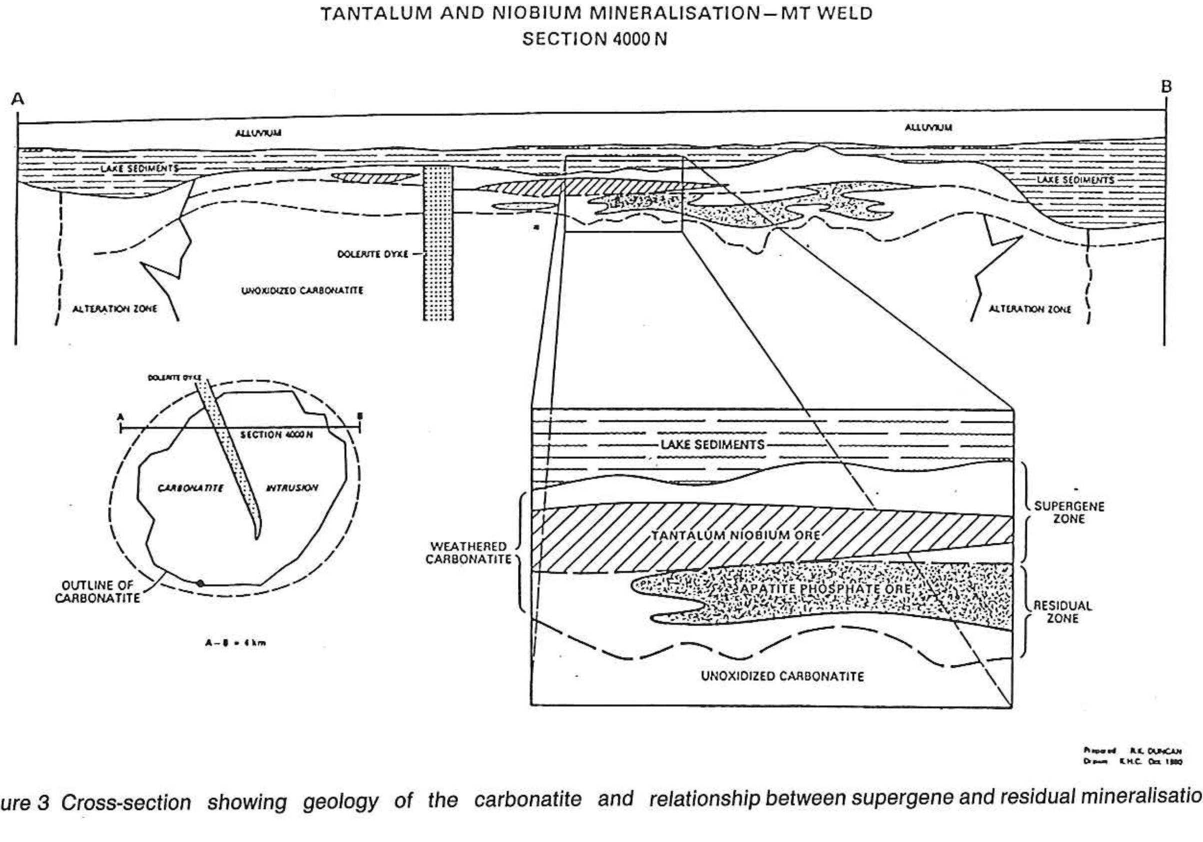


Figure 3 Cross-section showing geology of the carbonatite and relationship between supergene and residual mineralisation.

The variation in degree of cementation is probably responsible for a wide range of observed ore densities from a low of 0.94 to an average in one core hole of 2.5. A conservative figure of 1.5 calculated from average density of core and confirmed by bulk sample drilling has been applied to all resource estimation.

Resources of lanthanides and yttrium were calculated by geostatistical estimation methods using lognormal kriging on 25 m × 25 m × 3 m ore blocks and are presented in Table 1 together with the total regolith resources at Mt Weld.

TABLE 1

MT WELD REGOLITH RESOURCES

COMMODITY	TONNAGE (millions)	GRADE (%)	CUT OFF GRADE (%)
PHOSPHATE			
Total inferred resource	250.0	18.1	10.0
Indicated resource	60.0	19.2	10.0
NIOBIUM (Nb_2O_5)			
Total inferred resource	273.0	0.9	0.5
TANTALUM (Ta_2O_5)			
Total inferred resource	145.0	0.034	0.02
RARE EARTHS			
(Total combined lanthanide oxides + yttrium oxide			
Measured + indicated resources	17.0	10.2	5.0
Measured + indicated resources	6.3	16.2	10.0
Measured + indicated resources	1.35	23.6	20.0

TANTALUM AND NIOBIUM RESOURCES

More than 100 drill holes, mainly at 200-250 m spacing have made intercepts of weathered carbonatite of at least 3 m assaying greater than 0.02 % tantalum oxide or greater than 1 % niobium oxide. Table 2 details the reasonably well defined localised tantalum and niobium resources.

TABLE 2

TANTALUM AND NIOBIUM RESOURCES

	TONNAGE (millions)	GRADE (%)	CUT OFF GRADE (%)
NIOBIUM			
Total inferred resource	273.0	0.9	0.5
including			
Local inferred resource	9.0	1.9	1.0
Local inferred resource	8.8	1.75	1.0
Local inferred resource	5.0	2.0	1.0
TANTALUM			
Total inferred resource	145.0	0.034	0.02
including			
Local inferred resource	14.0	0.053	0.05
Local inferred resource	2.2	0.099	0.05

The resources have been calculated with the help of geostatistical estimation from relatively wide spaced drill holes, generally 200-250 m spaced but with some 50 m spaced holes. The stratiform nature of the deposits lends confidence to the tonnage estimations, but estimates of grade are almost certainly low due to inability of the hydrocyclone dewatering plant used in exploration sampling to capture fully tantalum and niobium enriched slime fractions. Limited diamond drilling and total capture reverse circulation drilling indicates that grades of niobium and tantalum are probably understated.

Recent total sample capture drilling has shown that the northern zone of mineralisation shown on Figure 2 probably contains the highest grades of both tantalum and niobium mineralisation in tonnages capable of sustaining a long term extraction program in an area of carbonatite regolith relatively amenable to open cut development. A typical ore block might be that intersected by drill hole RC417 with 8 m of ore grading 5.7 % Nb_2O_5 and 0.18 % Ta_2O_5 and a stripping ratio of 6.5 : 1. An adjacent core hole produced an exceptional intercept of 30 m @ 0.13 % Ta_2O_5 including 15 m @ 0.21 % Ta_2O_5.

Although comparatively large resources of disseminated pyrochlore exist within the residual apatite phosphate deposits, grades are generally very low and extraction can only be economic as a by-product of phosphate mining.

COMPARISON OF RESOURCES

The monazite hosted REO resources at Mt Weld possess favourable distributions of lanthanides compared to the light lanthanide enriched bastnasite hosted resources at Mountain Pass, California (25 Mt @ 5-10 % REO), the only current producer of REO's as a primary commodity. Nearly all other western world sources of REO are from monazite as a by-product of mineral sand mining. It might be expected that development of anatase deposits by Du Pont on the Tapira carbonatite, Brazil (190 Mt @ 21.9 % TiO_2, will eventually reduce demand for mineral sands ilmenite and rutile, and hence the sources of by-product monazite.

Niobium resources at Mt Weld (273 Mt @ 0.9 % Nb_2O_5) can best be compared with the major western world producer, CBMM at Araxa, Brazil, with reserves of 460 Mt @ 2.5 % Nb_2O_5.

With respect to tantalum, Mt Weld resources of 145 Mt @ 0.034 % Ta_2O_5, including 2.2 Mt @ 0.099 % Ta_2O_5 compare favourably with the major world deposits of Ta_2O_5 :

Tanco Canada, 1.0 Mt @ 0.144 %;
Greenbushes W.A., 32 Mt @ 0.050 %;
China, 100 Mt @ 0.015 %;
Zaïre, 27 Mt @ 0.003 %; and
Egypt, 70 Mt @ 0.016 %.

EXTRACTIVE METALLURGY

Extensive bench scale and pilot plant beneficiation work based on phosphate flotation has produced monazite concentrates acceptable to conventional cracking and rare earth extraction processes. This has required the development of novel techniques and reagents currently the subject of patent applications. Plans for development of the rare earth resources envisage a beneficiation plant at Mt Weld producing approximately 10 000 tpa concentrates which will be further processed at a plant in the Perth region.

Tantalum and niobium beneficiation has not yet been thoroughly investigated. Because of the fragile physical condition of altered pyrochlore in the ore zones and the geochemical dispersion of niobium and tantalum into a number of fine grained secondary mineral phases, attempts at beneficiation using conventional physical methods have not been successful, most forms of crushing or attrition resulting in loss of tantalum and niobium to slimes. The recently developed technology for flotation of rare earth phosphates may be applicable to the tantalum and niobium resources, but no experimental work has been attempted to date. Similarly, experiments with hydrometallurgical extraction have only received tentative consideration to date, and no clear route to economic separation from the phosphate matrix has been demonstrated. The hydrometallurgical route appears particularly attractive if the value of accompanying rare earths and zirconium might be realized in conjunction with tantalum and niobium.

CONCLUSIONS

Although extensive resources of tantalum and niobium exist within the regolith of the Mt Weld carbonatite at grades generally considered economic, extractive metallurgy has not yet been developed to exploit the deposits. However, equally significant rare earth resources are now being subjected to full feasibility studies and a start to mining as early as 1994 is envisaged. Marketing studies have supported the feasibility of supplying approximately 10 % of the world lanthanide market with a number of specific high grade products. The substantial reserves at Mt Weld will ensure a long term future for the planned Carr Boyd (Ashton Mining Ltd) rare earths development.

REFERENCES

- DUNCAN, R.K., 1988. Discovery of the Mt Weld carbonatite, in *R & D For The Minerals Industry, Western Australian School of Mines, Conference '88,* pp. 86-93.
- LOTTERMOSER, B.G., 1987 (a). Supergene, secondary monazite from the Mt Weld carbonatite laterite, Western Australia. *N. Jb. Min. Mh.,* 2 : 67-70.
- LOTTERMOSER, B.G., 1987 (b). Churchite from the Mt Weld carbonatite laterite, Western Australia. *Mineral. Mag.* 52.
- MARIANO, A.N., 1984. On the mineralogy of Nb, Ta and REE in the Mt Weld laterite. Confidential report to Molycorp Inc. (unpublished).
- WILLETT, G.C., DUNCAN, R.K., and RANKIN, R.A., 1989. Geology and economic evaluation of the Mt Weld carbonatite, Laverton, Western Australia, in *Kimberlites and Related Rocks, Vol. 2 : Their Mantle/crust Setting, Diamonds and Diamond Exploration,* Geol. Soc. Aust. Spec. Publ. 14. 1215-1238.

TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER — Rue Washington 40, 1050 Brussels - Tel. (02) 649 51 58 - Telex 65080 INAC B
Fax (02) 649 32 69
PRINTED BY PUVREZ, avenue Fonsny 59, 1060 Brussels.