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THE TIN INDUSTRY[1])

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INTRODUCTION

Although the history of tin covers a period of perhaps 7000 or 8000 years the metal continues to play an important part in the development of our civilisation. Tin is at present an essential component in our communications and electrical systems and is also widely used in small but vital proportions in the packaging industry in the form of tinplate. The aim of this paper is to briefly review the history, the geology, the exploration, mining and processing methods employed and also the uses of the metal and to discuss the future prospects of the tin industry.

HISTORICAL

Tin is an important commercial material in our society and has been of considerable value for thousands of years. In fact, the production of tin is one of the oldest industrial activities of mankind. At a very early date the metal was alloyed with copper to make bronze for tools and ornaments and for weapons such as spearheads and axes and this great technical advance marked the commencement of the Bronze Age.

Since very little native tin has ever been recorded, the availability of the metal at such an early period of history was undoubtedly due to the ease with which it could be obtained from its ores. The ores of tin were not widely distributed over the earth's surface (unlike, for instance, the ores of iron which were used during the Iron Age) and a few specially favoured areas became well known in the ancient world as sources of tin, for instance, Cornwall, Spain, Brittany, Bohemia and Saxony.

Tin readily forms a series of alloys with copper and, since many of the earlier-found tin deposits also contained copper, it is probable that the first bronzes were accidentally produced during tin smelting operations.

When simple bronze weapons and tools were eventually replaced by iron the need for tin declined and it was only when tin was again used in large quantities for military bronze cannons and for the production of pewter utensils in the Middle Ages that there was any further significant increase of activity in the tinfields.

In the early nineteenth century the bronze cannons were themselves replaced by iron weapons and, in addition, pewter pots were replaced by china utensils (the raw materials for which were, ironically, obtained from the world's busiest tinfield!) and the position of tin as a major metal of commerce was once again jeopardised. However, at about this time, the invention of tin-alloy bearings (of the Babbit-metal type) introduced a new, important use for tin and the development of the tinned steel can for food preservation in the mid-nineteenth century demanded new high levels of tin production. In addition, the growing printing and electrical industries and the introduction of lead-based plumbing systems further increased the demands for tin metal for use as type-metal and solders.

Since that period the number of tinned cans produced each year has steadily increased and so also have the scale of the printing, the electrical and the

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	Tin	Aluminium	Copper	Nickel	Lead	Zinc
1925	148.7	173.1	1.418.1	36.7	1.451.9	1.087.1
1930	156.6	190.9	1.326.3	58.6	1.406.9	1.114.6
1935	137.5	269.6	1.364.3	74.3	1.329.6	1.250.6
1940	148.6	745.3	1.995.8	127.0	1.519.7	1.602.5
1945	95.6	878.8	1.899.8	128.2	1.230.7	1.211.5
1950	146.5	1.318.1	2.094.9	125.1	1.651.1	1.798.3
1955	144.0	2.563.5	2.615.0	159.2	1.934.4	2.245.1
1956	150.1	2.658.6	2.677.7	179.5	1.968.2	2.129.6
1957	143.2	2.337.8	2.757.3	180.8	1.937.9	2.132.3
1958	136.3	2.441.2	2.788.6	137.2	1.824.3	2.130.0
1959	148.5	3.159.9	2.914.5	185.8	1.962.5	2.291.3
1960	162.5	3.186.1	3.133.8	213.1	2.018.5	2.401.2
1961	157.9	3.404.9	3.402.4	224.2	2.073.0	2.538.1
1962	158.3	3.809.4	3.358.1	211.9	2.154.7	2.620.4
1963	161.5	4.297.8	3.559.5	231.0	2.262.1	2.813.2

Generally excluding the U.S.S.R. Mainland and Eastern Europe.

Fig. 1a
World consumption of some non-ferrous metals since 1925 (after Robertson).
This figure shows how the consumption of tin has fluctuated about an average value of approximately 150,000 tons/year for nearly 50 years whilst the other common metals have shown significant increases in production in that period.

"plumbing" industries. Unfortunately, the amount of tin required per unit of production (i.e. the amount of tin per can, or per electrical joint, etc.) has steadily decreased and the total amount of tin required per year has remained comparatively unchanged for decades.

Metal	Tonnes of metal produced per year	Tonnes of ore treated per year (approx.)	Value of metal produced
Tin	2×10^5	2×10^9	£ 280×10^6
Lead	2×10^6	4×10^7	£ 200×10^6
Zinc	2×10^6	2×10^7	£ 200×10^6
Copper	5×10^6	5×10^8	£ 2000×10^6
Iron	6×10^8	1×10^9	£ 2000×10^6
Coal	2×10^9	4×10^9	£ 6000×10^6
(Sand and gravel)	1×10^9	$>1 \times 10^9$	£ 1000×10^6

Fig. 1b
Tonnages of ore treated and the value of some of the metals produced by the mineral industry.
This figure shows the comparative position of tin in the "big league" of the mineral industry. A number of assumptions have had to be made regarding the average grades of ore being treated in various sectors of the industry.

TIN PRODUCTION

As shown in Fig. 1a, the weight of tin consumed is quite small when compared with many other common metals. The relative importance of the tin industry is, however, much more apparent if the *value* of the metal produced each year is used as a basis for comparison (see Fig. 1b), or if the total amount of ore mined or treated per year is taken into consideration (see below). Predictions of the probable future consumption trends do not suggest any major increase in the demand for tin in the foreseeable future.

The great bulk of the world's production is obtained from only 6 countries, see Figs. 2a and 2b, see also Fig. 3, which between them produce approximately 140,000 t/year. These countries have been notable in the recent past, for the high degrees of political uncertainty that they have shown! By far the most important tin producing area is South-east Asia (comprising Thailand, Malaysia and Indonesia) where in recent years more than 100,000 tonnes of the metal have been produced each year. The importance of the area may be gauged from the fact that the total recorded output since 1900 is approximately 5,000,000 tonnes as compared with the 2,000,000 tonnes produced in Cornwall in the past 3000 or 4000 years. The industries of Indonesia and Bolivia

Period	Malaysia	Bolivia	Thailand	Indonesia	Nigeria	Congo	Others	Total
1900–1904	47,500	11,500	4,000	15,600	2	– –	9,000	87,600
1905–1909	49,600	17,700	4,800	16,200	150	– –	12,300	100,900
1910–1914	49,000	23,100	6,200	20,300	2,400	10	15,200	116,200
1915–1919	43,900	25,100	8,800	20,600	5,800	90	12,900	117,200
1920–1924	39,300	29,500	7,000	26,600	5,700	800	8,700	117,500
1925–1929	57,400	37,200	7,900	33,600	8,600	1,000	11,800	157,500
1930–1934	42,600	25,000	10,700	21,600	5,700	1,600	11,700	118,900
1935–1939	55,400	25,900	13,800	29,000	9,100	8,100	18,900	160,100
1940–1944	42,700	39,500	10,000	26,100	12,300	15,500	15,500	161,700
1945–1949	27,700	37,000	3,300	16,600	9,800	12,700	9,900	116,900
1950–1954	57,900	32,000	9,900	33,600	8,300	12,400	11,900	165,900
1955–1959	51,800	24,900	10,900	27,200	7,700	11,400	12,600	146,500
1960–1963	56,600	21,200	13,900	17,900	8,100	7,500	13,700	138,900
1967	72,100	27,100	22,500	13,600	9,300	7,000		171,900

Congo includes Rwanda to 1942.

After Robertson.

Fig. 2a

Major producers of tin-in-concentrates.

This figure gives the 5-year average values for the annual production of tin-in concentrates by the six major producing countries since 1900. It clearly shows Malaysia's position as the major producer; the dominant role of South East Asia; the increasing importance of Thailand; the recent serious fall in production in Indonesia; and the cyclical fluctuations in total production from about 110,000 tons/year to 160,000 tons/year.

are nationalised whilst the industries of the other countries are run by private enterprise.

Because of the rather unstable political features of the tin producing countries, and also because of the almost total lack of tin in the major consuming areas, a number of co-operative efforts have been made to regulate and stabilise the price of the metal. The first attempts were made in 1921 when the Malayan and the Netherlands East Indies governments pooled a large stock of unwanted tin which they later sold off in small amounts as the market warranted. In 1929 the Tin Producers Association was formed and this was made up of leading mining interests in the main tin producing countries. This association recommended that tin prices should be maintained by restricting the output of the metal. The International

	1964	1965	1966	1967	1968
Mine production					
Major producers	131,000	136,000	146,000	152,000	156,000
Others	16,000	16,000	18,000	20,000	20,000
Sino-Soviet block	51,000	51,000	51,000	51,000	50,000
World Production	198,000	203,000	215,000	223,000	226,000
Consumption					
Western World	168,000	165,000	166,000	165,000	170,000
Sino-Soviet block	52,000	53,000	54,000	57,000	58,000
World Comsuption	220,000	218,000	220,000	222,000	228,000
World Surplus (+) or deficit (–)	–22,000	–15,000	–5,000	+ 1,000	–2,000

Fig. 2b

World tin statistics 1964-68.

This figure shows a summary of the *world* production and consumption figures for tin between 1964 and 1968. The major deficit of the earlier years has been overcome and the production and consumption figures are now in virtual balance.

	1947	1957	1967
Rwanda	1400	1800	1300
South Africa	500	1500	1800
Brazil	300	300	1600
Burma	1800	700	300
Japan	100	900	1200
Laos	–	300	300
Portugal	500	1100	600
Spain	400	500	100
U.K.	900	1000	1500
Australia	2400	2000	5600

Fig. 3
Principal minor producers of tin-in-concentrates.
The table shows the output of the principal minor producing countries in 1947, 1957 and 1967, and clearly indicates the growing importance of Brazil and Australia.

Tin Committee was formed in 1931 with delegates appointed by the governments of the main producing countries and this committee took power to restrict tin output for a few years. This agreement was continued, and was supported by buffer stocks of metal, until 1939. In 1956 an International Tin Agreement was ratified and, as a result, the International Tin Council was set up with headquarters in London. It is composed of delegates from six tin-producing and sixteen tin-consuming countries which represent 90% of Western world production and about 50% of consumption. Its aims are to prevent excessive fluctuations in the price of tin and to alleviate the difficulties arising from shortage or surplus of the metal.

These aims are now backed by a buffer stock with a potential total value of £ 30,000,000 (i.e. amounting to about 20,000 tonnes of tin metal). The International Tin Council provides support for tin when the price is low by buying metal and the Council sells metal only to prevent the price from becoming unnecessarily high. The current (March 1969) buying and selling prices are £ 1280 and £ 1630/ton respectively, i.e. when the price of tin on the open market falls below £ 1280/ton the Tin Council *must* buy all the tin that is offered, and when the price of tin exceeds £ 1630/ton the Council *must* sell tin from its tock in an attempt to reduce the price. In periods of gross oversupply the Council is empowered to restrict the output of tin and at present (1969) tin restrictions are in force. These efforts, by producers and consumers to control violent price fluctuations in a basic commodity have already achieved considerable success and both groups of people can, therefore, invest with confidence in new plant, new capital, long-time exploration, etc., and so maintain the long-term production and use of tin. The success of the International Tin Council's policy is partly due to the fact that tin production is obtained from only a few countries and that direct consumption of tin in those countries is negligible. Consequently, tin *must*, in general, cross frontiers between the areas of production and the areas of consumption and it can, therefore, be fairly readily controlled. In addition, the amount of secondary, or scrap, tin that is available in the consuming countries is small and this has little effect on the availability of the metal.

GEOLOGY OF TIN

Tin is not an especially rare metal but (as previously indicated) it is distributed very sporadically throughout the world. In nature the metal is almostly invariably associated with highly acidic, intrusive, granitic rocks but, unfortunately, all granitic rocks do not carry workable amounts of tin. The reasons for the association of tin with acid, igneous rocks have not been adequately explained but it is an undoubted fact that tin is concentrated in the later facies of differential igneous masses.

It has been shown that in tin-bearing granites that contain appreciable amounts of amphiboles the metal is contained in the lattices of these minerals (the ionic radii of Sn, Fe and Mg are very similar). On the other hand, in granites that contain appreciable quantities of sodium, fluorine and mica, the tin usually occurs as the distinct mineral cassiterite. It is possible that tin, originally contained in mica, could have been released from that mineral by "emanations" rich in sodium and fluorine and then re-deposited as cassiterite (see below).

The paragenetic significance of cassiterite has not yet been clearly established; in Nigeria (and possibly in Brazil) the main occurrences of the mineral are associated with the crustal tension that gives rise to ring structures and cauldron subsidences, whilst in Bolivia, Cornwall and South-east Asia the tin is always associated with compressional, orogenic granites.

The most extensive and productive tin province stretches from China, Yunan and North Burma throughout the length of Thailand and Western Malaysia to the "Tin Islands" of Indonesia and Sulawesi (See Fig. 4). The age of the associated

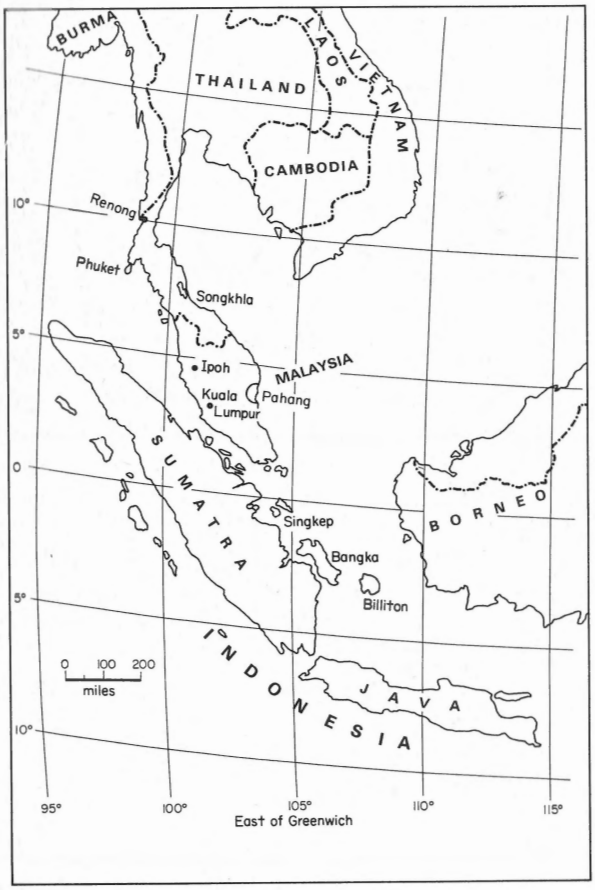


Fig. 4
The tin province of South East Asia.
The map shows the location of the main tin producing centres in Thailand, Malaysia and Indonesia.

granites in this area is post-Triassic, presumably Jurassic. Some of the granite bodies in this vast area show great similarities of texture and mineral composition but a number of local variatons have been recorded from small areas near Haad Som Pan, Thailand and from Malaysia. These local facies contain variable amounts of tin – from 0.0025 to 0.0076% near Ipoh – and the highest tin proportions in these rocks occur in the biotite granites, for example, at Sungei Besi, Malaysia which has a tin content of 0.01%.

The main tin-bearing mineral in these granites is cassiterite and recent work has clearly shown that the cassiterite occurs as a primary, accessory constituent, e.g. in Odegi, Nigeria (see Fig. 5); Sungei Besi, Malaysia; Haad Som Pan, Thailand; and that the mineral *can* occur in amounts up to 0.06 percent as in Odegi. Enormous volumes of these granites exist and they comprise very large potential sources of tin. For example, a granite containing 0.06% cassiterite (by weight) and having an outcrop area of 1000 x 1000 metres contains about 1620 tonnes of tin per metre of depth.

The granites that contain large proportions of tin are fequently decomposed, in situ, to depths of up to 100 metres. This decomposition is possibly of pneumatolytic origin but may also, in part, be due to the late-stage, small-scale shattering that took place in the immediate post-solidification period. This shattering produced stockworks of narrow quartz and/or feldspar veins along which ground waters could readily penetrate into the granite. These veins occasionally contain cassiterite in addition to that found within the granite, e.g. Sungei Besi.

A number of the low-grade, soft-rock deposits that are *at present* being worked may in fact be decomposed granites. Unfortunately, a thoroughly decomposed granite cannot readily be differentiated from an alluvial (or an eluvial) deposit by the commonly used methods of sample examination and the true

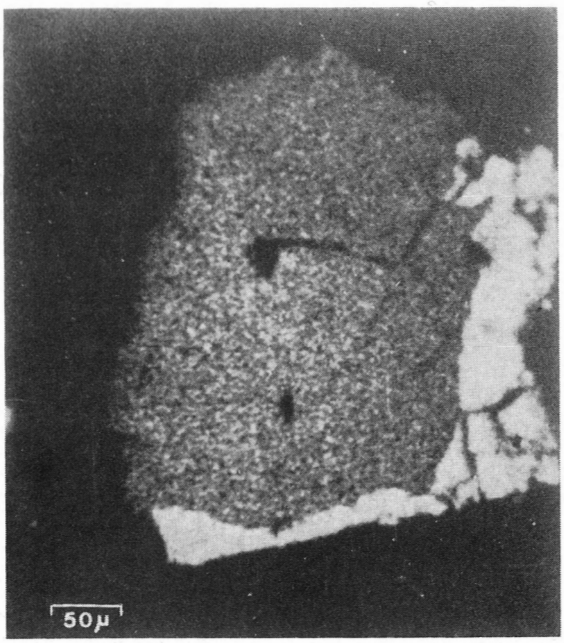


Fig. 5
Cassiterite as a primary, accessory constituent of granite.
This is a composite electron probe X-ray microanalyser picture of cassiterite (the central core) almost completely surrounded by columbite which was found in a thin section of an unweathered, albite-biotite granite from Odegi, Nigeria.

nature of these deposits is seldom recognised. The systematic determination of mineralogical assay and size distribution data is, however, invariably successful in differentiating between the various types of stanniferous deposits and such systems are now employed in a few areas.

It was at one time thought that maximum depths of decomposition were only achieved in tropical areas where high rainfall is interspersed with periods of desiccation, e.g. Northern Nigeria, South-east Asia; but the deeply decomposed granitic clay pits of Cornwall must be of the same general origin as the stanniferous granites of the tropics.

New evidence is gradually becoming available that suggests that the decomposed stanniferous granites may have been the original sources of much of the secondary, alluvial cassiterite found in parts of Nigeria and South-east Asia, and possibly in Brazil.

However, the sources of primary cassiterite most often described in the literature are the "lodes" of Cornwall and Bolivia, etc., and the pegmatites and "contact zones" between granite and country rock in Malaysia, Brazil and the Congo. These deposits have been classified as follows:

1. *Pegmatites* – contain cassiterite with columbite/tantalite and beryl, e.g. in Nigeria, Congo and Brazil. The tin content of the pegmatites is *irregular* and is, on average, apprximately 0.3%. These pegmatites show a close spatial relationship to granite. The best known and by far the largest pegmatite is the *Manono* pegmatite in the Congo which is 14 Km x 200 m x 50 m and is said to contain approximately 1,000,000 tonnes of tin.

2. *Contact Metamorphic Zones* – contain cassiterite and/or malayaite and occur in the immediate vicinity of granite, e.g. Pahang, Malaysia. The average tin content of these zones is very approximately 0.5 percent and large amounts of tin are likely to be available in this form.

3. *Pneumatolic-hydrothermal deposits* – form "lodes" in or near biotite granite. The cassiterite occurs either in *greisen* veins with chlorite, and frequently, wolframite, or in *sulphide* "lodes" with chlorite, tourmaline, and the sulphides of iron, copper, lead, zinc, bismuth, arsenic, silver, etc. The cassiterite is often fairly uniformly distributed in these "lodes" but is frequently of very fine grain size, e.g. Pinyok, Thailand; Klapa Klampit, Indonesia; Wheal Jane, Cornwall. These lodes contain approximately 1% tin but values of up to 6% are not uncommon. The usual lodes vary in width from a few centimetres to a metre or so but, at the junction of a number of lodes, the width may be considerably increased. The richest of these lodes generally occur above, and in close proximity to, granite cupolas.

In addition to the staniferous granites, all these other primary sources of cassiterite contribute to the secondary accumulations of cassiterite that form such a large proportion of the present reserves of tin. Where the topography and the climate are favourable and where suitable isostatic readjustment of the earth's crust is taking place, it is possible to form very extensive and economically attractive alluvial piles that contain between 0.1 and 0.01% tin, e.g. Kinta Valley, Malaysia, and the Tin Islands of Indonesia. Some of these alluvials have been partly submerged by recent marine incursion, e.g. Renong and Phuket in Thailand, and Bangka in Indonesia.

It is a curious feature of tin geology that very few, if any, "fossil" alluvial deposits have been located, although the deposits at Leeuwpoort and Nieuwpoort in South Africa, which are flat and conformable with Pre-Cambrian strata, *may* be of sedimentary origin.

GEOCHEMISTRY OF TIN

In meteorites the Fe/Ni phase is the richest in tin and contains an average of approximately 100 ppm* of the metal (the chondritic phase contains 5 ppm and the trioilite phase 15 ppm).

The two common ions of tin, Sn^{4+} (stannic) and Sn^{2+} (stannous), substitute in common minerals for iron, titanium and calcium to produce tin analogues of other minerals such as sphene (tin sphene, malayaite = $CaSnSiO_5$). Tin can also be dispersed in a number of minerals that contain iron, titanium and calcium, for example, biotite can contain some hundreds of ppm of tin, rutile is said to contain up to 900 ppm and andradite up to 1.7%.

In 1849 Daubrée synthesised cassiterite by the action of steam on stannic fluoride.

$$SnF_4 + 2H_2O \rightleftharpoons SnO_2 + 4HF$$

This reaction may be responsible for the formation of

* ppm = parts per million ≡ g/tonne.

the cassiterite found in close association with fluorides in many granites. There are, however, a number of tin occurrences that do not contain fluorides and it is possible that tin may also be transported as a stannate, e.g. Na_2SnO_3.

MINERALOGY OF TIN

Tin is found in a number of distinct mineralogical forms as shown in the list below:

Mineral		Occurrence
Native tin	Sn	Very rare
Cassiterite	SnO_2	Main tin mineral of commerce
Hydrocassiterite	$SnO_2.nH_2O$	Occasionally common
Thoreaulite	$Sn\ Ta_2O_7$	Occasionally common
Hochschildite	$Pb\ SnO_3.nH_2O$	Rare
Stannite	$Cu_2Fe\ Sn\ S_4$	Common but not economically important
Teallite	$Pb\ Sn\ S_2$	Rare
Franckeite	$Pb_5Sn_3Sb_2S_{14}$	Rare
Cylindrite	$Pb_3Sn_4Sb_2S_{14}$	Rare
Herzenbergite	SnS	Rare
Canfieldite	Ag_3SnS	Rare
Stokesite	$H_4Ca\ Sn\ Si_3O_{11}$	Very rare
Malayaite	$Ca\ Sn\ Si\ O_5$	Rare
Nigerite	tin silicates	Rare
Arandisite		
Nordenskioline	$Ca\ Sn\ (BO_3)_2$	Very rare
Hulsite	tin borates	Rare
Paigeite		

occasionally found in smelter concentrates.

Cassiterite, which is often called "tin-stone" and, incorrectly, "tin ore", is the major mineral of the tin industry. The details of the mineralogy of cassiterite are only imperfectly known. The colour of the mineral can range from "white" through grey to brown and black, but the reasons for this variation of colour are not understood: e.g. it was once believed that the lighter colours indicated greater purity, but a black cassiterite from the Kinta Valley contains 77.6% Sn whilst a white cassiterite from the same area, rather surprisingly, contains only 74.2% Sn. Individual grains of cassiterite are often impure and can contain large numbers of microscopic inclusions of columbite, wolframite, ilmenite, iron oxides, etc., (see Figs. 6a to 6d). These impurities markedly affect many of the physical properties of the cassiterite, e.g. the magnetic permeability, the chemical reactivity, etc., and frequently cause difficulties during the extraction of the mineral. For example, cassiterite that contains iron oxide inclusions is usually markedly ferromagnetic whereas normal cassiterite is paramagnetic. Cassiterite is normally insoluble in hydrochloric acid but a variety containing 74% Sn and 1% Fe from a granite/limestone contact zone at Pin Yok, Thailand, is readily dissolved in concentrated hydrochloric acid. It has been suggested that this acid solubility is related to the very small grain size and the enormous surface area of the mineral from this locality. However, it has also been shown that iron oxides catalyse the reaction $2HCl + H_2 + SnO_2 \rightarrow SnCl_2 + 2H_2O$ (see Fig. 7) (niobium inhibits the reaction and tantalum has no effect on the kinetics of the reaction). It is, therefore, possible that the solubility of the Pin Yok cassiterite may, in part, be controlled by its iron oxide content.

EXPLORATION FOR TIN

The prospects of finding completely new tinfields were, until recently, considered to be rather remote but the developments currently taking place in Rondonia, Brazil, may lead to the most important tin finds of the century. In addition the stanniferous deposits that have been found in Alaska may also prove to be of considerable significance.

The ores of tin are nowadays located either by geochemical surveys which use assay methods claimed to be capable of detecting 0.5 ppm of the metal, or by rather inefficient manual panning for the mineral cassiterite. Much of the cassiterite in decomposed primary granites is too fine-grained to be readily collected by these panning methods and, in addition, the metal occurs in proportions that are too low for all but the most sophisticated chemical assay methods. Consequently, there is considerable danger that economically attractive primary granitic deposits may have been missed by the existing prospecting methods. The use of detailed mineralogical analyses during prospecting for "soft-rock" deposits has not been widely adopted but the example given in Nigeria, with such techniques, (which were initially developed for finding columbite deposits) is slowly being followed by the tin industry.

The search for tin frequently takes place in swampy or marine locations that are difficult of

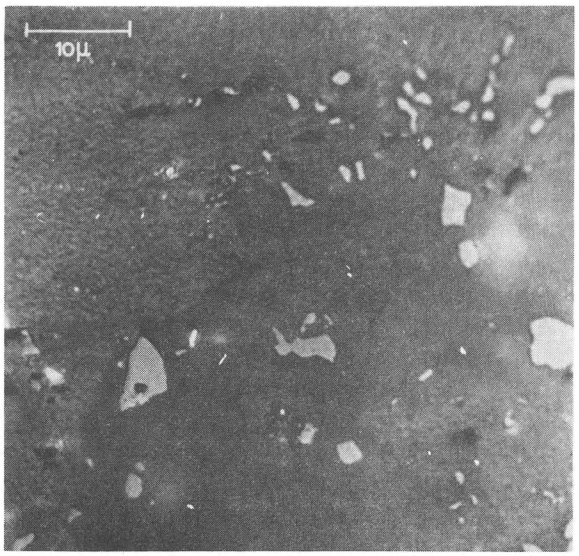


Fig. 6a

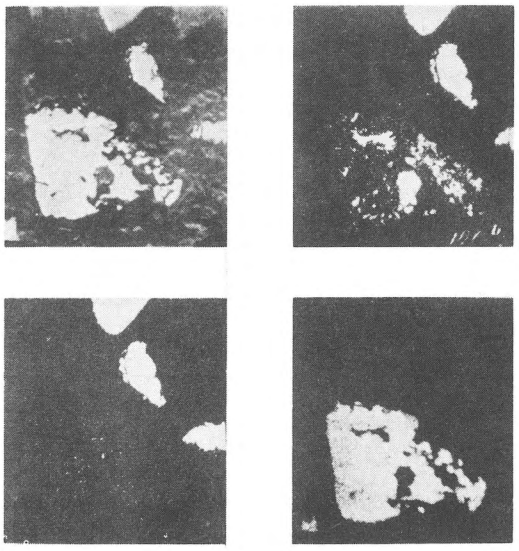


Fig. 6b

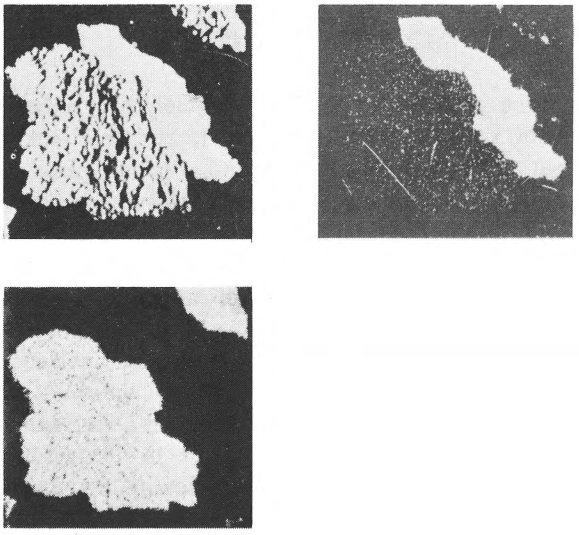


Fig. 6c

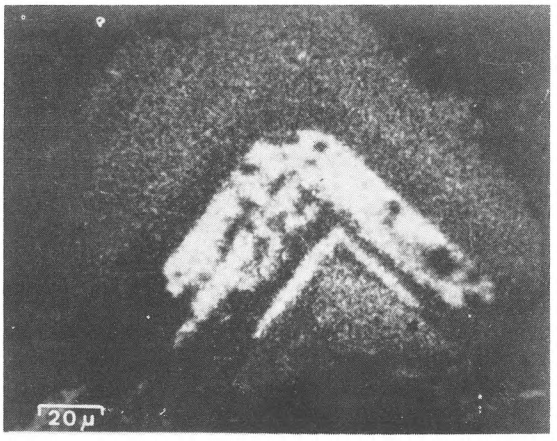
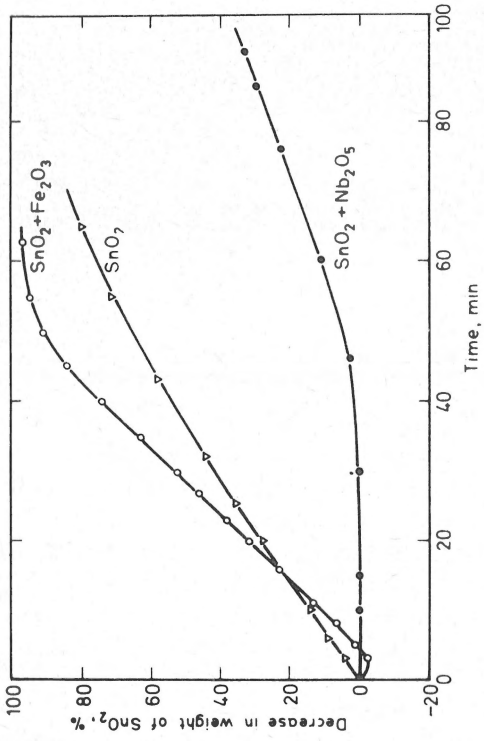


Fig. 6d

Fig. 6
Impurites in cassiterite.

a. Optical micrograph of a fragment of banded cassiterite showing multiple inclusions of columbite from an alluvial deposit, Nigeria.
The lighter areas are columbite. The darker matrix is cassiterite. The speckled area is an area of unresolved, finegrained intergrowth of columbite and cassiterite.
b. Electron probe X-ray microanalyser pictures of a cassiterite grain from a Cornish lode deposit that contains inclusions of magnetite. (The three associated grains are wolframite).
c. Electron probe pictures of Bolivian cassiterite with galena impurity.
d. Composite electron probe picture showing banded cassiterite from an alluvial deposits in Nigeria. The outer bands contain columbite inclusions and the central bands contain iron oxide inclusions.



Influence of additions of 4·4% of Fe_2O_3 and Nb_2O_5 on the rate of reaction between SnO_2 and excess H_2–HCl gas mixture. Conditions: 550 C, p_{H_2} = 3·3 kN m^{-2}; p_{HCl} = 2·7 kN m^{-2}

Fig. 7
The influence of niobium and iron on the chemical reactivity of tin oxide. (after A.P. Prosser)
Iron oxide initially inhibits but later catalyses the reaction between tin oxide and a hydrogen-hydrochloric gas mixture at 550°C. Niobium oxide, however, significantly reduces the rate of the above reaction.

access and present many logistic problems to the prospector. Furthermore, it is not easy to obtain good samples from loosely aggregated materials that may contain only small proportions of very heavy particles and the manual drilling techniques that have been commonly used for this work in the past have not always been very successful e.g. Banka drills.

In Nigeria manually-dug prospecting pits, which are seldom more than 50 cm in diameter, are used for the evaluation of tin deposits to depths of 10 m or more. Improved mechanical drilling tools and techniques are now being employed but despite these advances the evaluation of "soft-rock" tin-bearing deposits often lacks accuracy. It is perhaps fortunate that the methods employed almost invariably *underestimate* the amount of tin available, for example, recent work in Indonesia shows that cassiterite recovery during Bangka drilling seldom exceeds 50 or 60% of the mineral. Whilst such underestimation of reserves can be a useful safety factor in the design of a suitable mineral recovery unit there is some danger that economically viable deposits may be missed by such unreliable prospecting methods.

"Hard-rock" evaluation relies almost entirely on core drilling followed by chemical assays for tin and such assays are frequently unreliable. The many new methods now available include atomic absorption analysis and X-ray analysis by portable fluorescence analyser. The latter technique offers the great advantage of providing very rapid analyses that can be carried out in the field or even in a mine stope.

EXTRACTION OF TIN ORES

Between 75 and 80% of the total output of tin is obtained by "on-surface" extraction techniques. These techniques are in use on *all* the soft-rock tin deposits since these deposits provide large volumes of low grade ore which are amenable to extraction by large-scale, earth-moving methods. Some hard-rock deposits of the "sulphide lode" type are worked from the surface in Thailand and a few small pegmatites are also worked by open-cast methods in various parts of the world.

The main areas of under-ground mining are Bolivia, Australia and Cornwall. It is interesting that many of the Bolivian and Cornish tin mines are extensions in depth of mines that were originally worked for copper.

Fig. 8 tabulates the mining methods that are employed in Malaysia for the extraction of tin ore. The total amount of tin *ore* extracted per year in that country is not readily determined but is estimated as approximately 200,000,000 tonnes. This enormous total compares with the total world copper ore tonnage of very approximately 500,000,000 tonnes.

The most important single mining method is gravel pumping whereby the loosely compacted alluvials (and also, on accasion, decomposed granite) are

	Percentages of total output			
	1928	1937	1961	1963
Dredging	30.24	48.14	52.9	45.9
Gravel pumps	45.05	38.22	34.5	39.7
Hydraulicing	8.39	4.32	2.4	2.0
Opencast mining	6.45	4.02	2.5	4.0
Lode mining	5.57	3.82	4.1	3.7
Dulang washing	1.82	1.33	1.9	2.7
Alluvial shifting	0.42	0.05		
Combined methods	2.04			
Other		0.09	1.7	2.0

Fig. 8
Tin extraction methods employed in Malaysia.
The latest (1968) values show that gravel pumping now accounts for almost twice the tonnage of tin-in-concentrates produced by dredges. Hard-rock (lode) mining accounts for only about 3 percent of the total tin output.

broken by high pressure water jets and the resulting slurry is pumped away for treatment. Many hundreds of such units are in use and, since they employ only small amounts of capital, they can be used to extract deposits of small extent and gravel pump mines can be rapidly re-opened after periods of closure due to production restrictions or other reasons.

The tin mining dredges are all large, bucket-ladder units, some of which are capable of moving almost 1,000,000 tonnes/month at a cost of only 50 Dutch cents per tonne (see Fig. 9). The maximum digging depth of these units is about 50 m and, in Thailand and Indonesia, many dredges are employed at sea in water depths of up to 30 m.

Dry open pit mining methods are not widely used in the tropical areas of Malaysia and Indonesia but have been widely employed in Nigeria. The alluvium or decomposed rock is dug by mechanical shovels or bucket-wheels and transported to the treatment plants by conveyor belts (see Fig. 10).

Traditional hard-rock mining for tin is carried out in Bolivia, Cornwall, Australia, etc., and these methods range from a few rare, block caving operations (such as Catavi, in Bolivia) to hand extraction from narrow lodes of variable width.

MINERAL TREATMENT

The tin industry is notable for its almost complete reliance on simple gravity methods of mineral separation. The cassiterite that is found in soft-rock ores is

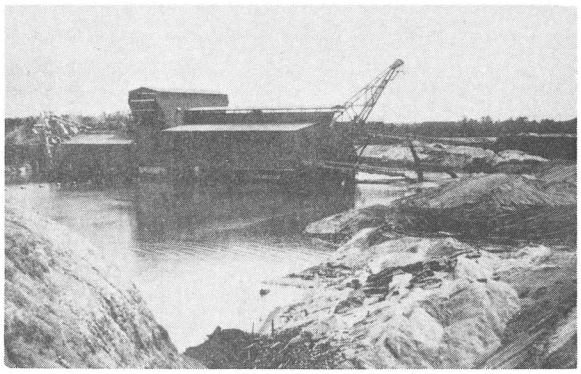


Fig. 9
Tin dredging.
The deepest digging dredge in the tin industry, Malaysia. This bucket-ladder dredge is digging nearly 50 m below the water surface and about 8 m above the water.

generally liberated from its matrix without undue difficulty by various scrubbing and washing devices, and the grain size of the mineral (2 mm to 100 μm) is commonly quite suitable for it to be concentrated by gravity methods. Furthermore, cassiterite, is notoriously difficult to concentrate by flotation and concentration methods such as volatilisation or chemical solution have not yet been effectively employed on any of the low-grade tin ores.

The liberation of cassiterite at a reasonably coarse size from "hard-rock" ores is often difficult since the mineral is brittle and tends to shatter readily.

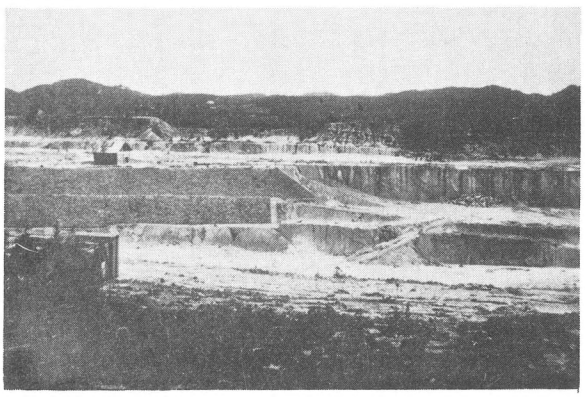
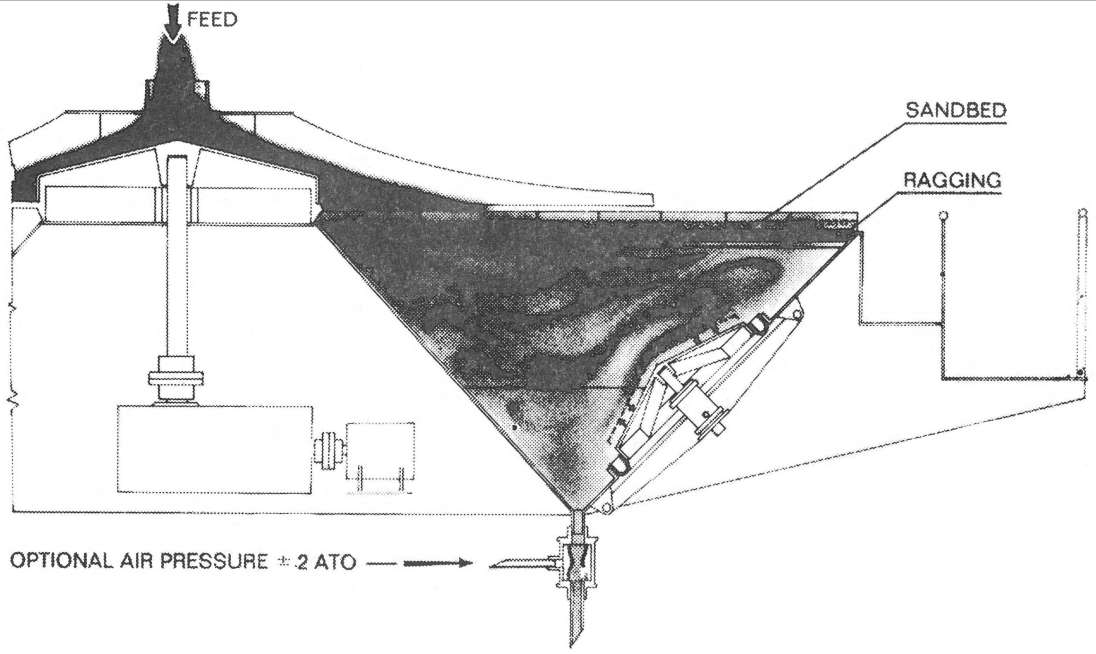


Fig. 10
Dry, open-pit extraction.
Bucket-wheel excavator working in decomposed granite in the Sungei Besi open-pit, Malaysia. The pit slopes are initially stabilised by thatching with straw and the slopes are eventually covered by a thick cover of grasses.



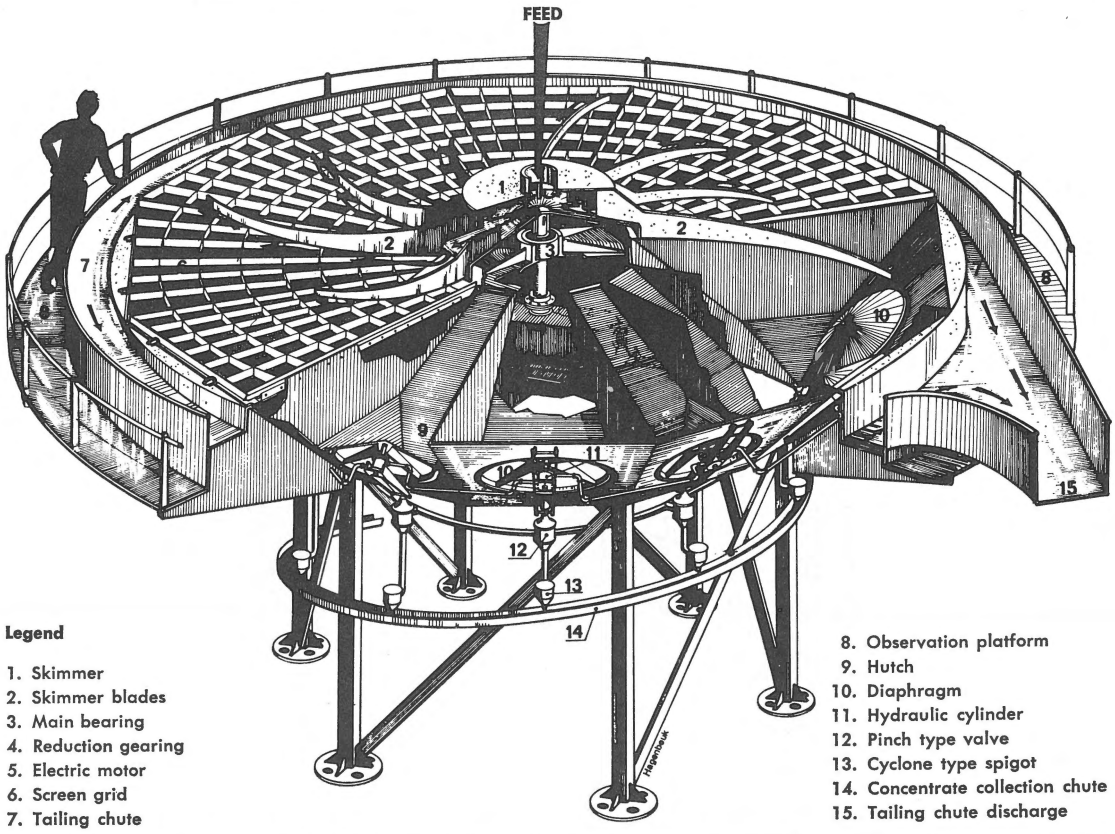


Fig. 11
Circular jig.
. This is a cross section of the right-hand side of the jig showing the pulp flow, the reciprocating diaphragm and the rotating plough that removes large fragments or light minerals that have settled on the bed of pulp.
. A schematic diagram showing the feed distributor, the rotating plough, etc. on a circular jig. The scale of the diagram is given by the operator.

Consequently there is a tendency for the usual liberation procedures of crushing and grinding to produce very fine-grained cassiterite that cannot adequately be concentrated by the gravity methods that are available. The shattering of cassiterite is reduced by using multi-stage comminution systems that work in closed circuit with separation units such as dense-media plants, jigs, tables, etc.

A preliminary sorting of barren material from the tin-bearing parts of an ore is frequently possible. With hard-rock ores the barren wall-rock can often be discarded by hand-sorting or by heavy media separation and when treating soft-rock ores the untreatable slimes and any coarse, barren gravels can be discarded by screening. The most commonly used gravity separators as jigs and circular jig units up to 7 m diameter, and capable of treating up to 600 tonnes/hour, are now employed on dredges (see Fig. 11). Shaking tables and sluices (or palongs) are widely used in the treatment of soft-rock ores and some vanners and strakes are in use for the separation of lode minerals. The gravity concentrates which are produced by these methods are seldom considered clean enough for shipment and further treatment stages are necessary. These stages include electrical and magnetic separations and, in addition, if significant quantities of sulphides are present, these minerals are removed by flotation with xanthates.

In the soft-rock sector of the industry the feed grade to the treatment plant is seldom known with any accuracy and, since the tailings are seldom assayed, it is only rarely possible to arrive at reliable values of tin recovery. It is obvious, however, that recovery values are often low since recently-discarded tailings from tin treatment plants are being repeatedly reworked at a profit.

In many of the major producing countries there is a considerable tax inducement to produce the maximum possible grade of tin concentrate and products containing over 75 percent tin are not uncommon. On the other hand, the concentrates from many of the hard-rock mines contain much less than 50 percent tin and these minerals can often present difficulties during smelting.

TIN SMELTING

The main tin smelting centres were at one time in the United Kingdom, the Netherlands and Malaysia. Nowadays, most producing countries smelt their own concentrates and modern smelters exist in Nigeria, Indonesia, Thailand, Bolivia, Australia, etc.

The smelting of high grade cassiterite concentrates is a fairly simple procedure. The overall reaction is:

$$SnO_2 + C \rightarrow Sn + CO_2$$

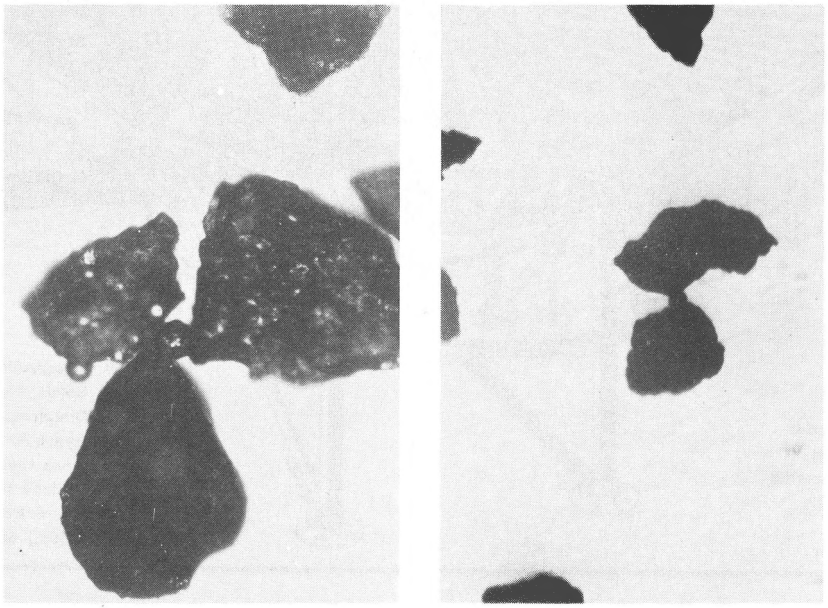


Fig. 12
Solidified droplets of tin metal formed at the surface of particles of quartz from a tin ore (after A.P. Prosser).
The largest particle is = 100 μm in size.

The carbon is supplied in the form of anthracite, coke or wood charcoal and the reaction is carried out at comparatively low temperatures in reverberatory or electric furnaces.

This simple process is quite adequate for smelting most of the products from alluvial mining but can be responsible for much waste when treating the concentrates from lode mining operations.

Many of the low-grade concentrates obtained from hard-rock ores contain deleterious impurities such as lead, copper, etc., and special care is necessary during the smelting process. A number of secret methods have been developed by various smelters who specialise in the handling of these types of ore.

At the Royal School of Mines recent work on the reduction of an ore containing about 1% tin (which occurred as unliberated cassiterite in a siliceous matrix) by hydrogen at 800°C showed that much of the tin metal was formed as spherical droplets and migrated to the surface of quartz. It is possible that, after solidification, such droplets could be separated from the matrix by screening or by flotation (see Fig. 12).

USES OF TIN

The man in the street is hardly ever a direct purchaser of tin and he is largely unaware of the importance of the metal to his way of life. This is largely because tin forms a relatively minor component of the finished article in most of its major uses, i.e. in tinplate, tinned domestic ware, bearings and bronzes. Fig. 13 shows the proportions of the total tin production used for various manufacturing purposes.

Tinplate is tinned steel sheet. This material is by far the largest single user of tin and most tinplate is used for food and beverage canning. In the past decade

	Nature of metal			*Representative Uses*
TIN	*As metal*	Cast	Foil	Lining valves and pipes
		Rolled	Sheet	food wrapping, electrical condensers, tobacco packaging lining tanks
		Powder		metal spraying, reagent
		Extruded	Collapsible tube	pharmaceuticals, adhesives, paints, toiletries
			Pipe	chemical-, beverage-, and food-handling equipment
		Molten		float glass.
	Coatings	Immersion		pins, buttons, staples, printed circuit boards, pistons
		Clad		copper alloys, steels
		Electrodeposited		table ware, petrol tanks, drawing instruments, musical instruments, radio chasses, food equipment *tinplate*
		Hot dipped		tinplate, dairy and brewery equipment, hot water apparatus, signs, fuel tanks
		Fluid bed		alloys for refractory metals
		Sprayed		food equipment, bearings
	Alloys	Solder		food cans, electronics, plumbing
		Bearing alloys		bearings for cars and heavy trucks
		Bronze		bushings, gears, coins, bells
		Type metals		linotype, monotype
		Pewter		domestic ware, jewellery
		Dental alloys		amalgams, brazing
		Fusible alloys		fusible links, die casting, solders
		others		Grey iron castings, superconductors, semi-conductors.
	Chemical Compounds	Inorganic		toothpastes, ceramics, dielectrics
		Organic		P.V.C., paint stabilizer, wood preservative, fungicide.

After Tin Research Institute.

Fig. 13
Tin and its uses.

there has been an almost total eclipse of the hot-dipping method of applying the molten tin to the steel sheets by electrolytic deposition methods and, as a result, there has been a major saving of tin; for example, the amount of tin per unit of steel sheet has been reduced from 1.68% to approximately 0.6%. The continuous electro-tinning of steel strip only began in the 1930's but there are now 115 such tinning plants in operation. The larger of these plants have capacities in excess of 250,000 tonnes of tinplate per year and the steel strip can be coated at speeds of greater than 500 m/min. By this method more than 60,000 tonnes of tin per year are used in a process involving about 10^{14} coulombs of electricity. The total annual weight of electrodeposited tin is greater than that of all other electrolytically deposited metals put together. Electrolytically prepared tinplate differs from most other metal coatings because the tin coating is thermally melted after deposition. This melting operation, which is known as "flow brightening" allows the tin to form an alloy with the steel base and, at the same time changes the tinplate surface from a matte finish to the bright, specular appearance associated with this material. The average thickness of the tin coating obtained by this method is less than 1 micrometre. Tinplate is nowadays under severe pressure from substitutes that range from "tin-free" steel cans protected by aluminium, chromium, nickel or lacquer coatings to aluminium cans and plastics. In addition, frozen and dehydrated foods, which are stored without the use of tinplate, are increasing in importance. However, the great value of tinplate in the preservation of food is well established and complete substitution will take a very long time.

Bronze: This material is basically an alloy of copper and tin in which the concentration of tin rarely exceeds 10 percent. The various types of bronzes now available are noted for chemical resistance, mechanical strength and ease of fabrication and are widely used in marine engineering, chemical engineering and in food handling equipment. Precision bars and tubes of bronze can now be made by a continuous chill-casting process. The continuously cast products are almost entirely free from porosity and internal flaws because only sound metal can enter the die whilst impurities and gas float on the metal reservoir and are removed.

Solder: most solders are tin-lead alloys. The tin confers the ability to stick metals together whilst the lead content controls the melting range of the solder. Solder for electrical joints needs a high fluidity and usually contains about 65 percent tin. The solder used in plumbing requires a wide "pasty range" and consequently has a high lead content. The number of solder joints in the communication and electronic fields increase each year but the size of an individual joint tends to decrease. Consequently, the total amount of tin used in this field has remained virtually unchanged for a number of years.

Anti-fraction metal bearings: Tin-rich "Babbit" metal bearings, which contain up to 90 percent tin, have been in use for more than 100 years. They are generally used in electrical machinery, marine engines and heavy diesel engines. Small Babbit-type bearings are also used in automobile engines. Aluminium/tin bearings (containing 20% tin) are also in wide-spread use in motor cars where superior fatigue strength is necessary. The use of tin-based bearings is under some competition from roller bearings and from plastic bearings.

Tin compounds: tin oxide is widely used as an opacifier in enamels and organotin compounds are used in wood preservatives, special paints and disinfectants. Rigid polyvinylchloride contains up to 1 percent of organotin compounds where they improve transparency and colour. The addition of tin compounds to polyurethane ensures greater speed of production of the foam that is now so widely used as "sponge rubber".

Some hundreds of tons of tin per year are sprayed onto agricultural crops as a fungicide. It is unlikely that such tin has yet figured in geochemical survey figures but it will obviously present a hazard for geochemists of the future.

It can be seen that most of the traditional uses of tin are under pressure from substitute materials: because of this pressure the industry has supported research into the properties and uses of tin by the *International Tin Research Council* since 1932.

The Research Council is financed by the major tin producing nations and has its headquarters at the Tin Research Institute in London. The Council controls a number of organisations for the technical development of tin in many other countries, e.g. Technisch Informatie Centrum voor Tin, The Hague. The declared objectives of the Council are to develop the consumption of tin by seeking new uses and to

improve existing products and processes that use tin in any form.

FUTURE PROSPECTS FOR TIN

As indicated above, the traditional uses of tin are under severe attack from improved technology and from substitution: the supply of tin metal is more than usually subject to political factors which are outside the control of the users of the metal; in addition, the reserves of the metal have always been claimed to be small. What then are the prospects of tin for the future? Fortunately, the metal and its compounds have a number of unique properties that will ensure their continued use: e.g.

1. low melting point of tin
2. molten tin wets and adheres to many common metals
3. tin has a high resistance to corrosion
4. coatings of the metal can be readily electro-deposited
5. coatings of the metal are non-toxic
6. tin readily alloys with many elements
7. tin possesses a low coefficient of friction and very thin coatings allow steel to be deep-drawn.
8. the oxide has a high opacity in glasses and enamels
9. tin forms a range of useful organic compounds.

W.R. Jones said in 1925 "lode-mining is far more likely to continue to yield large outputs for a long period of future years than will the mining of secondary stanniferous deposits that are fast being exhausted, as in the Dutch East Indies . . . . . 10 to 12 years hence the bulk of the rich secondary deposits of South-East Asia will have been exhausted".

Such dismal prophesies for the future of tin have been made regularly for over 50 years but production from South East Asia is still approximately 100,000 tons of metal/year and almost all of this is obtained from deposits that Professor Jones would (in 1925) have called "secondary stanniferous deposits".

The definition of tin "ore" is now, of course, very different to what it was in 1925. As extraction and treatment methods improve, it will be possible to work even lower grade deposits than at present and such deposits exist in vast quantities in South East Asia and elsewhere. Consequently, there is little danger of any long-term shortage of tin. Even short-term fluctuations of production are now less likely than in the immediate past because of the work of international bodies such as the Tin Council and the Tin Research Council.

The history of tin has been one of marked fluctuations of supply and demand but, it can be claimed with confidence, that its future as an important industrial metal is now assured and that adequate reserves of ore exist to meet any foreseeable demands.