Assessment Manual

Heavy Minerals of Economic Importance

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Sillimanite and Andalusite, Staurolite, Garnet, Chromite, Magnetite,
Cassiterite, Columbite-Tantalite, Wolframite and Scheelite)

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[218 p., 31 fig., 125 tab.]

Heavy minerals (ilmenite, leucoxene, rutile, zircon, monazite, xenotime, kyanite, sillimanite, andalusite, staurolite, garnet, chromite, magnetite, cassiterite, columbite-tantalite, wolframite, scheelite), genesis, deposits, quality, use, parameters, technological properties, occurrences, production, reserves

[Heavy minerals of economic importance]

Abstract: Usually, heavy minerals are not the first thing on the mind of working geologists in Germany. However, on a global scale, they are of crucial economic importance as non-metallic and metallic raw materials alike. Economic heavy mineral deposits are mainly located in tropical and sub-tropical countries. Heavy minerals are traded globally as bulk and bagged minerals. The economics of the various heavy minerals is the subject of this monograph. The group of heavy minerals described includes ilmenite and leucoxene, rutile, zircon, monazite and xenotime, kyanite, sillimanite and andalusite, staurolite, garnet, chromite, magnetite, cassiterite, columbite-tantalite, as well as wolframite and scheelite.

The report starts with an outline of the ore genesis of heavy mineral deposits and how they are mined. It is followed by data on the mineralogy, petrography, chemistry and ore genesis of each of the heavy minerals, plus extensive information on their application, their uses in various products, and their potential substitutions by other materials. Background information, reserves and production data, as well as a selection of basic references, conclude each chapter.

[Schwerminerale von wirtschaftlicher Bedeutung]

Kurzfassung: Schwerminerale stehen nicht so sehr im Bewusstsein des in Deutschland tätigen Geologen. Weltweit sind sie als nichtmetallische aber auch metallische Mineralrohstoffe jedoch von großer wirtschaftlicher Bedeutung. Vor allem in Ländern der tropischen und subtropischen Zone finden sich bauwürdige Anreicherungen von Schwermineralen. Fast alle Schwerminerale werden weltweit und in großen Mengen gehandelt. Die wirtschaftliche Bedeutung der verschiedenen Schwerminerale ist Gegenstand dieser Monographie. Die Gruppe der hier beschriebenen Schwerminerale umfasst Ilmenit und Leukoxen, Rutil, Zirkon, Monazit und Xenotim, Disthen, Sillimanit und Andalusit, Staurolith, Granat, Chromit, Magnetit, Cassiterit, Columbit-Tantalit sowie Wolframit und Scheelit.

Zu Beginn der Abhandlung steht ein Überblick über die Genese von Schwermineralllagerstätten und deren Abbau. Die einzelnen Schwerminerale werden danach getrennt mineralogisch, petrographisch, chemisch sowie lagerstättengenetisch beschrieben. Es folgen umfangreiche Informationen zur Verwendung der Minerale und der aus ihnen gewonnenen Produkte einschließlich der Möglichkeiten ihrer Substitution. Hintergrundinformationen und Zahlen zur Vorratssituation und Produktion sowie eine Auswahl grundlegender Schriften schließen jedes Kapitel ab.

[Minerales pesados de importancia económica]

Resumen: Minerales pesados no tienen un gran papel en la consciencia de los Geólogos en Alemania. Sin embargo los minerales pesados metálicos y no-metálicos tienen una gran importancia económica a escala mundial. Especialmente en los países de la zona tropical y subtropical se encuentran enriquecimientos de minerales pesados que son dignos de explotar. Casi todos los minerales pesados se venden y además en gran cantidades a escala mundial. La importancia económica de los distintos minerales pesados es el objeto de esta monografía. El grupo de los minerales pesados aqui describidos comprende ilmenita y leucoxeno, rutilo, circón, monacita y xenotima, distena, silimanita y andalucita, estaurolita, granate, cromita, magnetita, cassiterita, columbita-tantalita así como wolframita y scheelita.

Al comienzo del tratado se encuentra una visión general de la génesis de los yacimientos de minerales pesados y de su explotación. La descripción mineralógica, petrográfica, química así como de la génesis de los yacimientos de los minerales pesados sucede por seperado. Siguen informaciónes extensos sobre el uso de los minerales pesados y de sus productos incluyendo las posibilidades de su sustitución. Informaciónes de trasfondo y cifras de las reservas y de la producción así como una selección de escrituras básicas concluyen cada capitulo.

[Importance économique des minéraux lourds]

Résumé: En Allemagne, les géologues ne sont pas conscients de l´importance des minéraux lourds. Cependant, ceux-ci sont d´une grande importance sur le plan économique en tant que matières premières minérales métalliques et non métalliques. Ils sont surtout localisés dans les pays tropicaux et subtropicaux. Presque tous les minéraux lourds sont exploités en grande quantité dans le monde entier. L´importance économique de ces différents minéraux fait l´objet de cette monographie. Le groupe des minéraux décrits comprend: ilménite et leucoxène, rutile, zircon, monazite et xénotime, disthène, andalousite et sillimanite, staurolite, grenat, chromite, magnétite, casssiterite, columbite-tantalite, wolframite et scheelite.

Un aperçu général de la genèse des gisements et de leur exploitation se trouve en début du rapport. Chaque minéral lourd est classifié de façon minéralogique, pétrographique et chimique et est décrit selon la génétique du gisement. On trouve par la suite des informations détaillées sur l´utilisation des minéraux lourds et des produits obtenus de leur exploitation ainsi que les possibilités de substitution de ceux-ci. Chaque chapitre se termine par des informations d´arrière-plan, des chiffres sur les réserves et sur la production ainsi qu´un choix de publications de référence.

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Introductory remarks

Heavy minerals – Geoscientists who deal with them for longer periods of time become fascinated by them. Whether mineralogists at the microscope entranced by their dazzling colors, their many shapes, and their use as a means of dating, or geologists because of their significance in stratigraphic and sedimentological investigations.

But heavy minerals are much more than this: in today's globalised economy they constitute important resources, employing tens of thousands in the production and international trading of millions of tonnes per year. Heavy minerals are used in the manufacture of very important construction and industrial products. Without ilmenite and rutile there would be no snow-white paints and airplanes; without zircon no control rods for nuclear reactors; without tantalite no transistors; and without cassiterite no tin cans. Some heavy minerals are not easily substituted and only available in a few countries. Many of them are thus very valuable and rare – wars have been and are still being waged because of them.

The structure of this monograph on "Heavy minerals of economic importance" is based on another publication series of the Federal Institute of Geosciences and Natural Resources (BGR): the "Manual on the Geological-technical Assessment of Industrial Minerals and Rocks" published between 1997 and 2007. The penultimate issue of this 13-piece series was the volume on "Heavy minerals". For reasons of comparability, much of the available data and many of the charts had to be omitted from this volume, and the compilation also had to be abridged significantly. In addition, the heavy minerals of economic importance – and only those are of interest from a raw materials point of view – also comprise minerals which are almost exclusively used for the production of metals. By definition they were therefore not included in the volume on "Heavy minerals" in the "Manual on the Geological-technical Assessment of Industrial Minerals and Rocks".

Thus, this monograph "Heavy minerals of economic importance" is the first nearly complete compendium of the economically important heavy minerals, which will be of interest to persons involved in this subject, such as economic geologists, mineral processing engineers, commodity traders and above all, users in the manufacturing and processing industries. The precious metals gold and platinum, as well as precious stones, such as diamonds, sapphires and rubies, have not been dealt with here, as they are already covered by sufficient and extensive special literature. Because heavy minerals occur and are traded globally, this monograph will be presented in English. The author hopes that this compendium of the economically usable heavy minerals will gain a wide audience in all the target groups.

The Author
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Introduction

Each chapter of this monograph is structured the same way as the series of publications issued under the title “Manual on the Geological-technical Assessment of Industrial Minerals and Rocks” by the BGR.

The section **Mineralogy, Petrography, Chemistry** contains mineralogical and chemical information on each heavy mineral or each heavy mineral group. Mineralogically closely related minerals or synonyms are specified and their typical chemical compositions delineated.

The section **Formation of deposits and occurrences** briefly reviews the essential processes that result in the enrichment of mineable deposits of the minerals discussed. A detailed look will however always be taken at placer deposits of each type of heavy mineral. Globally important placer deposits are listed with their data.

Under the heading **Applications** the main industrial application areas of the heavy minerals described in each chapter are specified. Important processing methods will be explained. An attempt is made to detail established as well as more recent, and even, still emerging intended uses.

The chapter **Substitutes** shows options on how heavy minerals or products made from them can be replaced by alternative raw materials and products. In these cases, please note that a potentially available substitution option in general will only be used when it is economically viable. In addition, some of the heavy minerals described are in turn substitutes for completely different primary minerals.

Of particular importance when evaluating each raw material, and therefore the heavy minerals, are its qualitative properties. These are described in tabular form in the chapter **Raw material and quality specifications** in relation to each possible area of application. The figures in the tables should be viewed as reference values (guidelines) that fluctuate within specific limits for various reasons.

The raw material and quality specifications define the physical, chemical and mineralogical properties of the heavy minerals for each specific usage, which usually but not necessarily involves concentrated material. There must therefore be a clear distinction between details relating to the *ore sand* and those that refer to the *concentrate* or even to the *final product*.

Only the exact knowledge of the material specifications of each specific mineral enables a statement to be made on the branches of industry where it can be used. Depending on the targeted area of application, the specifications for the raw material can sometimes vary significantly within very broad limits: a mineral that does not meet the specifications for a specific area of application can still be eminently suitable for another area of application where other specifications apply.

The reader should also be aware that the disclosed numbers are only the reference values that usually apply, but do not necessarily exclude the use of raw materials with differing values. This is due to the fact that in many cases there are technical processes or certain economic circumstances and pressures that still make utilization of the raw material possible (or even necessary). *Therefore, the reference values specified in this section must not be misconstrued as numbers that are absolutely binding and universally applicable.*

The quantitative aspects of evaluating placer deposits will be taken into account in the section **Size of deposits and occurrences**. Here an attempt is made to quantify the relative terms “large”, “medium” and “small” using absolute numbers. Because the heavy mineral mining industry is international, a deposit should only be termed "large" if it is of significance on a global scale, but not if it is only large on a domestic scale. Up-to-date data on the worldwide reserves situation of each mineral are listed in a table.

In the section **Important producing countries,** the most important countries and their production are detailed – often after a short outline of the historical development. Please note that reliable data for many countries is not generally available. Great care has been taken, however, to collect production data from the best available sources that is as reliable and as current as possible.

A selection of basic references on each heavy mineral has been compiled in the section entitled **References**. Predominantly standard works and publications were selected that facilitate delving further into the subject matter by specifying more detailed references themselves.

1 Overview

1.1 Classification and definition

Heavy minerals are defined as minerals having a higher density than quartz, the most common rock-forming soil mineral with a density of 2.65 g/cm^3. In practice, only those minerals that are heavier than the dense media most commonly used in the lab – bromoform (2.84-2.89 g/cm^3) or tetrabromomethane (2.94 g/cm^3) – i.e. that sink in these media, are included in the group of heavy minerals. In contrast, minerals with a lower density than heavy minerals, e.g. most mica minerals, dolomite, aragonite, anhydrite, magnesite and quartz, are called light minerals.

Heavy minerals (German: *Schwerminerale*, Spanish: *minerales pesados*, French: *minéraux lourdes*) exist in all sediments and sedimentary rocks. Deposits are only formed when there is a very large enrichment (cf. below) of heavy minerals. (Mineable) concentrations of relatively heavy or hard minerals which have accumulated as a result of physical processes are called *placer(s)* or *placer deposits*. Because many heavy minerals are opaque and darken the sediment when they reach large concentrations, the terms *black sands* or *mineral sands* or the abbreviation *minsands* have become established based on Australian literature.

Of the numerous heavy minerals, only a few have economic significance due to their properties and prevalence. These are called *valuable heavy minerals*, abbreviated as *VHM*. English references also use the terms *heavy mineral concentrate*, abbreviated as *HMC*, and *total heavy minerals*, abbreviated as *THM*, for the total volume of heavy minerals within a deposit, and *trash minerals* for heavy minerals that cannot be utilized.

Furthermore, a distinction is made in the references according to the density of the useable heavy minerals:

- the heavy heavy minerals with a density of 6.8-21 g/cm^3 (mainly gold, platinum, cassiterite),
- the light heavy minerals with a density of 4.2-6.7 g/cm^3 (mainly ilmenite, rutile, zircon, monazite, magnetite, chromite),
- gemstones with a density of 2.9-4.1 g/cm^3 (mainly diamond).

Producers, however, use a different classification, also according to the density of the heavy minerals:

- the light (largely not exploitable) heavy minerals with a density of <3.7 g/cm^3 (sillimanite, epidote, hornblende, andalusite, tourmaline, kyanite etc.),
- the heavy (mostly exploitable) heavy minerals with a density of >3.7 g/cm^3 (ilmenite, leucoxene, garnet, rutile, zircon, monazite, xenotime etc.).

Heavy minerals enriched in placers that can be exploited commercially include:

- ilmenite and its weathering products up to leucoxene,
- rutile and anatase,
- zircon,
- monazite and xenotime,
- staurolite,
- aluminum silica minerals, i.e. kyanite, andalusite and sillimanite,
- minerals of the garnet group,
- magnetite,
- chromite,
- cassiterite,
- tantalite-columbite,
- wolframite and scheelite

as well as

- precious metals, i.e. gold and platinum,
- gemstones, i.e. diamond, ruby and sapphire,

which are, however, not the subject of this monograph, as there are sufficient and comprehensive references already available on them.

1.2 Genesis of Placers

Heavy mineral placers are formed by early settling of the heavy minerals from a transport medium when the flow energy abates. Gemstone placers, however, are formed as a residue from the weathering of particularly hard minerals. The references specifiy a multitude of possibilities for classifying placers. Based on MACDONALD (1983), however, we can distinguish essentially between:

- **Eluvial placers**
  Eluvial, also called residual, placers are formed at the early stages of placer development. They are formed when rocks rich in heavy minerals (kimberlite, granite, pegmatite etc.) lose their structure due to different types of weathering and are therefore increasingly exposed to erosion. The lighter elements are transported away first by deflation or denudation. This results in a relative in situ concentration of heavier or more resistant minerals forming a placer. Examples of important eluvial placer deposits are Greenbushes in Western Australia with the valuable minerals cassiterite and tantalite, and Round Mountain in Nevada with the valuable mineral gold.

- **Colluvial placers**
  After their release from the parent rock, the heavier minerals are also subject to erosion. Even purely gravitative processes such as earth flows, mudflows or rock falls can sort the components and therefore form placers. Mining of these colluvial placers is of no global economic importance, but regionally some of the screes formed in this way are mined (e.g. India: gold, Southeast Asia: cassiterite)

- **Fluvial placers**
  a) Alluvial fans
  With increasing denudation and erosion, the minerals are exposed to the hydraulic properties of water. The heavy minerals are concentrated in so-called alluvial fans. They are mostly formed in the arid to semi-arid climates of the transitional regions between mountains and plains. With decreasing relief energy and reduction in the transport force, heavy minerals initially settle in alluvial fans, while the light minerals can still be transported further away. This is how the world's largest rutile deposits (cf. Chapter 3.6) were formed in Sierra Leone. The gold placers of the Witwatersrand District in South Africa were formed in the transition from these alluvial fans to delta-type alluvial accumulations.

  b) Flood plains
  In rare cases, placers can be formed by river floods. These can break their banks and deposit fine material in the surrounding flood plains. Because of the huge range in flow energies, this can lead to accumulations of heavy minerals such as gold in particular.

c) Point bars
The intense decrease in flow velocity in the slip-off slopes of meandering streams lowers the transport power of the water. The resulting sedimentation of heavier minerals can form placers with high concentrations of gold, for example.

d) Braided bars and islands
Mineable fluvial placers are also formed on riverbanks where sharp changes in flow velocities occur. This sweeps away lighter minerals and concentrates heavy minerals, especially gold, but also cassiterite, etc. Due to the high erosive power of such rivers, these placers are mostly temporary occurrences. However, they can have high mineral concentrations.

e) Lag gravel, riffles, potholes
Large accumulations of heavy minerals can be found in riverbeds when strong flow velocities prevent the sedimentation of light minerals or erode such light mineral accumulations. The pore spaces between gravel particles migrating along riverbeds provide another possibility for the accumulation of heavy minerals (*interstice entrapment*). Irregularities (e.g. outcrops of rock layers) in the riverbed or scours also change flow velocities and often result in the formation of placers.

Fluvial placers of types c) to e) are globally important economically for the accumulation and mining of gold, platinoids and gemstones. Lighter heavy minerals are much less likely to form mineable fluvial placers. Exceptions to this rule however are, for example, the placers of Horse Creek in Aiken County, South Carolina, where predominantly monazite and xenotime were mined from 1955 to 1959; the monazite placers of Magang in Hubei Province, China; and the ilmenite placers of Central Virginia.

- **Glacial placers**

  Glaciofluvial placers are formed by the change in flow velocities of glacial rivers in the glacier forelands. Here the fine material transported in the river, that may for example contain gold, sediments out and forms its own deposits. Mineable placers of this kind are, however, almost only known in locations where further secondary sorting is done in rivers or on beaches (e.g. gold placers of Nome, Alaska).

  The *Port Leyden delta* glaciolimnic placers in the US State of New York were created by the discharge of a delta into a former glacier lake.

  The glacial drifts of gold-bearing ores or diamond-bearing kimberlite found in some Scandinavian or Canadian moraines, however, are not real placers, but serve only as index rocks for the prospecting of parent rocks outcropping at other places.

- **Littoral placers**

  a) Beach
  Globally, very large deposits of lighter heavy minerals such as ilmenite, rutile and zircon form so-called beach placers. These are formed through physical processes that are complicated in detail and have been researched extensively. According to this work, it is particularly important that after the deposit of a sediment skin by a breaking wave, all the minerals initially exist in an unsorted assemblage. Because the wave flowing back no longer has enough energy to remobilise the heavy minerals (*selective entrainment*) these are left as *lag deposits* after removal of the light minerals. This lag deposit is often easily visible by the gradations in color of the minerals on the beach where they were deposited and sorted according to their density. Micro-vibrations caused by the surf cause a secondary inverse gradation (light minerals migrate to the top, heavy minerals move to the bottom) and therefore the additional selection out of erodable light minerals (*dispersive equivalence*).

Depending on the pre-concentration of the heavy minerals in the *nearshore* area, the wave energy and wave height, these processes result in accumulations of heavy minerals in typical lamellae. The beach placers therefore always appear very well layered. Normally, because of the strong surf, heavy mineral concentrations are eroded away again by the following waves. During periods of high wave energy (heavy storms), however, larger volumes of sand are sorted, and there is a strong concentration of heavy minerals in the foredune areas. Beach placers formed in such a way have very high concentrations averaging 10 to 50 % heavy minerals, at maximum even 100 %. They mainly form concentrations of heavy minerals of economic interest (e.g. rutile, monazite, zircon, ilmenite, garnet) rather than lighter heavy minerals (e.g. epidote, hornblende). For such placers to be preserved in the long-term, there must also be a fall in sea level (regression, uplift of the land etc.).

The geomorphological characteristics of such beach placers are their narrow width (on average 100 m, up to 1000 m), large length (on average 1-2 km, up to >15 km) and low thickness (on average 3 m, up to 11 m). Petrographically, they usually have very low concentrations of fine particles <63 µm (a few % by mass). Almost all heavy mineral placer deposits in Western Australia (Eneabba, Capel, Jurien etc.), in the Murray Basin in Victoria, Australia (Gingko, Mindarie, Wemen etc.) and also the large heavy mineral placer deposits at Lake Malawi, were formed as beach placers.

b) Spits
Littoral placers of a slightly different kind are found alongside fossil and recent sand spits where the physical processes described above also result in heavy mineral accumulations. In addition, the effect of longshore drift also plays a role. Such a deposit related to beach placers was mined in Panama for magnetite.

- **Eolian placers**

  a) Coastal dunes
  Coastal dunes are formed by the blow-out of beach placers. Due to the preferred incorporation of light minerals, dunes should generally be less rich in heavy minerals than the adjacent beach sands – there are exceptions however because sorting also takes place in dunes: in the windward area by the wind, and on the leeward side through simple gravitational processes. Furthermore, there are field observations of all minerals being blown in from the sea by strong day winds and only light minerals being blown back from the shore by the weaker night winds (PIRKLE et al. 1989). Therefore, there is not only preservation of blown-in heavy minerals in dunes, but also independent sorting.

  Coastal dunes worldwide constitute very large but frequently also relatively low-grade deposits. An important example of this is the Richards Bay deposit in KwaZulu-Natal Province, Republic of South Africa.

  b) Inland dunes
  All those dunes whose genesis occurs largely independently of coastal winds or those that no longer lie on the coast today, are called inland dunes. The sorting and concentration of heavy minerals in inland dunes is similar to coastal dunes. The world's most important inland dune placer is the Trail Ridge deposit in Florida/Georgia, USA.

- **Marine placers**

  When classifying marine placers, a distinction is made between primary sorting and concentration processes, and secondary sorting of placers formed at other locations and subsequently "drowned".

Primary marine placers

a) Shoals

Some rivers transport large amounts of sediment which leads to the formation of large sandbanks in front of the river mouths when the flow energy decreases on a flat shelf. It is thought that the settling of coarse and heavy sediment fractions in connection with the sorting effect of longshore drift and tidal flows leads to the formation of placers, some of which are high-grade. These placers are not currently mined because exploration in an area often intensely frequented by ships is difficult and cost-intensive, not to mention the complex technical specifications involved in extraction in river mouth areas.

b) Ocean currents, tides

Numerous observations, mainly from the Dutch and German tidal flats, reveal the direct influence of ocean currents and tides on the sorting of ocean floor sediments and the associated formation of placers. Despite relatively high concentrations of (mostly not valuable) heavy minerals on the sediment surface, no data exists on the depth and therefore the mineability of these placers.

c) Storms

One of the largest known heavy mineral deposits in the world, which is however currently not exploitable due to its fine grain size, is the WIM 150 placer in the Murray Basin, Victoria, Australia. According to WILLIAMS (1990), its inner structure and the fineness of the grains indicates that this placer formed as a result of storm effects on the ocean floor.

d) Nearshore bars

In Russian literature (e.g. NEVESKII 1960) it has been assumed for a long time that waves that break on the flat ocean floor near the shore, and therefore decrease in energy, can result in the accumulation of sediments in bars parallel to the coastline – and therefore the formation of placers. Because sampling and observing such areas is very difficult, there is no solid data available. However, ELSNER (1992b) was able to provide evidence that several heavy mineral placer deposits in Northeastern Florida, USA, were created by this process.

Secondary marine placers

e) Mainly former fluvial placers

Large cassiterite deposits of today's Southeast Asian tin belt are found in a flat shelf area. They were formed during the last ice age through the erosion of weathered material (residual placers), but mostly through the sorting of fluvial placers. Gold placers in the *offshore* areas of Alaska, Siberia and Nova Scotia can also be traced back to the sorting of former fluvial placers.

f) Mainly former littoral placers

Accumulations of lighter heavy minerals are, amongst other things, known from the flat shelf areas of Australia, New Zealand, Senegal and Sri Lanka. These are strongly sorted littoral placers deposited during glacial periods that largely provided the base material for the Holocene coastal placers of today. The littoral diamond placers of South Africa have a similar genesis. Another subgroup of this type is the heavy mineral placers of the Mozambique Shelf. According to KUDRASS (1987, 1989), the Zambezi River delivered such huge amounts of heavy minerals to form beach placers during glacial periods that these, only slightly reworked during the Holocene transgression, still form independent *offshore* deposits today.

1.3 Extraction and Processing

One to two years before the extraction of heavy minerals proper begins, work is carried out to remove trees and shrubs covering the area to be mined. The wood is supplied to the local wood and paper industry, if possible including their root systems. The topography is then usually carefully surveyed to be able to restore it as closely as possible to its original condition once the mining operations have finished. Detailed mapping of the flora and fauna is carried out first during the *environmental impact study* that is always required by the authorities today.

The topsoil together with the seeds and spores it contains is carefully removed using bulldozers or scrapers a few months before mining begins. It is piled up in flat heaps for later restoration, which is almost always renaturisation.

The proper extraction processes for heavy minerals depend on the depth of the groundwater level, the degree of consolidation of the sediment and its particle size. If the groundwater level is sufficiently high and the sediment finely grained, extraction is mostly economic if large-scale cutter wheels or cutter head suction dredges that mechanically break up solidified horizons are used. In the case of very high extraction banks, the ore sand can be pushed towards the suction dredger ship using bulldozers. When gravel and stones are involved (e.g. gold extraction in Alaska, cassiterite extraction in South East Asia) floating bucket wheel dredges are used. If the groundwater level is very low, scraper bulldozers are used.

The sand/water mixture sucked in by the powerful vacuum pumps of suction dredger ships is transferred via floating pressurized pipelines to a wet mill that is also usually floating. When extracting coarse debris, the fine grained material, including valuable heavy metals, is separated on board and then supplied to the wet mill via conveyor belts. The debris is immediately dumped again. If scraper bulldozers are used for mining, the intermediate transfer into the wet mill via dumper trucks is required.

The heavy minerals contained in the ore sand are strongly pre-concentrated (on average 80-85 % by mass) in the wet mill using purely gravitative processes. Humphrey spirals or Reichert cones arranged in series are mainly used for this purpose. The separated gangue material is later used for restoring the mined area.

After running through the wet mill, the still wet heavy mineral pre-concentrate is dried, usually in a rotating kiln. The minerals are roasted if there are granular cavities filled with impurities. If there are organic coatings on the mineral grains, these are removed by “scrubbing” (so-called “attrition”) with caustic soda solution. In the dry mill, the minerals are then separated by way of their different magnetic and electrostatic behavior, and in part also their different apparent densities. The major differences in the magnetic and electrostatic properties of minerals are therefore of special interest to processing engineers.

When they leave the dry mill, the valuable heavy minerals are available as processed, saleable concentrates – frequently already separated into different grades. They are sold packed in bags or in bulk.

1.4 Notes on Prospecting and Exploration

The type and distance of the parent rocks to the placer is irrelevant when **prospecting** for heavy minerals, with the exception of the less resistant minerals cassiterite, tantalite-columbite, wolframite and scheelite. The original concentration of the minerals contained in the parent rocks is also of no importance. Rather, prospecting is based on knowing as exactly as possible the geomorphologic processes resulting in the local and regional formation of placers, as well as the properties of the valuable heavy minerals that enable detection using geophysical prospecting methods.

Geomorphological work:

- stratigraphic-sedimentological examinations. Objective: genetic classification of sediment sequences
- evaluation of satellite photos and aerial pictures. Objective: identification of locations with diminishing transport energy
- evaluation of hydrographic-oceanographic data. Objective: identification of coastal currents and sedimentation processes
- *side-looking airborne radar* (SLAR). Objective: identification of geomorphological structures underneath cover/vegetation

Geophysical prospecting:

- shallow seismic refraction survey. Objective: identification of old river valleys
- aero-radiometrics. Objective: identification of monazite deposits
- induced polarization, Objective: identification of ilmenite deposits
- (aero)magnetics. Objective: identification of magnetite deposits

Drilling boreholes or *offshore* sampling using grab samplers is indispensable for the **exploration** of heavy mineral placers. The so-called Bangka (or Banka) drilling method has proved successful worldwide for the exploration of placers, mainly in developing countries, since the end of the 19th century. This method, however, only yields very disturbed sediment samples. In manual drilling mode (4” or 6”), sediment depths of up to approx. 20 m can normally be drilled through using the Bangka drilling equipment. Using diesel engines (8”, 6” or 4”), depths of approx. 60 m can be attained.

Furthermore, when exploring for heavy minerals the following applies:

- boreholes drilled below groundwater level must be cased and if possible cored.
- optimally, the placer shall be drilled through to its full assumed depth.
- offshore, merely sampling the sediment surface is meaningless from an economic-geological point of view.
- sampling locations must be mapped!

For evaluating the economic-geological context, samples that are as large as possible (several kg) should be extracted from pooled areas. Sampling volumes of several tonnes are necessary for meaningful processing tests performed in highly skilled plant manufacturing and research laboratories.

Eeach sample should undergo granulometric, mineralogical and chemical analysis. For a meaningful economic-geological classification, microscopic analysis of the entire heavy mineral spectrum, i.e. not only the valuable minerals, is required. For an economic-geological assessment, the chemical composition of the valuable minerals (RFA), as well as the chemical composition of the ore sand, are of interest. In this case, qualified laboratories should be engaged to carry out more detailed analysis.

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2 Ilmenite and leucoxene

[German: *Ilmenit*, Spanish: *ilmenita*, French: *ilménite*]
[German: *Leukoxen*, Spanish: *leucoxeno*, French: *leucoxène*]

2.1 Mineralogy, Petrography, Chemistry

Pure **ilmenite** has the following characteristics:

Formula	$FeTiO_3$
Chemistry	52.66 % by mass TiO_2, 47.34 % by mass Fe_2O_3
Density	4.72 g/cm^3
MOHS hardness	5 – 5 ½
Color	black to black-brown
Magnetic property	intensely paramagnetic
Electrostatic property	conducting

Ilmenite is the most common titanium mineral in the Earth's crust. It is the most important dispersed accessory mineral in almost all intrusive and extrusive rocks. It has overriding significance as a titanium mineral in norites, gabbros and anorthosites. There is seamless miscibility at high temperatures (>600 °C) between ilmenite and hematite (Fe_2O_3). In the mixed crystals though, part of the Fe can be replaced by Mg, Mn and Al, as well as part of the Ti by Mg. As the temperature drops, hematite and ilmenite become segregated forming titano-hematite: here, thicker or thinner lamellae of hematite in varying amounts are intercalated with ilmenite.

Another important mineral is titanium magnetite. The two spinels magnetite ($Fe^{2+}Fe_2^{3+}O_4$) and ulvite (Fe_2TiO_4) are seamlessly miscible at high temperatures. Furthermore, part of the Fe^{2+} can be replaced isomorphously by Ti, Mg, Mn and other elements, and part of the Fe^{3+} can be replaced by Ti, Al, V and Cr in the magnetite. As the temperature declines, there is segregation into magnetite, ilmenite and ulvite. Complete segregation into pure magnetite and ulvite does not take place. In addition, ilmenite is precipitated in the form of fine lamellae on the octahedral faces of the magnetite. The slower the cooling, the coarser the segregation structure.

Due to the preferred intercalation of Fe instead of Ti, the TiO_2 content in ilmenite can be far below the stoichiometric value of 52.66 % by mass. The numerous possibilities for the incorporation of impurity ions in ilmenite also partly explain the difference in the chemical analyses of ilmenite concentrates (cf. Table 2.15). Impurities due to the incorporation of mineral impurities in solution cavities or by insufficient processing are not uncommon.

Figure 2.1 shows the FeO- Fe_2O_3- TiO_2 system in a triangle chart (GARNAR 1978). This also includes the weathering sequence of ilmenites from solid rocks (A) to ilmenites from sediments (B and C) and to leucoxenes from sediments (D) and finely crystalline, secondary rutile.

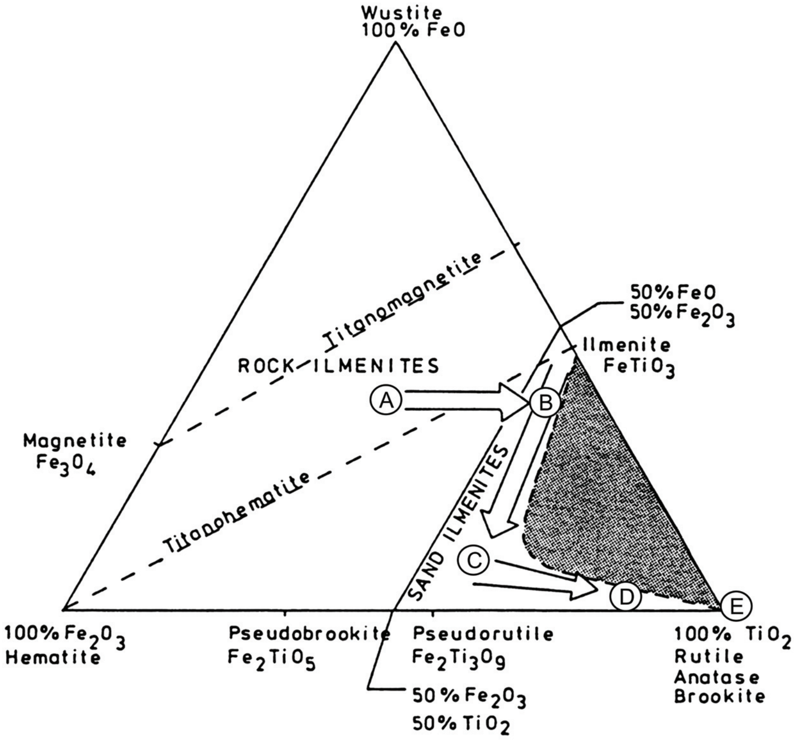

Figure 2.1: Representation of the FeO- Fe_2O_3- TiO_2 system in a triangle chart, according to GARNAR (1978). There are no known analyses of titanium minerals in the dark field.

After the ilmenite is released from solid rocks, it is subject to weathering. Particularly under humid tropical conditions, iron increasingly dissolves and titanium becomes relatively enriched. The final member in the weathering process is the mineral mixture **leucoxene**, predominantly consisting of Ti oxides and, to a far lesser degree, Fe oxides. The process of weathering is therefore called leucoxenization. Leucoxenization only occurs above groundwater level. The influence of humic acids plays an important role. As the TiO_2 content of ilmenites is of outstanding significance in an economic-geological and processing context, the process of leucoxenization has been thoroughly investigated. Starting at the grain and structural boundaries, disintegration of the ilmenite structure and formation of an amorphous iron/titanium oxide mixture occurs. FeO is increasingly oxidized to Fe_2O_3, Fe oxides dissolve. The amorphous TiO_2 recrystallizes as finely crystalline rutile, more rarely anatase or brookite. This finely crystalline mineral mixture consisting predominantly of TiO_2 is called leucoxene. The dissolution of the iron oxides induces the relative increase in TiO_2 and the reduction of magnetic susceptibility. MÜCKE & CHAUDHURI (1991) were able to very closely define the minerals of the ilmenite → leucoxene conversion series in a mineralogical and crystallographic context: ilmenite ($FeTiO_3$) → “leached out” ilmenite → pseudorutile ($Fe_2Ti_3O_9$) → “leached out” pseudorutile ($FeTi_3O_6(OH)_3$) → leucoxene.

According to TEMPLE (1966), the inherent color of "leucoxene“ directly depends on its TiO_2 content (cf. Table 2.1).

Table 2.1: Dependence of the color of leucoxenes on their TiO_2 content (TEMPLE 1966).

TiO_2 (%)	Color
52 – 63	dark gray
63 – 68	reddish gray
68 – 75	auburn
75 – 80	yellowish-brown
80 – 85	yellow orange
85 – 90	yellowish-gray
90 – 95	yellowish-white
95 – 100	white

According to GARNAR (1980), ilmenites and partially weathered ilmenites are opaque and completely soluble in sulfuric acid when the TiO_2 content lies between 45 – 65 % by mass. Leucoxenes are also opaque, have TiO_2 contents between 68 – 92 %, a light gray color when heated to 550 °C under the influence of oxygen, and are not completely soluble in sulfuric acid. Rutiles are reddish brown and translucent and have a TiO_2 content of 92 – 98 %.

GARNAR (1985) (cf. Table 2.2) and ELSNER (1992) (cf. Table 2.3) listed further distinguishing characteristics of ilmenite, leucoxene and rutile.

Table 2.2: Changes in chemical and magnetic properties with increasing weathering of ilmenite (GARNAR 1985).

Name of the Mineral	TiO_2 (%)	Density (g/cm^3)	Magnetic susceptibility
Ilmenite	40	4.7	very strongly paramagnetic
Ilmenite	50	4.7	strongly paramagnetic
Ilmenite	60	4.2	paramagnetic
Weathered ilmenite	70	4.1	slightly paramagnetic
Leucoxene	85	3.5	very slightly paramagnetic
Rutile	95	4.2	nonmagnetic

Table 2.3: Differentiation of ilmenite, leucoxene and rutile in the industry (ELSNER 1992).

Mineral	Density	Magnetic susceptibility
Ilmenite	> 4.1 g/cm^3	magnetic
Leucoxene	< 4.1 g/cm^3	nonmagnetic
Rutile	> 4.1 g/cm^3	nonmagnetic

2.2 Formation of deposits and occurrences

Ilmenite is found as an accessory in almost all magmatic rocks. It is also typical of the epizonal and mesozonal or catazonal metamorphosis zone (cf. Chapter 3: Rutile). New autochthonous formations of ilmenite in sediments are not known. Table 2.4 shows an overview of the most important deposit types for titanium minerals, including ilmenite.

Table 2.4: Types of titanium mineral reserves, their mineralogy and their economic significance according to FORCE (1991).

Category	Type	Typical mineralogy	Importance	Example
Metamorphic	Eclogite	Rutile	B	Piampaludo, Italy
	Aluminosilicate	Rutile	E	Evergreen, Colorado
	Contact ultramafic	Rutile	E	Dinning, Maryland
Magmatic	Magmatic ilmenite	Ilmenite	A	Allard Lake, Canada partly Roseland, Virginia
	Anorthosite marginal	Rutile, ilmenite	C	partly Roseland, Virginia
	Albitite (kragerite)	Rutile	E	Kragero, Norway
	Alkaline	Perovskite Nb-rutile Nb-brookite	C	Powderhorn, Colorado Magnet Cove, Arkansas
	Carbonatitic	Anatase	B	Tapira, Brazil
Hydrothermal		Porphyritic rutile	C	Bingham, Utah
Sedimentary	Fluvial	Ilmenite, rutile	A	Gbangbama, Sierra Leone
	Glaciolacustrine	Ilmenite	C	Port Leyden, New York
	Beach (and eolian)	Ilmenite, weathered ilmenite, rutile	A	Richards Bay, South Africa North Stradbroke Island, Australia Trail Ridge, Florida

A: currently of major significance, B: probably of major significance in the near future, C: of possible significance,
D: currently of moderate significance, E: currently of minor global significance

Mineable solid rock reserves of ilmenite are associated with anorthositic rocks. Its genesis is described by JACKISCH (1967):

Concordant deposits in gabbro rocks: When relatively dry, juvenile basaltic magmas are emplaced on discontinuities in the Earth's crust, initially a heat-insulating, solidified border facies is formed, which allows inferences to be made on the original composition of the magma. Mg-Fe silicates (olivine, bronzite) are precipitated as the first differentiates and form an ultrabasic to basic cumulate. Under certain circumstances, enrichment of chromite ores takes place in the peridotitic phase, and the segregation of iron sulfide in the noritic phase. Following the bronzites, Ca-rich plagioclases crystallize out. They have a tendency to rise in the earth's gravity field and form anorthosite layers. The magnetite-ilmenite ores of the gabbro phase are also precipitated at approximately the same time as the precipitation of the monoclinal pyroxenes (augites). This only occurs if the titanium content has reached a concentration of approx. 2.5 % TiO_2 due to the limited ability of titanium to become incorporated in olivine, rhombic pyroxene and plagioclases, and the removal of these silicates from the liquid rock.

The direction of differentiation and the formation of the different deposit types in gabbros in this context is an extremely complex process. Apart from the shape and size of the intrusion chamber, intrusion level, cooling and crystallization rate, and magma movement and concentration ratios, numerous other factors, which are partly very difficult to determine and are interrelated to each other, also play a part. Numerous examples show that major fractionation and differentiation can only be expected in very large intrusion complexes with a correspondingly slow cooling period.

Discordant deposits in anorthosites: From a juvenile tholeiitic basaltic magma, olivine alkali basaltic magma is formed through intermediate differentiation at a great depth at pressures of >20,000 bar. This intrudes in the deep crust into highly metamorphic, already strongly dehydrated rocks in the border areas of old shields. As the magma can only absorb insignificant volumes of water due to the assimilation of the arid rocks, its extreme dryness is maintained. There is early precipitation of plagioclases, which leads to the formation of rocks of the mangerite suite. The plagioclases rise gravitatively in the liquid rock and form anorthosite massifs. Due to the higher alkali content – attributable to intermediate differentiation – and higher formation pressure, the composition of the plagioclases shifts towards albite.

Whereas the silicate components slowly crystallize, the residual melt rich in Fe-Ti remains liquid. Before their final solidification, tectonic stress mobilizes or even transports the rock masses over short distances. In doing so, the residual liquid rock rich in Fe-Ti is squeezed out into fracture zones and zones of weakness in the anorthosite massifs. The changes taking place in the residual melt typically increase the oxidation potential in such a way that mainly the hematite-ilmenite-(rutile) association is found in the iron-titanium deposits in anorthosite massifs.

In the case of the “Virginia special type”, segregation processes occur in the liquid state in the Fe-Ti rich melt due to higher fluorine and phosphorous contents. Here, Fe-Ti oxide/apatite is formed on the one hand, and a silicate phase on the other. The Fe-Ti melt rich in apatite is squeezed into the anorthite massifs, where the further segregation of Fe-Ti oxide and apatite can occur due to the fall in temperature.

Currently, ilmenite is only mined in five solid rock deposits. This production, however, accounts for approx. 1/3 of global ilmenite production:

- Tellnes (Tellnes, Storgangen) district, Norway (mining since 1916)
- Sanford Lake (Tahawus, MacIntyre) District, New York (mining since 1942)
- Allard Lake (Lac Tio) District, Quebec (mining since 1951)
- Otanmäki, Finland (mining since 1953)
- Gusevogorsk, Russia (mining since 1963)

Erosion leads to breakdown of the rock matrix and the exposure of the ilmenite. Here, ilmenite is released in large quantities mainly from metamorphic and anorthositic complexes. Due to its stability against physical, and to a lesser degree against chemical weathering, ilmenite belongs to the ubiquitous heavy minerals. Progressive chemical weathering - leucoxenization - always results in an increase in the primary TiO_2 content and therefore an increase in their value. The heavy mineral ilmenite, concentrated in placers and, where possible, chemically weathered, is therefore the preferred prospecting target of the titanium mining industry.

2.3 Applications

The significance of ilmenite as the most important, rock-forming titanium mineral is not due to the extraction of titanium metal but the production of titanium dioxide TiO_2. TiO_2 is easily the most significant white pigment in the world, and is used, amongst other things, in paints and varnishes, printing inks, plastics, rubber, linoleum, artificial fibers, paper, glass, enamel, and ceramics. Approx. 94 % of the titanium minerals (ilmenite, leucoxene, rutile) extracted worldwide are used for the production of TiO_2 pigments. With only a few exceptions, the white materials in almost all applications worldwide owe their “color” to TiO_2 pigments!

There are two industrial processes for the manufacture of TiO_2 pigments.

The older sulfate process requires as initial raw materials either ilmenite with a TiO_2 content of 45 – 65 % or a titanium slag (cf. below) with 70 – 80 % TiO_2.

The sulfate process for manufacturing titanium dioxide was developed in 1915 and has been applied industrially since 1919, and is still of significance today. The finely ground and enriched titanium ore is broken down by concentrated sulfuric acid. In doing so, the iron oxide contained in the ore reacts to become iron sulfate, while the titanium ore becomes titanium oxysulfate.

$$FeTiO_3 + 2H_2SO_4 \rightarrow FeSO_4 + TiOSO_4 + 2\ H_2O$$

During this process, large quantities of sulfur dioxide are produced, which is largely neutralized with caustic soda solution so that only a relatively small portion of sulfuric dioxide is nowadays released into the environment. The iron sulfate is separated from titanium sulfate by crystallization. Due to its superior solubility in water, the iron sulfate crystallizes out as green iron (II) sulfate ("green salt"), which can then be removed. By boiling in large vats with water, titanium oxysulfate relatively easily breaks down into titanium oxide hydrate, again with the parallel production of large quantities of "dilute acid" as an undesirable by-product.

$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4 \text{ ("dilute acid")}$$

The titanium oxide hydrate is annealed to pure white titanium dioxide in large rotating kilns at temperatures between 800 and 1000 °C following a lengthy washing process.

$$TiO(OH)_2 \rightarrow TiO_2 + H_2O$$

To improve the optical and physical properties, the fine pigment particles are post-treated using different substances and processes (e.g. renewed washing, grinding or vapor depositing a coating onto the pigment particles).

For each tonne of TiO_2 produced using the sulfate process, approx. 2.7 tonnes of ilmenite (45 % TiO_2) and 4.0 tonnes of sulfuric acid, or 1.4 tonnes of titanium slag (80 % TiO_2) and 2.3 – 3.0 tonnes of sulfuric acid are required. In addition to 0.6 – 2.7 tonnes of iron sulfate, around 6 – 8 tonnes of dilute acid with a sulfuric acid concentration between 20 and 22 % by volume are produced. This dilute acid cannot be processed further due to its low sulfuric acid content. In the 1950s, it was released into rivers in Germany and after 1964 it was dumped from ships in the North Sea. The dilute acid is also usually contaminated with heavy metal salts such as lead or chromium salts. Dumping the dilute acid into the North Sea was stopped by law after years of negotiations and campaigns by individuals and environmental protection organizations. Since 1990, the German TiO_2 manufacturers are obliged to treat the dilute acid. The treatment process was already developed as long ago as 1958 by Bayer AG and is applied by most titanium dioxide manufacturers today. In a process consuming relatively large amounts of energy, the acid content is increased and the metal salts - predominantly the iron sulfate - are crystallized out. The higher concentrated sulfuric acid produced in this way can then be recycled back into the process. The iron sulfate is used in wastewater treatment as "green salt". It converts phosphate salts in the wastewater from fertilizers and detergents into iron phosphate that is insoluble in water. This can then be extracted from the water using the usual separation methods in sewage treatment plants. The iron oxides produced during TiO_2 production are in part recycled or dumped in landfills (cf. Table 2.5).

The more recent chloride process requires intensely weathered ilmenite, leucoxene, natural rutile, synthetic rutile (cf. below) or a titanium slag (cf. below) with >85 % TiO_2 as the basic raw materials.

The chloride process was developed in 1959 by E. I. du Pont de Nemours and Company (DuPont) for the use of high-grade titanium minerals from their newly exploited Trail Ridge placer deposit in Florida. In this process, ore rich in TiO_2 is initially mixed with coke and then with chloride gas at approximately 1000 °C in a fluidized bed furnace particularly resistant to chloride. There the chloride reacts with the titanium dioxide in the ore and the added carbon to form gaseous titanium tetrachloride and carbon dioxide (chlorination) according to the formula:

$$TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$$

Iron (II) chloride produced by chlorination is dissolved in water and separated out. At the same time, hydrochloric acid is produced as a result of the reaction between the chloride with the residual moisture contained in the raw ore, and is leached out and can be sold as a raw material. Following this, the gaseous titanium tetrachloride is condensed into a solid substance and this is treated repeatedly by distillation to remove impurities.

After re-condensing, pure titanium tetrachloride is produced that can be supplied to the next processing step. Pure titanium dioxide is produced by heating the titanium tetrachloride to high temperatures and adding pure oxygen:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

In doing so, the titanium tetrachloride oxidizes to form titanium dioxide, and pure chlorine is released again, which is returned to the reaction process.

The major advantage of the chloride process is the fact that no sulfur dioxide and no dilute acid are produced because the released chlorine is recycled back into the chlorination process. The reaction furnace for the chlorination has a lifetime of approximately one year, and must then be renewed – the corresponding work taking several months. The manufacture of one tonne of TiO_2 using the chloride process requires approx. 1.0 – 1.1 tonnes of rutile, 0.1 – 0.2 tonnes of chlorine, 0.1 – 0.3 tonnes of coke and 0.45 – 0.5 tonnes of oxygen. In this process, approx. 0.4 – 0.9 tonnes of iron chloride are produced as a by-product. When using more low-grade titanium slag, the chlorine requirement increases up to 0.7 – 0.9 tonnes and more iron chloride is produced as well. The latter is used in wastewater treatment, amongst other things (cf. Table 2.5).

Currently approx. 65 % of the 4.9 million tonnes of TiO_2 pigment produced worldwide are produced using the chloride process.

Table 2.5: Excerpts from the life cycle assessment of ilmenite processing using the sulfate and the chloride process (KUMAR et al. 1991).

Substance	**Sulfate process**	**Chloride process**
Liquid substances		
Waste acid m^3/t TiO_2	65.0	-
Other process flows m^3/t TiO_2	41.7	32
Coolant m^3/t TiO_2	375.0	600 – 900
Dilute acid m^3/t TiO_2	2.4	-
Iron in the waste water t/t TiO_2	0.16-0.26	0.002
Solid substances		
Iron sulfate t/t ilmenite	2.4	
Residual ore t/t TiO_2	0.13-0.2	Negligible
Waste sludges of the process water treatment t/t TiO_2 (lime neutralization)	4.5	0.07

Low-grade titanium ores can be processed to form titanium slag or synthetic rutile using various processes to increase their primary TiO_2 content in a secondary manner.

Titanium slag can be utilized for pigment manufacturing using the sulfate process as well as the chloride process. As a byproduct, *pig iron* is always extracted in large quantities. Production data from the few titanium slag producers and comparative compositions of the raw materials used and the titanium slags extracted from these have been summarized in Tables 2.6 and 2.7.

Table 2.6: Global production of titanium slag.

Country Occurrence	Properties of the material	Properties slag	Capacity production
Canada Allard Lake	Ilmenite-hematite-ore (on average 34.3 % TiO_2, 27.5 % FeO, 25.2 % Fe_2O_3)	Sorel slag (on average 80 % TiO_2, 8 % FeO) "*upgraded slag*" (UGS) (on average 94.5 % TiO_2, 1 % Fe_2O_3)	1.1 Mt/year 1.01 Mt (2007)
Rep. of South Africa Richards Bay	Placer ilmenite (on average 49.7 % TiO_2, 36.6 % FeO, 11.1 % Fe_2O_3)	RBM-slag (on average 85% TiO_2, 12 % FeO)	1.05 Mt/year n.a.
Rep. of South Africa Namakwa	Placer ilmenite (on average 52 % TiO_2)	Namakwa-slag (on average 86 % TiO_2, 10 % FeO)	200,000 t/year 159,000 t (2008)
Rep. of South Africa Hillendale	Placer ilmenite (on average 46.6 % TiO_2)	KZN-slag (on average 86 % TiO_2, 12 % FeO)	250,000 t/year 113,000 t (2008)
Norway Tellnes	Titanium magnetite ore (on average 44.4 % TiO_2, 34.0 % FeO, 12.5 % Fe_2O_3)	Tinfos slag (on average 75 % TiO_2)	240,000 t/year n.a.

Table 2.7: Chemical compositions (%) of titanium slag produced worldwide (GILMAN & TAYLOR 2001).

	Sulfate slag		**Chloride slag**		
	Sorel slag	*Tinfos slag*	*RBM slag*	*Namakwa slag*	*UGS*
TiO_2	80	77	85.5	86.0	95.0
Fe_2O_3	9	-	-	-	-
FeO	-	8	10.8	9	1.17
SiO_2	2.4	4.5	2.1	1.8	1.95
MgO	5.0	6.0	1.1	0.7	0.6
Al_2O_3	2.9	1.7	1.3	1.4	0.60
Cr_2O_3	0.17	0.12	0.17	0.09	0.03
U + Th	<5 ppm	-	15-30 ppm	20 ppm	<5 ppm

Synthetic rutile serves as the basic raw material for the chloride process and is therefore also usable for metal production using the Kroll process (cf. below). The process for the manufacture of synthetic rutile consists of the complete or partial reduction of the iron bound in the ilmenite, and subsequent leaching and separation from the titanium dioxide. In the meantime, numerous special processes have been developed, which even allow reducing minor contaminants (cf. Table 2.8).

Table 2.8: Comparison of the chemical composition (%) of the raw material ilmenite and synthetic rutile produced from it using various processes (SCHMIDT et al. 1980).

	Western titanium process 1)		Benilite process 2)		Wah Chang process 3)				Ishihara Sangyo process 4)	
					Quilon		Manavalakurichi			
	Ilmenite	Synthetic rutile	Ilmenite	Synthetic rutile	Ilmenite	Synthetic rutile	Ilmenite	Synthetic rutile	Ilmenite	Synthetic rutile
TiO_2	54.4	91.1	53.1	92.1	59.30	92.66	53.88	92.57	59.62	96.34
Fe (total)		0.63	32.2							
FeO	19.8	4.91	33.6		10.77	2.66	31.76	3.39	9.49	
Fe_2O_3	19.0		8.7	2.62					24.62	1.07
Cr_2O_3	0.2	0.05	0.05		0.15	0.07	0.12	0.04	0.16	0.13
Al_2O_3	1.5	1.10		1.17	1.44	0.45	1.13	0.25	1.32	0.51
V_2O_5	0.12	0.17	0.02		0.18	0.09	0.18	0.09	0.20	0.21
Nb_2O_5		0.48		0.35	0.21	0.44	0.21	0.40		0.61
P_2O_5	0.02	0.02	0.09	0.27		0.20		0.20		0.19
MnO	1.4*	2.08*			0.41	0.01	0.36	0.01	0.48	0.01
MgO	0.45	0.36			0.65	0.02	0.80	0.13	0.78	0.04
CaO	0.04*	0.12*			0.31	<0.01	0.36	<0.01	0.09	0.00
ZrO_2	.			1.16	0.59	0.55	0.12	0.39	0.86	0.24
SiO_2	0.7	0.71	0.36	0.86	1.41	1.57	1.52	1.93	0.70	0.57
SO_3										0.00

1) also called Becher process, process steps: a) oxidation of the FeO in the ilmenite to form Fe_2O_3 b) complete reduction to form metallic iron c) oxidation (artificial roasting) of the iron in aqueous NH_4 solution by means of atmospheric oxygen to form iron hydroxide, and re-precipitation

2) Process steps: a) partial reduction of the iron oxide to form FeO b) leaching of the FeO with 18-20% HCl c) separation of the iron as Fe_2O_3 d) recovery of the acid

3) also Dhrangadhra process or *Chlorine Technology* process, process steps: a) partial reduction of the iron oxide to form FeO b) leaching of the iron with concentrated HCl c) separation of the iron as $FeCl_2$ d) recovery of the acid

4) Process steps: a) partial reduction of the iron oxide to form FeO b) leaching of the iron using diluted H_2SO_4 c) separation of the iron as iron sulfate d) recovery of the waste sulfuric acid

* possibly transposed numbers

The structure of the titanium mineral processing industry, and the possibilities for further processing different titanium raw materials depending on their TiO_2 content, are shown in Figure 2.2 and Table 2.9.

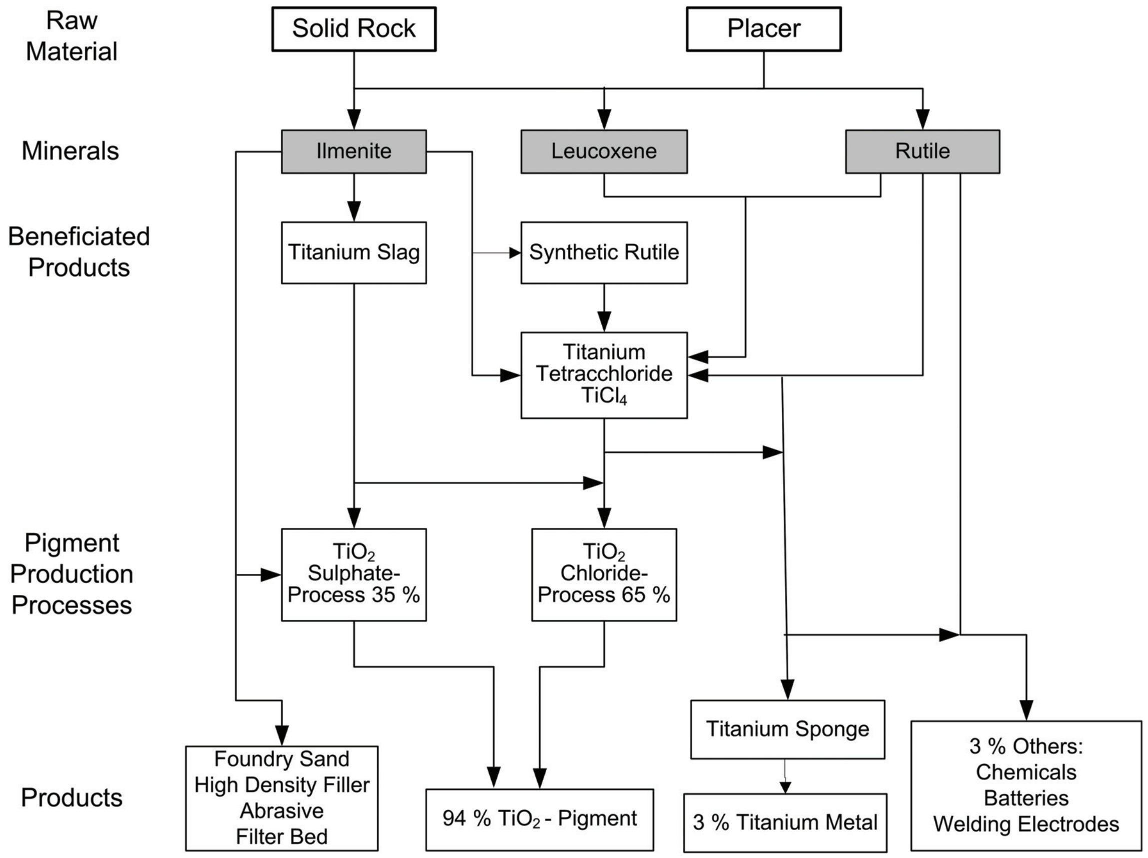

Figure 2.2: Structural overview of the titanium mineral processing industry from the raw material to the final product.

Table 2.9: Use of titanium raw materials as a function of their TiO_2 content, according to HARBEN (2002).

Raw material	TiO_2 (%)	Use
Ilmenite-concentrate of ilmenite/magnetite or ilmenite/hematite rock, e. g. Tellnes/Norway, Allard Lake/Quebec	44-45	Sulfate process or titanium melt
Ilmenite in beach placers, e. g. east and west coast of Australia, Florida, India and Sri Lanka	48-51	Refractory industry, sulfate process, production of synthetic rutile
Ilmenite from placers, e.g. Australia, USA, India, Sri Lanka, Ukraine and Malaysia (tin production)	54-60	Sulfate process, production of synthetic rutile
Weathered ilmenite from placers, e. g. Eneabba, Western Australia, Green Cove Springs, Florida	$\geq$60	Sulfate process, production of synthetic rutile
Leucoxene, e. g. Bunbury/Capel area, Western Australia and Florida	$\geq$68	Choride process and welding rods
Titanium slag from Quebec by melting ilmenite/hematite rocks	75-80	Sulfate process
Titanium slag through melting ilmenite from Richards Bay, Rep. of South Africa	85	Sulfate and chloride process
Anatase concentrate from carbonatites in Minais Gerais/Brazil	90	Chloride process
Upgraded Slag (UGS) from Quebec through melting and concentrating ilmenite/hematite rocks	95	Chloride process
Synthetic rutile through reduction of iron and chemical leaching of ilmenite, mostly from the USA, Australia, Japan, Taiwan and India	92-95	Chloride process
Natural rutile from placers, e. g. from Australia, Sierra Leone, Rep. of South Africa, Ukraine, Sri Lanka, India	94-96	Chloride process, welding rods and coatings, titanium metal

Titanium dioxide is the most popular white pigment worldwide. Its advantages are:

- high refractive index of 2.55 or 2.70, for high opacity (covering power),
- good reflectivity causes luminosity and whiteness,
- inertness and chemical stability (insoluble in acids, bases, organic solvents and air pollutants),
- high resistance to UV degradation (color retention),
- non-toxicity,
- high thermal stability.

TiO_2 pigments are available in two crystalline textures: rutile and anatase. The rutile texture is denser than the anatase texture and therefore has a higher refractive index. Due to its higher chemical stability, the rutile texture is preferably used in exterior paints, plastics, printing inks and in cosmetics. The anatase texture has a bluish base tone and is less resistant. It is used in interior paints, paper, textiles, rubber products, soaps and medicines. The physical properties of the two TiO_2 crystalline textures are compared in Table 2.10.

Table 2.10: Properties of TiO_2 pigments (HARBEN 2002).

	Rutile-TiO_2	**Anatase-TiO_2**
Appearance	Pure white powder	Pure white powder
Apparent density (g/cm^3)	4.2	3.9
MOHS hardness	6-7	5 ½-6
Refractive index air	2.70	2.55
Refractive index water	2.1	1.9
Refractive index oil	1.85	1.7
Specific heat (kJ/°C kg)	0.7	0.7
Dielectric constant (powder)	114	48
Melting point (°C)	1855	Turns into rutile
Brightening properties (Reynolds)	1650-1900	1200-1300
Relative light scattering ability	800	600

Due to its outstanding properties and its non-toxicity, TiO_2 has displaced many other formerly common white pigments, e.g. lead oxides.

White pigments must scatter the emitted light as much as possible. The optimum light dispersion capability of TiO_2 pigments is achieved at particle sizes of 0.2-0.3 µm (200-300 nm). The particle size distribution curve must also be as narrow as possible. Pure TiO_2 is a colorless, pure white powder with a refractive index that exceeds all other colorless substances (including diamond). It therefore has such a high light dispersion capacity that it can reflect almost all of the light at any wavelength. A comparison of the most important properties of different white pigments is shown in Table 2.11.

Table 2.11: Characteristic values of some white pigments (KENT 1974).

	Refractive index	**Relative brightening properties**	**Relative covering power**
Rutile TiO_2	2.70	100	100
Anatase TiO_2	2.55	71	78
Zinc sulfide	2.37	36	39
Lithopone (72 % $BaSO_4$, 28 % ZnS)	-	16	18
Antimony oxide	2.09	17	15
Zinc oxide	2.02	12	14
Alkaline lead carbonate	2.00	9	12
Alkaline lead sulfate	1.93	7	10
Alkaline lead silicate	-	5	8

In recent times, the application of TiO_2 pigments in the form of highly concentrated, pourable, pumpable suspensions (*slurries*), which can be metered volumetrically, has increased. These slurries contain up to 75 % TiO_2 and are rheologically set up to prevent the formation of sediments, even after longer periods of storage. They represent a dust-free form of application of the TiO_2 pigments.

Only approx. 3 % of the titanium minerals extracted worldwide is used for the production of **titanium metal**. 84 % of present day industrial production uses the Kroll process, which was invented in 1938, but has only been used on a large industrial scale since 1946. Feedstock for this process is the titanium tetrachloride previously produced using the chloride process. It is based on the principle of the separation of the titanium from titanium tetrachloride by means of magnesium:

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

The reduction of the $TiCl_4$ is performed using argon to create an inert atmosphere, since titanium, as a relatively base metal, has a high affinity to atmospheric gases. The process is carried out in a reactor made of steel or chromium-nickel steel. Its interior walls must be brushed clean. Depending on the size of the reactor, 1.5-7 tonnes of titanium sponge are produced in each batch. At the beginning of the process, magnesium is melted in the reactor. $TiCl_4$ is then continually added dropwise over the course of several days or fed from above into the reactor in gaseous form. The magnesium chloride is liquid and sinks to the reactor floor due to its higher apparent density compared to titanium and magnesium. The liquid $MgCl_2$ therefore accumulates below the magnesium melt and can be extracted discontinuously. The titanium sponge, however, precipitates in the reactor and forms a solid crust above the magnesium melt. Due to capillary action, the magnesium rises through the porous titanium sponge to its surface to react further with the gaseous $TiCl_4$. The addition of $TiCl_4$ is stopped when the magnesium placed in the reactor at the beginning is consumed. Afterwards, the titanium sponge must be cleaned of magnesium and $MgCl_2$ residues.

Today, this process is performed in most cases by vacuum distillation. To this end, a vacuum bell connected via a vacuum line to a second reactor is set on top of the reduction reactor. A vacuum of around 10^{-3} mbar and a temperature between 900 and 1,000 °C is produced in the reduction reactor and in the distillation reactor. Under these conditions, the impurities (metal chloride, mainly magnesium chloride and titanium tetrachloride, as well as magnesium) pass into the gaseous state. They are transferred to the second distillation reactor that serves as a condenser where they condense out leaving behind in the reduction reactor the titanium sponge in its cleaned form. Condensed magnesium and $MgCl_2$ form two separate phases in the condenser, and can thus both be removed separately. The titanium sponge cake is removed mechanically from the reactor and reduced to small pieces afterwards.

Due to its porosity and remaining impurities, the titanium sponge must now be melted into blocks. This is usually done in a high vacuum arc furnace with consumable electrodes made from titanium sponge and water-cooled copper crucibles. Induction or arc furnaces with cooled tungsten or carbon electrodes are used to a lesser degree. Up to 40 % titanium scrap can be added during the smelting process.

Titanium metal is valued for three main positive characteristics:

- Low **apparent density** (4.507 g/cm^3). Volume for volume, titanium is 43 % lighter than steel (7.85 g/cm^3) and only 66 % heavier than aluminum (2.70 g/cm^3). This means that 1 m^2 steel sheet metal has the same weight as 1.75 m^2 titanium sheet metal of the same thickness.
- Titanium and its alloys at room temperatures have close to the same **strength characteristics** as steel and therefore generally higher strengths than light alloys. During continuous stress at elevated temperatures of up to around 500 °C, the relationship between strength and apparent density is particularly advantageous.
- The **corrosion resistance** of titanium - particularly in oxidizing and chloride-ion containing media - allows economic combination options in the different areas of application.

Other outstanding characteristics are:

- high melting point: 1668 °C
- good thermal conductivity: 21.9 W/m · K
- small coefficient of expansion: 8.36 [10^{-6} K^{-1}]
- high electrical resistivity: 54 µΩ · cm
- non-toxicity and non-irritation of human skin.

For the above reasons, titanium metal and its numerous alloys (with Fe, Nb, Sn, V, Al, Zr, Mn, Ni, Cr) are used in the following areas:

- aircraft engineering: landing gear support beams, engine supports, fuselage, engine blades, rotor blades, compressor disks, spacers, suspensions, bolts, exterior skin, exterior skin jacking points, spars, spar frames, wing spar box, undercarriage components
- helicopter engineering: gearbox, boom, rotor hub, tail rotor driveshaft, fasteners, exterior skin and floor pan components, rotor leading edge
- spacecraft: helium and nitrogen tanks, hydrogen tanks, jet components, rings, bracers in the propulsion area, spars, spar frames
- drive systems: connecting rods, valves, butterfly valves, rocker arms, water jet propulsion systems, maglevs, batteries
- chemical and industrial plant engineering: pumps and valves and fittings, chemical and seawater pipes, bleach tanks in paper mills, hydrogen tanks, anodes in chlorine, chlorate and hypochloride production, catalysts, nuclear fuel canisters
- defense: submarine cladding, weapons systems
- IT, electronics: supercomputers, cryoelectronics, superconductor systems
- casting and molding: rotors, suction covers, housing components for plate valves and y-valves, ball valves, valve plates
- jewelry and watchmaking industry: watches, rings, frames for glasses, body piercing jewelry
- sports: golf clubs, tennis rackets, baseball bats, racing bike frames, billiard cues
- housing: roofs, air conditioning systems
- medicine: prostheses, surgical implants and devices, dental technology, pacemaker covers

Titanium metal powder is used in pyrotechnics and serves as the initiator for the inflation of airbags. It is also an alloying agent for the manufacture of magnets, and a deoxidizer.

Other areas of application for titanium and titanium dioxide are:

- **Fillers**: Ultra fine (20 – 40 µm) TiO_2 particles should still be viewed as relatively coarse. They are not effective in dispersing light and are highly transparent in various media (metallic paints, cosmetics). Special paint effects can be achieved when mixed with aluminum flakes.
- **Nanotechnology**: In sunscreens, clear wood varnishes and plastic films, ultra fine TiO_2 (1-50 nm) generates high UV protection due to its property of strongly absorbing and dispersing UV light. Deposited on glass with a thickness of approx. 15 nm, ultra fine TiO_2 gives the glasses self-cleaning properties. Further areas of application are emerging in the areas of electro-ceramics and photocatalysis.
- **Batteries**: Titanium has been used as an insulator in alkaline batteries for a long time. Recently it has been used in rechargeable Mn-Ti-Li batteries that use an Li-Mn complex oxide cathode and an Li-Ti oxide anode (e.g. Energizer®). The Li-Ti oxide and the cell structure improve electron flow and lead to an increased capacity in miniature format, superior charging properties and excellent voltage and overload resistance characteristics.
- **Chemistry**: TiO_2 is the raw material for various titanium chemicals such as:
    - Titanium iodide, TiJ_4, a black-green crystalline powder that is used as a catalyst in the stereo-specific polymerization of butadiene.

- Barium titanate, $BaTiO_3$, a light gray powder with ferro-electric properties and with a high dielectric constant, semi-conducting and piezo-electric properties that is used for special electro-ceramic purposes. Barium titanate works by generating an electric voltage field dependent on the pressure of the substrate. Conversely, the material also changes its form as a function of the electric field acting on it. Applications in high technology are underwater sonar, guided missiles, sonar mines, ultrasound cleaning, measuring equipment, sound reproduction, filters and ultrasound therapy.
- Strontium titanate, $SrTiO_3$, crystallizes in the cubic Perovskite structure (special ceramic material, electronic and electric insulators), can then be cut (microwave utilization, super and semi-conductor substrates, thin films) and polished (synthetic gemstones, optical and piezoelectric applications).
- Titanium tetrachloride, $TiCl_4$, a liquid which is only colorless after distillation, and that fumes strongly upon contact with moist air. Intermediate product of titanium metal, TiO_2 and organic titanium production, changes the structure of aluminum alloys, special glazes for glasses and ceramic products, feedstock for pharmaceuticals.
- Alkyl and butyl titanate, colorless to yellow liquids. Their areas of application are: Catalyzation (polymerization of polyethylene, polypropylene, polybutadiene; esterization of plasticizers and different esters, transesterization of polyesters for fibers, films, casting resins and paint binders); binders between different casting resins; surface modification (leaving a TiO_2 film when heating) to improve surface hardness, adhesion, of color effects, iridization, heat and light reflection and/or corrosion resistance (plastics, oils, greases, paint, printing paper, glass treatment, metal treatment, pigmented coatings); adhesion promotion (printing inks, coatings, laminates, demolding enhancers, wire coatings, sealants) and direct use (in sunscreen gels, catalysts, special glass, greases and metal titanate coatings).
- Titanium oxide chloride, $TiOCl_2$, a pearlescent pigment frequently used for coatings, cosmetics and sanitary products, packaging, plastics and printing inks. It is also used in metal treatment and as a feedstock for the manufacturing of barium titanate and inorganic titanates.
- Titanium oxide sulfate, $TiOSO_4$, a colorless to light yellow liquid (barium titanate production, manufacture of polymerization catalysts, pearlescent pigment production for cosmetics)
- Potassium titanate, $K_2O(TiO_2)_{n\ n\ =\ 4\text{-}7}$, occurs as needles, bars or is powdery with low thermal conductivity, has high reflectivity between the ultra red and infrared spectrum and good friction properties (high quality welding bars, car brakes, special paints, heat insulation materials). In the modification as extremely fine individual fibers or strings with 0.3-0.6 nm diameter and 10-20 mm length (1/1000 the size of a typical glass fiber) potassium titanate has great strength and form stability, stiffness, abrasion and corrosion resistance, as well as good packing, lubricating and machining properties (reinforcement of special plastics, friction materials in cars and precision filters).
- Titanium disulfide, TiS_2, a black, crystalline solid (Li-TiS_2 batteries). It is a substitute for graphite as an anode material with LiCoO as the anode and a suitable low-temperature electrolyte in rechargeable electro-chemical lithium-ion cells that can operate at temperatures $<20\ ^{o}C$.
- Titanium hydride, TiH_2, a gray powder that explodes when combined with oxygen. Areas of application: pyrotechnics, manufacture of vacuum tubes, bronzing aids when applying ceramics on metals, titanium feedstock for alloys, reservoir for high purity hydrogen (450 l H_2 in 1 kg TiH_2 powder); foaming agent for expanding aluminum, feedstock for the manufacture of titanium carbide and titanium nitride.
- Titanium carbide, TiC, a hard (Mohs: 9), dense refractory with high thermal shock and abrasion resistance as well as low friction resistance. Used in powder metallurgy in cutting tool end fittings, fittings, wear parts and high strength coatings; additive for plastic or rubber replacement parts instead of metals; in mixed crystals such as (Ti,W)C, (Ti,Ta,W)C, (Ti,Ta,Nb,W) C for hard metals.

- Titanium nitride, TiN, a yellow brown crystalline solid with a melting point of 2,950 °C and Vickers hardness of 2,100. Used in crucibles for melting lanthanum alloys, coatings on cemented carbides and golden yellow coloration on jewelry.

Because of its high bulk density, ilmenite without chemical processing is used as a weighting medium (drilling mud, high weight concrete), abrasive (blasting abrasive powder) and filtration media (water and industrial waste filtration).

2.4 Substitutes

Depending on the area of application, titanium minerals, titanium dioxide, titanium metal and titanium chemicals can only be replaced to a limited extent by other mineral resources or chemicals; some possibilities are as follows:

- weighting agent: barite, coelestine, hematite, magnetite, iron ore
- blasting agent: bauxite and aluminum (electrocorundum), corundum/emery, diamond, diatomite, feldspar, garnet, hematite, magnetite, nepheline syenite, olivine, pumice, silica sand, slag, staurolite, tripoli, silicon carbide
- filter medium: activated carbon/anthracite, asbestos, cellulose, diatomite, garnet, magnetite, olivine, perlite, pumice stone, silica sand
- pigment: lithopone, zinc oxide, lead oxide (an equivalent substitute for TiO_2 is not known!)
- metals and alloys: aluminum, magnesium, stainless steel, various super alloys (partially with completely different properties)
- fillers: aluminum tri-hydroxide (ATH), barite, calcium carbonate, diatomite, feldspar, kaolin, mica, nepheline syenite, perlite, talc, microcrystalline silica, ground silica dust, wollastonite

Leucoxene is an affordable substitute for rutile in welding electrodes.

2.5 Raw material and quality specifications (reference values)

According to HARBEN (2002), the ilmenite concentrates for TiO_2 pigment manufacture based on the **sulfate process** should have:

- TiO_2 contents between approx. 50-60 % (<50 % often too many foreign substances; >60 % often not completely broken down by sulfuric acid),
- a high FeO/Fe_2O_3 ratio (must react with sulfuric acid),
- a low Fe content (low quantities of Fe sulfate as by-product),
- low Cr, V and Nb contents (act as color pigments and form toxic waste materials),
- low Ca and P contents (impede optimum crystallization),
- low U, Th and Ra contents (continually decreasing lower limits for radioactivity in educts, products and waste materials).

The physical properties of ilmenite have no significance as long as it can be precipitated cleanly from the mineral spectrum of the placer using conventional methods.

Ilmenite/leucoxene concentrates for TiO_2 pigment manufacture using the **chloride process** should have the following properties according to HARBEN (2002):

- TiO_2 contents >60 % (<60 % too many foreign substances that occur in the form of waste materials),
- low alkaline values: <0.2 % CaO, <1 % MgO (form liquid chlorides at 1000 °C and impede the distillation of the titanium tetrachlorides as a result),

- a low Fe content (leads to formation of iron chloride, that melts at 700 °C and blocks the lines),
- <0.5 % Cr_2O_3 and V_2O_5 (color change of the white pigment, toxic waste materials, form liquid chlorides that clog the reactor bed),
- low Sn and As contents (accumulate with the titanium tetrachloride),
- <2 % SiO_2 (coats grains and impedes the reaction),
- low U, Th and Ra contents of <500 ppm in total (always lower limits for radioactivity in educts, products and waste materials).

To be suitable as a raw material for the chloride process, it must have a particle size of 50-100 µm and a sufficiently high apparent density after processing. A narrow particle size spectrum is advantageous because this avoids *blow over* effects during chlorination in the reactor, and dust losses.

GROSZ (1987) compiled the chemical specifications for the raw materials required for the manufacture of **TiO_2 pigments** from ilmenites (cf. Table 2.12).

Table 2.12: Specifications for the ilmenite raw materials for the production of white pigments according to GROSZ (1987). Critical impurities are shown in bold typeface.

Oxides	**Sulfate process** (%)	**Chloride process** (%)
TiO_2	45-58	50-60
FeO	10-40	10-35
Fe_2O_3	5-27	5-27
Al_2O_3	0.2-1.2	**0.1-0.6**
Cr_2O_3	**0.01-0.1**	0.1-0.2
V_2O_5	**0.01-0.15**	**0.01-0.3**
Nb_2O_5	**0.04-0.2**	unimportant
P_2O_5	**0.01-0.2**	0.01-0.1
SiO_2	**0.1-0.5**	**0.1-0.5**
MnO	**0.1-3.0**	**0.1-1.0**
CaO	0.01-1.0	**0.01-0.02**
MgO	0.01-?	**0.01-0.04**
ThO_2	<200 ppm	<200 ppm
U_3O_8	<10 ppm	< 10 ppm

In Japan, the limit for all imported ores, that also covers ilmenite concentrates, is 500 ppm U + Th.

For **slag manufacture,** the TiO_2 minimum content in the raw material is 35 %.

Leucoxene must contain sulfur and phosphorous <0.03-0.05 % to be considered a substitute for rutile. Also of importance is a narrow particle size range, constant chemical composition for each supply, and a high TiO_2 content >92 %.

For the Western-Titanium process (cf. Table 2.8), weathered ilmenite with 57-63 % TiO_2 is required. For the Benilite process (cf. Table 2.8), however, a wide range of ilmenites can be used since the acid also reduces the interfering Mg, Ca, U and Th.

In China, there is a standard for ilmenites from placers (cf. Table 2.13).

Table 2.13: Chinese standard YB 835-87 for placer ilmenites (WEN LU 1998).

	Grade (%)			
	I-1	**I-2**	**II-1**	**II-2**
TiO_2	>50	>50	>49	>49
Fe_2O_3	<10	<13	<10	<13
P	<0.02	<0.02	<0.02	<0.025

Unlike western industrialized countries, Chinese standards prescribe minimum and maximum contents for different ilmenite *grades*; the customer then chooses a product corresponding to the intended use.

In Germany, the specifications for TiO_2 pigments are governed by DIN EN ISO 591-1, the chemical composition of titanium by DIN 17850, the chemical composition of titanium alloys by DIN 17851, and the material properties of titanium and titanium alloys by DIN 17869. However, these standards do not contain any specifications for the raw materials.

The average TiO_2 contents of ilmenite concentrates more rarely mentioned in technical references and produced or producible from placers have been compiled in Table 2.14.

Table 2.14: Average TiO_2 contents of ilmenites mined or mineable from placers worldwide.

Country	**Deposit area or deposit**	**Designation**	**TiO_2 content (%)**
Australia	Murray Basin	ilmenite	50 – 55
		weathered ilmenite	58 – 63
Kazakhstan	Satpayevskoye	ilmenite	55
Malaysia	in Amang	ilmenite	53.1
Mozambique	Congolone	*standard ilmenite*	57.5
		sulfate ilmenite	53.7
Russia	Tugansky, Tomsk	ilmenite	>58
Sierra Leone	Gbangbama Range	ilmenite	60
Rep. of South Africa	Geelwal Karoo	ilmenite	50.83
Ukraine	Irshansky GOK	ilmenite	55 – 56
	Volnogorsky GOK	ilmenite	61 – 63
Vietnam	Degi	ilmenite *Grade A*	52.07
		ilmenite *Grade B*	51.70

Tables 2.15 to 2.19 show examples of compositions and physical parameters of titanium mineral concentrates (ilmenite, leucoxene, mixed concentrates) from placers.

Table 2.15: Chemical composition (%) of ilmenite concentrates.

	Capel WTC-Grade RGC Minerals Sands Ltd. Western Australia 1)	**Eneabba** RGC Minerals Sands Ltd. Western Australia 1)	**North Stradbroke Island** Cruzor Ilmenite Consolidated Rutile Ltd. Queensland, Australia 2)	**Chavara** Q-Grade Indian Rare Earths Ltd. Kerala, India 2)	**Manavalakurichi** MK-Grade Indian Rare Earths Ltd. Tamil Nadu, India 2)	**Chapura (OSCOM)** OR-Grade Indian Rare Earths Ltd. Orissa, India 2)	**Kollam** Kerala Minerals and Metals Ltd. Kerala, India 2)	**Tamil Nadu Leases** KPM 53 %-Grade V.V. Mineral Tamil Nadu, India 2)	**Tamil Nadu Leases** TIS 52 %-Grade V.V. Mineral Tamil Nadu, India 2)	**Tamil Nadu Leases** PON 51 %-Grade V.V. Mineral Tamil Nadu, India 2)	**Pulmoddai** Ceylon Mineral Sands Corp. Sri Lanka 3)	**Malyshev. Volnogorsk** VSMMP Dnepropetrovsk, Ukraine 4)
Guaranteed												
TiO_2	≥54.0						≥58.0				≥53.0	≥63.0
Cr_2O_3	≤0.05											0.4
Typical												
TiO_2	55.3	60.80	50.7	60.1	55.1	50.50	59.88	53.50	52.00	51.50	54.58	63.9
Fe (total)	29.5	23.60					25.34					
FeO	22.0	3.70	27	10.50	20.3	34.04	8.4	28.00	25.00	33.50	18.11	
Fe_2O_3	18.3	29.50	17	26.30	19.9	12.43	26.98	15.00	10.00	13.00	23.15	
Cr_2O_3	0.035	0.20	0.30	0.13	0.09	0.048	0.04	0.05	0.04	0.04	0.07	0.4
Al_2O_3	0.8	0.98	0.45	0.70	0.9	0.45	1.16	0.30	0.40	0.30	1.18	2.9
V_2O_5	0.15	0.22	0.22	0.15	0.22	0.23	0.2	0.20	0.18	0.19	0.09	0.19
Nb_2O_5	0.20	0.12	0.05	n.d.	0.2	n.d.		0.13	0.14	0.14		
P_2O_5	0.03	0.08		0.14	0.12	0.022	0.19	0.03	0.02	0.02	+	0.12
MnO	1.3	1.07	1.30	0.40	n.d.	0.51	0.4	0.40	0.30	0.37	0.37	0.8
MgO	0.22	0.27	0.85	0.40	n.d.	0.64	0.79	0.75	0.80	0.64	0.85	0.48
CaO	0.01	0.02	0.02	n.d.	n.d.	0.04	0.00	0.08	0.12	0.08	0.08	n.d.
ZrO_2		0.23	0.12	0.20	0.06	n.d.		<0.01	<0.01	<0.01	0.02	0.3
SiO_2	0.55	0.77	0.44	0.75	1.5	0.71	0.83	0.30	0.70	0.50	1.51	1.8
Zn								410 ppm	545 ppm	450 ppm		
Pb								70 ppm	35 ppm	40 ppm		
U	3 ppm		<10 ppm	~10 ppm	200 ppm 5)	<6 ppm		<10 ppm	<10 ppm	<10 ppm		60 ppm 5)
Th	60 ppm		<10 ppm	~160 ppm		~43 ppm		50 ppm	20 ppm	20 ppm		
LOI			~0.12				0.98	<2.50	<3.50	<3.30		0.1

Table 2.15: continued.

	Trail Ridge Du Pont Florida, USA 11), 12)	**Green Cove Springs** Iluka Resources Ltd. Florida, USA 11), 13)	**Jacksonville** Humphreys Gold Corp. Florida, USA 11), 14)	**Folkston** Humphreys Gold Corp. Georgia, USA 11), 15)	**Sai Lao Processing Plant** Hainan Island Guangdong Province, China 8)	**Beihai Processing Plant** Fluvial Ilmenite Guangxi Province, China 8), 10)	**Beihai Processing Plant** Beach Ilmenite Guangxi Province, China 8), 9)	**Kwale Central** Trial Product Tiomin Resources Inc. Kenya 16)	**Pooncarie Project** Chloride Ilmenite Murray Basin NSW, Australia 6)	**Egypt** Nile delta 17), 18)	**Madagascar** 17), 19)	**Athabasca Oil Sands** 7)
Typical												
TiO_2	64.89	63.67	62.95	59.78	51.48	53.50	55.04	48.90	64.5	52.51	61.47	64.3
Fe (total)						32.89	29.17					
FeO					33.99	37.15	23.80					
Fe_2O_3	28.27	28.94	30.44	31.77		5.75	15.25	51.46	32.5	43.82	32.62	29.5
Cr_2O_3	0.06	0.09	0.09	0.11		0.045	0.047	0.09	0.14	0.22	0.05	0.13
Al_2O_3	1.48	1.43	1.32	1.82	0.75	0.42	0.73	0.31	0.74	0.34	0.79	1.2
V_2O_5	0.14	0.14	0.14	0.13		0.14	0.11	0.21	0.25	0.29	0.15	0.14
Nb_2O_5	0.19	0.20	0.21	0.22	0.039	0.16	0.18		0.09	0.09	0.26	
P_2O_5	0.17	0.19	0.16	0.34	0.018	0.032	0.070	0.09	0.12	0.10	0.07	0.36
MnO	1.02	1.19	1.38	1.48	1.46	1.50	1.55	0.65	0.94	0.82	0.37	0.20
MgO	0.31	0.30	0.27	0.34	0.12	0.10	0.10	0.76	0.86	0.81	0.48	0.2
CaO	0.07	0.17	0.06	0.36	0.31	0.044	0.057	0.04	0.06	0.09	0.02	0.1
$Zr(Hf)O_2$	0.04	0.05	0.13	0.21	0.14	0.20	0.43	<0.01	0.09	0.13	0.18	0.45
SiO_2	0.05	0.19	0.10	0.84	0.79	0.71	1.44		0.60	0.85	0.24	1.9
Zn	232 ppm	213 ppm	241 ppm	304 ppm		300 ppm	360 ppm			205 ppm	359 ppm	
Pb	219 ppm	224 ppm	140 ppm	129 ppm		67 ppm	95 ppm			88 ppm	162 ppm	
U	<5 ppm	<5 ppm	<5 ppm	32 ppm				<0.5 ppm	<10 ppm	8 ppm	14 ppm	40 ppm
Th	53 ppm	114 ppm	71 ppm	215 ppm				30 ppm	72 ppm	40 ppm	103 ppm	80 ppm
LOI	2.67	2.56	2.09	1.59					0.92	-0.46	2.90	

1) Company data sheets 2) Company information 3) CLARKE (1983) 4) O´DRISCOLL (1998) 5) incl. thorium 6) EVERETT et al. (2003) 7) OXENFORD et al. (2003) 8) WARD & TOWNER (1985) 9) 67 ppm As, 170 ppm Cu, 48 ppm Ni, 100 ppm Sn 10) 25 ppm As, 60 ppm Cd, 21 ppm Cu, 44 ppm Ni, 67 ppm Pb, 100 ppm Sn 11) ELSNER (1992) 12) 12 ppm As, 44 ppm Co, 157 ppm Cu, 8 ppm Ni, 35 ppm Sn, 81 ppm Ta 13) 11 ppm As, 47 ppm Co, 123 ppm Cu, 24 ppm Sn, 78 ppm Ta 14) 10 ppm As, 54 ppm Co, 111 ppm Cu, 29 ppm Sn, 92 ppm Ta 15) 27 ppm As, 61 ppm Co, 33 ppm Sn, 63 ppm Ta 16) BALDERSON & ROSS (1998) 17) BGR analysis 18) 29 ppm As, 96 ppm Co, 111 ppm Cu, 22 ppm Sn, 45 ppm Ta 19) 43 ppm As, 41 ppm Co, 55 ppm Cu, 29 ppm Sn, 106 ppm Ta + traces

Table 2.16: Mineralogical composition and physical parameters of ilmenite concentrates.

	Capel WTC-Grade RGC Minerals Sands Ltd. Western Australia [1), 4)]	**Tomago Sand Beds** RZM Mines Pty Ltd. New South Wales [4)]	**North Stradbroke Island** Cruzor Ilmenite, Consolidated Rutile Ltd. Queensland, Australia [2), 4)]	**Chavara** Q-Grade Indian Rare Earths Ltd. Kerala, India [2)]	**Manavalakurichi** MK-Grade Indian Rare Earths Ltd. Tamil Nadu, India [2)]	**Chapura (OSCOM)** OR-Grade Indian Rare Earths Ltd. Orissa, India [2)]	**Madagascar** [4)]	**Trail Ridge** Du Pont Florida, USA [3)]	**Green Cove Springs** Iluka Resources Ltd. Florida, USA [3)]	**Jacksonville** Humphreys Gold Corp. Florida, USA [3)]	**Folkston** Humphreys Gold Corp. Florida, USA [3)]
Mineralogical composition (%)											
Ilmenite	98.3	81.6	98.2	98.47	~96.4	~98.6	85.5	81.0	78.2	74.5	83.0
Leucoxene		8.3		0.22	~0.3		14.1	18.8	21.3	23.3	13.4
Rutile	1.3	5.0		0.52	~0.6	0.3			0.1	1.5	1.3
Zircon	0.3	1.1	+	0.25	0.1	+	0.4			0.3	0.2
Monazite	+	+	+	0.13	0.2	+		+	0.1	0.1	0.6
Sillimanite				0.03	+	+					
Staurolite			+					0.1	0.1	0.1	0.1
Garnet		+	0.1	0.20	n.d.	0.9				0.1	0.4
Tourmaline			1.4								
Epidote			0.3					+	0.2		1.0
Spinel		4.0									
Quartz (free)	0.1		0.1	0.14	2.3	+	+			0.1	+
Others			+	0.04	+	0.2					
Physical parameters											
Apparent density (g/cm^3)	4.2-4.3		4.45-4.54	4.45-4.54							
Bulk density (t/m^3)	2.4-2.7		2.6-2.85	2.6-2.85							
Repose angle	30^o										
Melting point ^{o}c			>1400	>1400							
Ph			6.0-7.0	6-7							

1) Company data sheets 2) Company information 3) ELSNER (1992) 4) BGR-analysis + traces

Table 2.17: Chemical composition (%) of leucoxene and titanium mineral mix concentrates.

	HYTI 70 Iluka Resources Ltd. Western Australia 1)	**HYTI 91** Iluka Resources Ltd. Western Australia 1)	**Residue** Du Pont, Trail Ridge Florida, USA 2), 3)	**Residue** Senegal DuPont Exploration 8), 10)	**Leucoxene** Humphreys Gold Corp. Folkston, Georgia 2), 4)	**Leucoxene** Iluka Resources Ltd. Green Cove Springs Florida, USA 8), 11)	**Leucoxene** Kerala Minerals and Metals Ltd. Kollam, Kerala, India 2)	**Leucoxene** Grade I Western titanium NL. Capel, Western Australia 5)	**Leucoxene** Grade II Western Titanium NL. Capel, Western Australia 5)	**Leucoxene** Pooncarie Project Murray Basin NSW, Australia 7)	**Leucoxene** for welding electrodes Western Australia 6)
TiO_2	70-80	91-93	80.89	67.22	81.23	62.95	79.65 9)	90.30	82.60	68.7	93.60
Fe (total)							5.60				
FeO							0.47	1.90	3.40		
Fe_2O_3	15-25	1.0-2.0	11.69	26.11	9.18	28.71	7.5	5.00	11.10	22.1	2.47
Cr_2O_3	0.10-0.15	0.1-0.2	0.09	0.22	0.13	0.11	0.06	0.16	0.15	0.55	
Al_2O_3	1.0-2.5	0.5-1.5	1.51	0.93	2.42	1.38	3.31	0.37	0.65	1.42	0.53
V_2O_5	0.15-0.3	0.3-0.5	0.19	0.30	0.18	0.07	0.28	0.21	0.12	0.30	0.30
Nb_2O_5			0.66	0.07	0.38	0.11				0.17	0.40
P_2O_5	0.05-0.15	0.04-0.07	0.20	0.09	1.12	0.24	0.35	0.08	0.12	0.20	0.109
MnO			0.39	0.28	0.47	1.19	+	0.13	0.23	0.73	
MgO			0.20	0.58	0.20	0.23	1.1	n.a.	n.a.	0.45	
CaO			0.08	<0.005	0.21	0.24	0.00	n.a.	n.a.	0.17	
$Zr(Hf)O_2$			0.87	0.26	1.33	0.08	0.65	0.43	0.23	0.20	0.59
SiO_2	0.5-1.5	1-2	0.31	0.70	1.00	1.24	4.18	0.86	0.67	1.39	0.89
Zn			128 ppm	145 ppm	182 ppm	312 ppm					
Pb			188 ppm	164 ppm	257 ppm	222 ppm					25 ppm
S	0.02-0.2	0.01-0.5		n.d.		<0.01		0.04	0.04	0.03	0.031
C											0.07
U	10-30 ppm	30-60 ppm	10 ppm	9 ppm	193 ppm	23 ppm				11 ppm	
Th	250-450 ppm	90-50 ppm	57 ppm	116 ppm	1345 ppm	72 ppm				173 ppm	
LOI			1.87	2.82	1.08	2.88	2.38	0.71	1.18	3.80	

1) Company information 2) Elsner (1992) 3) 0.15 % Na2O, 29 ppm As, 30 ppm Co, 193 ppm Hf, 47 ppm Mo, 894 ppm Sn, 242 ppm Ta, 222 ppm W 4) 0.07 % Na2O, 28 ppm As, 10 ppm Co, 158 ppm Cu, 217 ppm Hf, 30 ppm Mo, 47 ppm Ni, 74 ppm Sn, 107 ppm Ta, 132 ppm W 5) Baker (1962) 6) Griffiths (1985) 7) Everett et al. (2003) 8) BGR analysis 9) guaranteed >75.0 % TiO2 10) 27 ppm As, 43 ppm Co, 83 ppm Cu, 36 ppm Hf, 45 ppm Ni, 59 ppm Sn, 32 ppm Ta 11) 10 ppm Bi, 291 ppm Ce, 38 ppm Co, 435 ppm Cu, 222 ppm Pb, 27 ppm Sn

Table 2.18: Mineralogical composition and physical parameters of leucoxene and titanium mineral mix concentrates.

	HYTI 70 Iluka Resources Ltd. Western Australia [1]	**HYTI 91** Iluka Resources Ltd. Western Australia [1]	**Residue** Du Pont Trail Ridge Florida, USA [2]	**Leucoxene** WTC-Grade, Capel RGC Minerals Sands Ltd. Western Australia [1],	**Leucoxene** Iluka Resources Ltd. Green Cove Springs Florida, USA [2] [3] ,	**Leucoxene** Humphreys Gold Corp. Folkston, Georgia [2]
Mineralogical composition						
Ilmenite	80-90	5-10	23.3			78.8
Leucoxene	10-20	80-95	24.4	70.4	97.3	2.2
Rutile	in Lx.	in Lx.	50.0	28.6	0.3	15.3
Anatase			0.4			0.2
Zircon	<1	2-2.7	1.1	1.0	0.3	1.8
Monazite	~0.5	~ 0.3			+	1.2
Xenotime					+	
Kyanite			0.2			+
Sillimanite			0.2			
Epidote					1.3	0.2
Garnet					+	
Cassiterite			0.3			
Staurolite	<1	<1	0.1		0.3	
Tourmaline					+	0.2
Titanite						+
Hypersthene					0.3	
Quartz	<0.5	<1	+	+	+	+
Physical parameters						
Apparent density (g/cm^3)	4.2	4.0-4.2			4.3-4.6	
Bulk density (t/m^3)	2.2	2.2			2.4-2.7	
Repose angle						
Ph	neutral	neutral			neutral	
Melting point (°C)	>1,000	>1,000			1,050	
AFS-number	83-95	83-95			75-90	

[1] Company information [2] ELSNER (1992) [3] BGR analysis + traces

Table 2.19: Grain size distribution (% by mass, screen residue) of ilmenite, leucoxene and titanium mineral mix concentrates.

µm	ASTM *mesh*	**Ilmenite** WTC-Grade RGC Minerals Sands Ltd. Capel, Western Australia [1]	**Ilmenite** Richards Bay Minerals KwaZulu Natal, RSA [3]	**Leucoxene** Richards Bay Minerals KwaZulu Natal, RSA [3]	**Ilmenite** Du Pont, Trail Ridge Florida, USA [4]	**Residue** Du Pont, Trail Ridge Florida, USA [4]	**Ilmenite** Iluka Resources Ltd. Green Cove Springs Florida, USA [4]	**Ilmenite** Humphreys Gold Corp. Jacksonville, Florida, USA [4]	**Ilmenite** Humphreys Gold Corp. Folkston, Georgia, USA [4]	**Leucoxene** Humphreys Gold Corp. Folkston, Georgia, USA [4]	**Ilmenite** Tamil Nadu Leases KPM 53 %-Grade V.V. Mineral Tamil Nadu, India [2]	**Ilmenite** Tamil Nadu Leases TIS 52 %-Grade V.V. Mineral Tamil Nadu, India [2]	**Ilmenite** Tamil Nadu Leases PON 51 %-Grade V.V. Mineral Tamil Nadu, India [2]
>700	>25	2	0.3	0.9					0.004				
600	30				0.007	0.004	0.015	0.003	0.004				
500	35				0.005	0.006	0.021	0.006	0.005	0.002			0.04
420	40				0.005	0.011	0.034	0.006	0.005	0.003	0.06	0.00	0.54
355	45				0.013	0.014	0.031	0.005	0.008	0.006	0.50	1.30	2.84
300	50				0.194	0.134	0.011	0.016	0.025	0.010	1.76	5.90	6.16
250	60				2.396	1.929	0.031	0.051	0.075	0.013	5.74	15.52	10.06
210	70	21	0.8	1.0	11.349	6.169	0.176	0.247	0.286	0.007	10.86	22.04	14.12
180	80		2.5	5.4	16.884	9.761	0.774	0.833	0.834	0.010	15.92	21.86	16.78
150	100	52	11.8	22.9	19.859	13.713	2.250	1.891	1.932	0.032	19.12	18.32	19.72
125	120		18.9	26.1	27.797	23.862	16.100	9.321	8.433	1.500	15.62	8.08	13.62
105	140	22	48.1	30.5	13.405	17.779	38.726	28.272	25.857	11.262	13.94	4.00	9.66
90	170		48.1	9.0	5.223	11.869	34.490	40.378	42.204	32.679	16.48	2.84	6.46
75	200		5.6	3.5	1.634	6.359	6.296	16.077	17.146	38.082			
63	230		0.3	0.7	0.578	3.726	0.838	2.672	2.974	14.577			
53	270				0.065	2,502	0.089	0.080	0.101	1.303			
45	325				0.268	0.788	0.023	0.057	0.052	0.436			
<45	<325				0.310	1.370	0.090	0.080	0.040	0.070			
mean (µm)					152.1	126.4	109.6	102.5	101.6	87.1			

[1] Company data sheets [2] Company information [3] FOCKEMA (1986) [4] ELSNER (1992).

2.6 Size of deposits and resources

The ilmenite/leucoxene concentration and their composition are not the only aspects important when assessing a placer deposit. Other accompanying valuable heavy minerals, mainly zircon and rutile, formerly also monazite/xenotime, provide significantly more added value per tonne (cf. Figure 2.3) and thereby make the mining of some deposits economically viable.

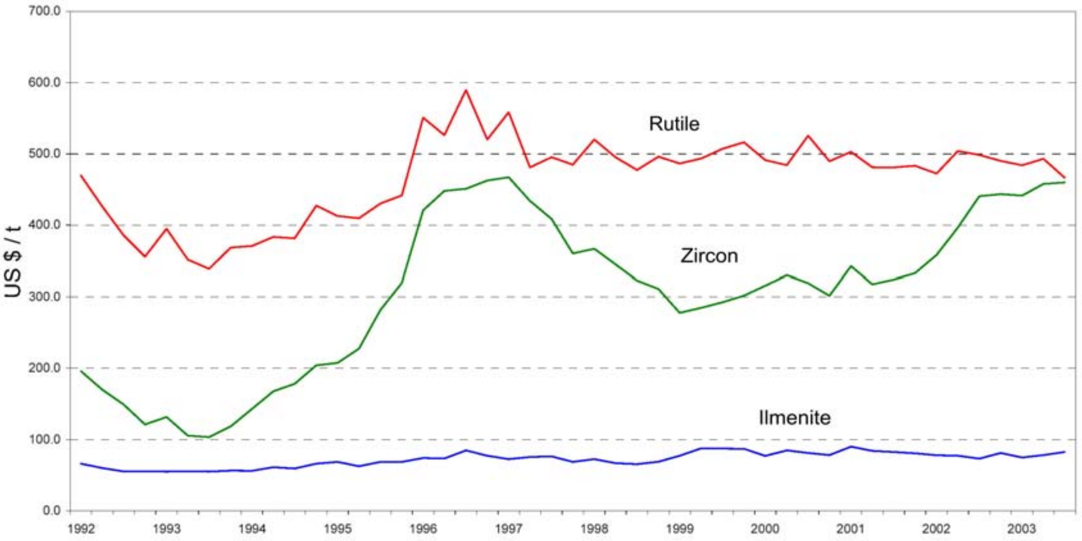

Figure 2.3: Pricing trends for ilmenite, rutile and zircon since 1992 (source: BGR database).

According to LYND & LEFOND (1983), undeveloped placer deposits must contain >1 million tonnes of mineable and usable TiO_2 in the form of titanium minerals (that is >2 million tonnes of ilmenite). For different mining areas, they also compiled the following minimum specifications:

- **South-eastern USA**
  - $\geq$1 million tonnes of mineable and usable reserves with TiO_2 contents:
  - on average 3-4 % by mass heavy minerals, *cut-off grade* 2 % by mass [Trail Ridge: 3 % by mass]
  - on average ~1 % TiO_2 in the ore sand
  - $\geq$5 m ore thickness (wet mining), *cut-off grade* 1.5 m
- **East Coast Australia (rutile and zircon)**
  - $\geq$300,000 tonnes of mineable and usable rutile reserves
  - on average 1 % by mass heavy minerals, *cut-off grade* ~0.5 % by mass
  - on average ~0.5 % TiO_2 in the ore sand, *cut-off grade* ~0.2 %
- **West Coast Australia (ilmenite, weathered ilmenite, rutile and zircon)**
  - $\geq$3 million tonnes of mineable and usable heavy mineral reserves
  - on average ~5 % by mass heavy minerals, *cut-off grade* ~2.5 % by mass

The most recent experience in the Murray Basin in Victoria, Australia, has also shown that despite all the processing technologies available today, the absolute majority of heavy minerals must be present in the particle size range >63 µm.

Ilmenites concentrated in placers with a TiO_2 content below the stoichiometric concentration of 52.66 % are - unless they are to be processed into titanium slag or synthetic rutile - normally not worth mining. This explains the lack of interest of the industry in several deposits that have been known for a long time, cf. Table 2.20.

Table 2.20: Comparison of placer ilmenite reserves of worldwide significance.

Country	Region of deposit	Occurrence	HM-content in the ore sand (% by mass)	Proportion ilmenite in the HM-concentrate (% by mass)	TiO_2-content in the ilmenite (%)	Percentage of leucoxene and weathered ilmenite in the HM-concentrate (% by mass)	Total reserves and resources of ilmenite as of: end of 2003 (million tonnes)
in production							
Australia	Western Australia	Capel	9.3	82	54.4 1)		52.7
		Eneabba	6.2	52	59.7-69.6 1)		30.4
		Jurien	6.3	53	54.5-63.0 1)	2.7	1.9
		Ludlow	0.8	77.8		7.3	0.7
		Cooljarloo	3.1	61	61.0 1)	3.3	11.4
	Queensland	N. Stradbroke Island	0.9	43	50.7		4.0
	Murray Basin	Douglas	8.4	45		6	9.5
		Snapper	5.4	43		10	2.2
		Gingko	3.2	44		21.5	5.3
India	Orissa	OSCOM	20.2	66	50.8 1)		20.3
	Tamil Nadu	coast	7-39	70	54.2		10.2
	Kerala	Chavara	9		60.6	2	62
Mozambique	coast	Moma	4.3	81.6	52-60		35.2
Sri Lanka	North-East coast	Pulmoddai	80	70-72	54.6		2 2)
Rep. of South Africa	Kwa-Zulu Natal	Hillendale	6.8	57.4	46.6 1)	0.9	4.4
		Richards Bay	13.8	~68	46-50 1)		27 2)
	Western Cape	Brand-Se-Baai	10	55	47-50 1)		23.6
USA	Florida	Trail Ridge	3.9	36.8	64.3	14.3	16.2
	Virginia	Old Hickory	9.5	68	53.6		5.5
Vietnam	coast	Cat Khanh			50-51		2.7
production planned							
Australia	Western Australia	Coburn	10	51		11	4.2
		Dongara		49		2	3.5
		Jangardup South		74.9		8.4	1.3
	Murray Basin	WIM 150	4.0	31.6	56.1	11.6	12.5
		KWR	9.3	37			20.1
		Culgoa		68	63	7	1.3

Table 2.20: continued.

Country	Region of deposit	Occurrence	HM-content in the ore sand (% by mass)	Proportion ilmenite in the HM-concentrate (% by mass)	TiO_2-content in the ilmenite (%)	Percentage of leucoxene and weathered ilmenite in the HM-concentrate (% by mass)	Total reserves and resources of ilmenite as of: end of 2003 (million tonnes)
production planned							
Gambia	coast	Sanyang amongst others	5.2	71.3	58.2		0.5
Kazakhstan	Northern Kazakhstan	Obukhovsky	9.4	36	55.5	8	0.5
Kenya	coast	Kwale	3.5-6.8	68	48.9-49.3		3.2
Madagascar	Fort Dauphin	QMM	4.5-5.5	75-80	63		60
Malawi	Lake Malawi	Chipoka	33	36-79	54		190
Mozambique	coast	Congolone	3.25	77.3	53.7-57.5		4.2
	Corridor Sands	West Block	7.47	55	1)		73
Senegal	Grand Cote	total	1.8	70	54.8		21.9
Rep. of South Africa	Kwa-Zulu Natal	Braeburn	4.7	62.0	1)	0.8	0.1
		Fairbreeze	5.9	58.7	1)	1.7	13.0
	Western Cape	Geelwal Karoo	42.3	21.7	50.8 1)	1.4	2.7
Transkei	coast	Xolobeni		54.0	1)		9
currently not mineable							
Egypt	Eastern Rafah, Nile Delta	El Arish amongst others	4	75	34-40		2.4
Bangladesh	coast	Cox´s Bazaar	21.9	27.6	40	2.4	0.9
Germany	Cuxhaven	Midlum	9.9	42.6	47.8		1.9
Liberia	coast	total		82	on average 28		0.5
Mozambique	Zambezi	offshore	5.0	45.5	49.5		51.3
New Zealand	South Coast	Barrytown			44-47		9.6
Rep. of South Africa	Free State	Bothaville amongst others		59.7	55	11.4	16.4

1) processed on site 2) estimated

The reference values specified in Table 2.21 can be applied to the size assessment of deposits that are predominantly mined for ilmenite/leucoxene.

Table 2.21: Reference values for the assessment of ilmenite-leucoxene deposits.

	All deposits [1)] **TiO_2-content**	**Placers** [2)] **mineral content**
Not mineable		2 million tonnes
Small	0.5-1 million tonnes	2-5 million tonnes
Medium	1-10 million tonnes	5-10 million tonnes
Large	10- >50 million tonnes	10-30 million tonnes
Very large		>30 million tonnes

[1)] LORENZ (1991) [2)] this work

The global reserves and resources of ilmenite/leucoxene – defined as known and published quantities of currently mineable heavy minerals not blocked by competing uses and extractable from placers or other sediments – are listed in Table 2.22.

Table 2.22: Currently known global reserves of placer ilmenite and leucoxene.

Country	**Total resources and reserves placer ilmenite and leucoxene** (million tonnes)	**Total resources and reserves heavy minerals** (million tonnes)
India	>348	>632
Australia	246	465
- Western Australia	*96*	*154*
- Murray Basin	*137*	*282*
- Queensland	*13*	*29*
Mozambique	237	372
Canada	183?	310-505
- Quebec	*58*	*116*
- Saskatchewan/Alberta [1)]	*125?*	*195-390*
Rep. of South Africa	82	133
Kenya	61	99
Madagascar	60	60
Namibia	36	39
USA	28	58
China	22	23
Senegal	22	31
Ukraine	~14	~20
Sri Lanka	~12	~18
Malaysia	~10	~15
Vietnam	8	9
Brazil	7	10
Sierra Leone	5	~18
Kazakhstan	~3	~5
Malawi	190 [2)]	>545
Total	**1,400**	**3,000**

[1)] from oil sands

[2)] ilmenite is not mineable due to its low TiO_2 contents, no processing industry and higher transportation costs

2.7 Important producing countries

Ilmenite was first mined in large quantities in Norway. The solid rock mine near Storgangen opened in 1861 and yielded more than 130 million tonnes of ilmenite hematite ore until its closure in 1964. The increasing use of titanium products in the following decades resulted in the development of new reserves, this time, however, consisting of heavy mineral placers. Until the end of the 1930s, the Indian placers supplied more than 70 % of the global ilmenite consumption. With the increase in Indian duties and the simultaneous discovery of large placers on the Australian East Coast in the first years after World War II, Australia became the leading worldwide producer of ilmenite, as well as rutile, zircon and monazite.

With the depletion or blocking of deposits on the Australian East Coast by competing uses, production increasingly moved to the Australian West Coast at the beginning of the 1980s. In these years, numerous other producing countries entered the world market, the most important being South Africa (from 1977). Currently, large reserves only discovered in the last two decades are being developed in the Murray Basin, Victoria, Australia, and on the East Coast of Africa (Mozambique, Kenya). Many reserves in the Murray Basin are negatively affected by several decameters (up to 64 m) of overburden, amongst other things!

Finally, Figures 2.4 and 2.5 show a direct comparison of the percentage distribution of the world production (2007) and currently known world reserves and resources of ilmenite and leucoxene from placers.

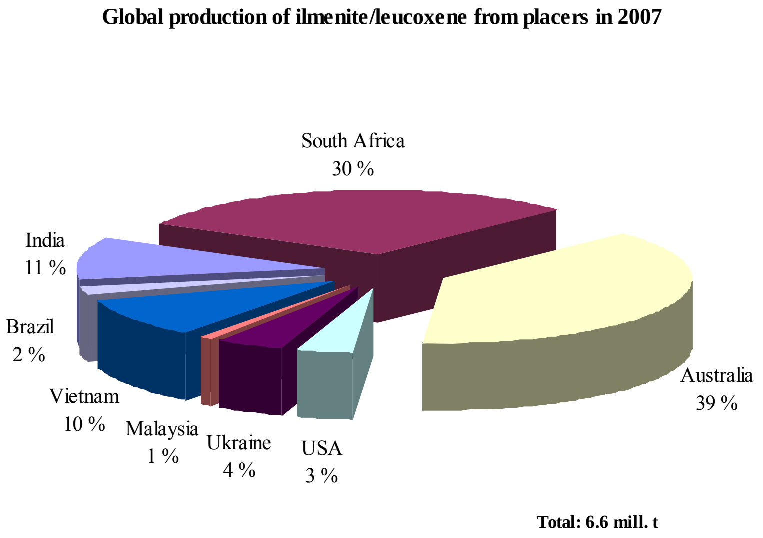

Figure 2.4: **Percentage distribution of the world production from placer ilmenite and leucoxene in 2007.**

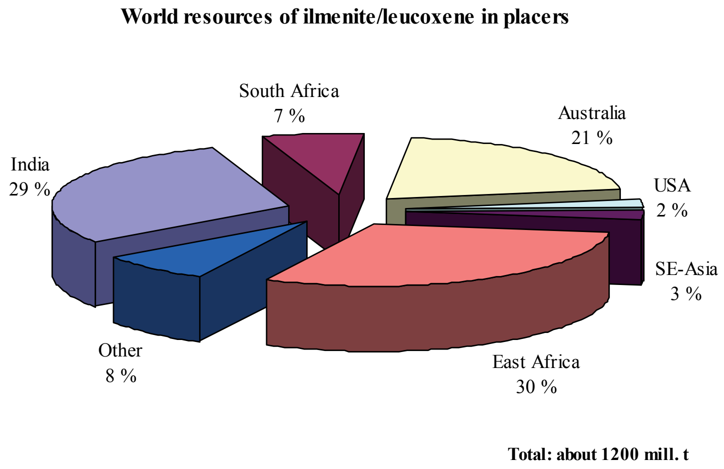

Figure 2.5: **Percentage distribution of the currently known world reserves and resources of placer ilmenite and leucoxene.**

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3 Rutile

[German: *Rutil*, Spanish: *rutilo*, French: *rutile*]

3.1 Mineralogy, Petrography, Chemistry

Of the three crystal modifications of natural titanium dioxide (rutile, anatase and brookite), **rutile** is the most important from an economic perspective (cf. Table 3.1).

Table 3.1: Crystal modifications of TiO_2 and their characteristics.

	Rutile	**Anatase**	**Brookite**
Formula	TiO_2		
Chemistry	(on average 100 % TiO_2)		
Density (g/cm^3)	4.21	3.90	4.14
MOHS hardness	6-6 ½	5 ½-6	5 ½-6
Color	brown, foxy red, yellowish, gray beige, bluish, violet	black, auburn, yellowish brown, dark blue, grey	dark brown to green-black
Magnetic properties	nonmagnetic		
Electrostatic properties	conductive		

Brookite is very rare and of no economic significance. **Anatase** can be created through transformation of rutile in placers, but is also rare in these cases.

The color diversity of rutile and anatase is thought to be attributable to different quantities of trace elements built into the crystal lattice. Nb, Ta, V, Cr and Fe can be built into the crystal lattice particularly well. According to MARTIN (1985), the coloring of rutiles is in direct relation to the ratio of the components $FeO\text{-}Cr_2O_3\text{-}Nb_2O_5$, whereas the proportions of Mg, Mn, V, Cu etc. do not play a part here. Rutiles particularly rich in Fe are called nigrines.

3.2 Formation of deposits and reserves

Rutile can be found as an independent mineral in almost all metamorphic facies areas. As a typical high-pressure and high-temperature version of TiO_2, it is predominantly found in highly metamorphic rocks mainly rich in Al. It is a characteristic mineral for the granulite and eclogite facies.

The following important mineral alterations during metamorphosis lead to the formation of rutile:

$$\text{sphene} + Al_2O_3 = \text{plagioclase} + \text{rutile}$$

$$\text{sphene} + CO_2 = \text{calcite} + \text{silica} + \text{rutile}$$

$$\text{sphene} + O_2 = \text{magnetite} + \text{rutile}$$

$$\text{sphene} + S = \text{pyrite} + \text{rutile}$$

FORCE (1991) provided an overview of the stability ranges of rutile in metamorphic rocks (cf. Table 3.2).

Table 3.2: Stability ranges of rutile in metamorphic rocks (FORCE 1991).

	Green schist facies	Amphibolite facies	Granulite facies	Eclogite facies
Al-rich rocks (sillimanite-kyanite-staurolite)	independent of the FeO/MgO ratio	at high pressure and temperature and low FeO/MgO ratio	independent of the FeO/MgO ratio	independent of the FeO/MgO ratio
"Common" rocks (chlorite-biotite-muscovite-garnet)			independent of the FeO/MgO ratio	independent of the FeO/MgO ratio
Ca-rich rocks (amphiboles-clinopyroxenes-calcite)				independent of the FeO/MgO ratio

In magmatites, however, rutile is relatively rare and only appears in acidic plutonites (granite) and then mostly as an accessory mineral in the form of small needles. Rutile is only very rarely found in pegmatitic veins. In amphibolites rich in biotite, albitites rich in rutile can occur as intrusive deposits. Albitite of this kind was mined for rutile until 1927 near Kragerø in Southern Norway.

In porphyries, rutile is formed during hydrothermal alteration at the expense of the pre-existing titanium minerals: biotite, hornblende, titanite, ilmenite and titanium magnetite. The titanium released here is precipitated as rutile, particularly at high CO_2 pressure. In the *porphyry copper ores* that are very important on a global economic scale, copper mineralization and rutile genesis are the results of the same processes. An economic process for the extraction of rutile as a by-product of the extraction of copper has, however, not been found so far.

In Italy, the Piampaludo eclogite deposit is located in the Ligurian Alps. This eclogite contains on average 6 % TiO_2, of which 80 % on average is rutile. Total ore reserves are estimated at 880 million tonnes and the theoretically extractable rutile reserves are estimated at 23 million tonnes. A similar deposit is known in Engebøfjellet in the Sunnfjord province of Norway. Due to the great hardness of the eclogite and the fine grained nature of the rutile, economic processing has so far not been possible in either case.

Authigenic formation is known for rutile. Microcrystalline rutile is also the end member of leucoxenization. It is no longer very resistant to the processes of physical weathering and therefore an indicator for in situ weathering under humid tropical conditions.

Rutile extraction around the world is restricted to placers. Apart from the deposits named in Chapter 2 referring to ilmenite, the fluvial placers of Sierra Leone are also of particular importance for rutile. High rutile contents also occur in the placers of the East Coast of Australia. The remaining deposits there are, however, largely blocked by competing uses (urbanization, tourism, environmental protection).

Anatase is also found as finely distributed ore in the thick (up to 200 m) weathering debris above the carbonatite deposits of Tapira (on average 21.6 % $TiO_{2,}$ ore reserves: 190 million tonnes) and Salitre (on average 23.5 % $TiO_{2,}$ ore reserves: 150 million tonnes) in the Federal State of Minais Gerais, and Catalão I in the Federal State of Goias in Brazil. Although these reserves have been known since the 1980s, anatase concentrates have so far only been produced for testing purposes.

3.3 Applications

Rutile as a high-quality titanium mineral is used in three areas:

- Manufacturing of titanium metal, similar to ilmenite and leucoxene (cf. Chapter 2.3)
- Manufacturing of TiO_2 white pigments, but only using the chloride process (cf. Chapter 2.3)
- Sheathing of welding electrodes for the stabilization of the electric arc, for the reduction of the melting viscosity and for the reduction of the surface tension of the metal drops on the electrodes.

3.4 Substitutes

Substitutes for rutile as a raw material for its areas of application in the specified three main fields are

- manufacturing of titanium metal
  - synthetic rutile
  - all other titanium minerals (cf. Chapter 2.3)
- manufacturing of white pigments
  - all titanium minerals that can be utilized using the chloride or sulfate process, if possible via the intermediate steps titanium slag or synthetic rutile, for the manufacture of TiO_2 white pigment (cf. Chapter 2.3)
  - lithopone, zinc oxide, lead oxide
- sheathing of welding electrodes
  - synthetic rutile, leucoxene (>92 % TiO_2)
  - fluorite, calcite, talc, clays, MnO_2, SiO_2, Fe oxides, silica, siliceous chalk, mica.

The most important substitute for natural rutile is synthetic rutile in all cases (cf. Chapter 2.3).

3.5 Raw material and quality specifications (reference values)

In China there is a standard for placer rutiles (cf. Table 2.13).

Table 3.3: Chinese standard YB 839-87 for placer rutiles (WEN LU 1998).

	Grade (%)			
	1	2	3	4
TiO_2	>93.0	>90.0	>87.0	>85.0
Fe_2O_3	<0.5	<0.8	<1.0	<1.2
P	<0.02	<0.03	<0.04	<0.05
S	<0.02	<0.04	<0.04	<0.05

Unlike western industrialized countries, Chinese standards prescribe minimum and maximum contents for different rutile *grades*; the customer then chooses a product corresponding to the intended use.

Rutiles to be used in welding electrodes must meet the following specifications according to GRIFFITHS (1985):

- ≥95 % TiO_2 (exceptions possible),
- ≤1 % ZrO_2,
- ≤1 % Fe_2O_3,
- narrow particle size band without oversize particles.

According to VENKATASUBRAMANIAN (1994), synthetic rutiles in comparison to natural rutile are measured against the following properties important for their utilization in the chloride process:

- composition: Natural rutile has the highest TiO_2 content and the lowest levels of impurities.
- hardness: Insufficient hardness leads to dust losses during chlorination. Natural rutile does not develop dust, synthetic rutiles produced by acid solution, do however.
- density: Low density leads to elutriation and therefore to dust losses during chlorination. The apparent density of synthetic rutiles produced by acid solution is only 1.3 g/cm^3.
- particle size: Particle sizes of the raw material <50 µm lead to dust losses during chlorination.
- particle size band: A wide particle size band negatively affects the control of the reaction processes.
- surface area size and porosity: High surface area size and porosity facilitate chemical reactions. These are very small in natural rutile, but very large in synthetic rutile manufactured by acid solution.

For the above reasons, industry always prefers natural rutile to synthetic rutile or titanium slag as the raw material for the chloride process, despite its high price.

Table 3.4 shows a comparison of the specifications of raw materials containing high levels of TiO_2 for the chloride process and the chemical composition of synthetic rutiles manufactured using different processes (cf. Table 2.8).

Tables 3.5 – 3.7 show the compositions and physical parameters of rutile concentrates produced globally from placers.

Table 3.4: **Comparison of the specifications for raw materials containing high levels of TiO_2 for the chloride process with the chemical compositions (%) of synthetic rutiles.**

	Specifications high-TiO_2-content raw materials for the chloride process [4]	**Ishihara Sangyo Process** Yokkaichi, Japan [1]	**Benilite Process** Kerr-McGee Mobile, Alabama, USA [1]	**Benilite Process** Pilot Plant, USA [1]	**Dhrangadhra Process** Quilon, India [1]	**Western Titanium Process** Capel, Western Australia [1]	**Becher Process** Iluka Resources Ltd. Narngulu Western Australia [2], [5]	**SREP Process** Iluka Resources Ltd. Narngulu, Western Australia [3]	**Mitsubishi Process** Pilot Plant, Japan [1]	**Summit Process** [1]	**Murso Process** [1]	**Chlorine Technology Process** Pilot Plant, Mt. Morgan Australia [1]
TiO_2	≥85	96.1	90.5-93.0	93.0	90-92	92.0	92.5	92-95	96.7	94.0	96.2	97.5
Fe (total)			1.5-2.6	2.0	3.0	3.6	2.4	1.0-3.0				0.46
FeO			0.1-0.6							2.0		
Fe_2O_3	<12	1.30	2.0-3.0						0.4		1.5	0.66
Cr_2O_3	≤0.2	0.15	0.05-0.12	0.04	0.2		0.10	0.2-0.3		0.10	0.15	0.11
Al_2O_3	≤0.6	0.46	<1.0-1.5	0.42	1.0	0.7	1.1	0.5-0.8	0.7	1.7	0.2	0.49
V_2O_5	≤0.65	0.20	0.10-0.25	0.06	0.25	0.12	0.22	0.25	+	0.15	0.04	0.04
Nb_2O_5	≤0.5	0.25	0.20-0.40	0.6			0.25	0.3				0.07
P_2O_5	≤0.05	0.17	0.05-0.09		0.2		0.03	0.01		0.1		0.072
MnO	≤0.1	0.03	0.05-0.15	0.22	0.1	2.0	1.1	0.8-1.2	0.06	1.7	0.05	<0.01
MgO	≤0.2	0.07	0.05-0.40	0.05	0.05	0.15	0.30	0.3			0.04	0.027
CaO	≤0.1	0.01	<0.35		0.05	0.03	0.03	0.07-0.15		0.7		0.065
ZrO_2	≤1.0	0.15	0.20-0.40	0.12	1.0		0.2	0.1		0.2		0.19
SiO_2	≤1.0	0.50	1.5-2.5	1.6	1.5	0.7	0.9	0.8-1.2	0.1	0.5		0.46
SnO_2	≤100 ppm [6]			0.14								0.003
As	≤20 ppm											
S		0.01	0.04-0.007	0.01		0.15	0.2	0.03		0.02		0.006
C			0.04-0.07			0.15						0.09
U	≤10 ppm						~ 10 ppm	10 ppm				
Th	≤100 ppm						80-450 ppm	80-90 ppm				
LOI			0.05-0.40		3.8							

[1] LYND & LEFOND (1983) [2] Company information [3] ELLIS et al. (1994) [4] DORMANN (1994) [5] CASSIDY et al. (1986) [6] as Sn + traces

Table 3.5: Chemical composition (%) of rutile concentrates.

	Eneabba WTN-Premium Grade RGC Minerals Sands Ltd. Western Australia 1)	**Eneabba** RGC Minerals Sands Ltd. Western Australia 16)	**Capel** Western Titanium N.L. Western Australia 9)	**Cudgen** New South Wales Australia 5), 6)	**Inskip** Queensland Australia 9), 7)	**Currumbin** Currumbin Minerals Pty Ltd. Queensland, Australia 1)	**North Stradbroke Island** Cruzor Rutile Consolidated Rutile Ltd. Queensland, Australia 2)	**North Stradbroke Island** Ibis Ore Body Consolidated Rutile Ltd. Queensland, Australia 16)	**Tomago Sandbeds** RZM Pty Ltd., Newcastle NSW, Australia 16), 18)	**Pooncarie Project** Murray Basin NSW, Australia 14)	**Malyshev, Volnogorsk** VSMMP Dnepropetrovsk, Ukraine 4)	**Sierra Leone** Sherbro Minerals 15), 17)
guaranteed												
TiO_2	≥95.0										≥94.0	
Fe_2O_3 (Fe total)	≤1.0										≤3.0	
Al_2O_3											≤0.6	
SiO_2											≤1.5	
ZrO_2	≤1.0										≤1.0	
typical												
TiO_2	95.5	95.22	96.10	96.80	96.80	95.05	95.5	94.90	94.61	96.3	95.2	96.29
ZrO_2	0.95	0.86	0.70	0.60	0.64	0.71	0.90	0.82	1.02	0.51	0.85	0.78
SiO_2	0.8	0.77	0.45	0.41	0.33		1.10	1.24	2.03	1.20	1.39	0.62
Fe_2O_3 (Fe total)	0.9	0.95	1.12	0.41	0.41	0.71	0.70	0.64	0.25	0.43	1.7	0.38
Al_2O_3	0.4	0.38	0.15	0.43	0.38		0.40	0.50	0.22	0.22	0.34	0.31
Cr_2O_3	0.15	0.14	0.16	0.24	0.23		0.25	0.20	0.12	0.13	0.13	0.19
V_2O_5	0.68	0.47	0.40	0.57	0.70	0.6-0.8	0.60	0.49	0.50	0.58	0.47	0.58
Nb_2O_5	0.35	0.37		0.40	0.40	0.3-0.35	0.40	0.37	0.40	0.33		0.15
P_2O_5	0.03	0.02	0.04					0.03	0.05	0.02	0.05	0.01
MnO	0.05	0.01	+	0.02	0.02			0.01	n.d.	0.01	n.d.	0.01
MgO	<0.01	<0.01	n.a.	0.15	0.10			0.06	0.04	<0.01	n.d.	<0.01
CaO	<0.01	<0.005	n.a.	0.03	0.02			<0.005	<0.005	0.01	0.08	0.01
S	0.02	<0.01	0.07		0.04			<0.01	<0.01	<0.01	0.02	<0.01
U	60 ppm	47 ppm					~50 ppm	64 ppm	69 ppm	39 ppm	60 ppm 8)	19 ppm
Th	60 ppm	46 ppm					~20 ppm	13 ppm	40 ppm	35 ppm		7 ppm
Moisture/LOI	0.04	0.34					~0.20	0.26	0.30	0.35	0.1	0.38

Table 3.5: continued.

	Namakwa Namakwa Sands Western Cape, RSA 10)	**Kwale** Trial Product Tiomin Resources Inc. Kenya 15)	**Mambrui** Trial Product Tiomin Resources Inc. Kenya 15)	**Pulmoddai** Ceylon Mineral Sands Corp. Sri Lanka 3)	**Kollam** Kerala Minerals and Metals Ltd. Kerala, India 2)	**OSCOM** OR-Grade Indian Rare Earths Ltd. Orissa, India 2)	**Manavalakurichi** MK-Grade Indian Rare Earths Ltd. Tamil Nadu, India 2)	**Chavara** Q-Grade Indian Rare Earths Ltd. Kerala, India 2)	**Green Cove Springs** Iluka Resources Ltd. Florida, USA 9), 11)	**Folkston** Humphreys Gold Corp. Folkston, Georgia 9), 12)	**Jacksonville** Humphreys Gold Corp. Florida, USA 9), 13)
guaranteed											
TiO_2	≥94.0			≥95.0	≥92.0						
Fe_2O_3 (Fe total)	≤1.0										
ZrO_2	≤1.2										
typical											
TiO_2	94.5	96.18	96.10	96.76	94.04	94.5	94.4	95.5	92.85?	95.09	94.65
$Zr(Hf)O_2$	1.1	0.72	1.09	0.38	0.64	0.90	1.8	1.40	0.11	0.73	0.37
SiO_2	2.0	0.94	0.80	0.64	0.58	0.90	1.8	1.0	0.09	0.31	0.11
Fe_2O_3 (Fe total)	0.80	1.25	<0.10	0.89	3.36	1.1	1.9	0.70	3.28	1.06	1.95
Al_2O_3	0.60	0.23	0.55	0.16	0.65		0.06		0.62	0.81	0.43
Cr_2O_3	0.14	0.17	0.12		n.d.		0.09		0.10	0.10	0.10
V_2O_5	0.33	0.52	0.58		0.36		0.05		0.22	0.27	0.27
Nb_2O_5	0.04					0.06	0.97		0.75	0.85	1.10
P_2O_5	0.02	0.00	0.01	<0.01	0.028		0.03	0.05	0.16	0.10	0.08
MnO	0.40	0.03	<0.01		0.05				0.15	0.05	0.09
MgO	<0.01	0.10	<0.05		n.d.				0.14	0.15	0.14
CaO	0.04	0.04	<0.02		n.d.				0.10	0.08	0.06
S	235 ppm			0.0				+			
U	40 ppm	28 ppm	54 ppm				~160 ppm 8)		<5 ppm	31 ppm	<5 ppm
Th	65 ppm	25 ppm	11 ppm						26 ppm	76 ppm	15 ppm
Moisture/LOI					0.22		0.4		1.39	0.36	0.81

1) Company data sheets 2) Company information 3) Clarke (1983) 4) Sokil (1998) 5) Baker (1962) 6) 0.05 % SnO2, 0.001 % CuO 7) 0.05 % SnO2, 0.07 % C, 0.001 % CuO 8) incl. Thorium 9) Elsner (1992) 10) Company information 11) 30 ppm As, 19 ppm Co, 60 ppm Hf, 57 ppm Mo, 144 ppm Pb, 166 ppm Sn, 258 ppm Ta, 225 ppm W, 198 ppm Zn 12) 22 ppm As, 67 ppm Cu, 110 ppm Hf, 37 ppm Mo, 81 ppm Pb, 179 ppm Sn, 267 ppm Ta, 258 ppm W, 14 ppm Zn 13) 16 ppm As, 16 ppm Co, 59 ppm Hf, 10 ppm Mo, 205 ppm Sn, 350 ppm Ta, 338 ppm W, 78 ppm Zn 14) Everett et al. (2003) 15) BALDERSON & ROSS (1998) 16) BGR analysis 17) 13 ppm As, 52 ppm Cu, 112 ppm Hf, 42 ppm Mo, 18 ppm Pb, 18 ppm Sn, 48 ppm Ta, 15 ppm W, 36 ppm Zn 18) 174 ppm Hf, 182 ppm Ta, 249 ppm W

+ = traces

Table 3.6: **Mineralogical composition (% by mass) and physical parameters of rutile concentrates.**

	Eneabba WTN-Premium Grade RGC Minerals Sands Ltd. Western Australia [1), 4)]	**Western Australia** Iluka Resources Ltd. [2)]	**North Stradbroke Island** Cruzor Rutile, Consolidated Rutile Ltd. Queensland, Australia [2), 4)]	**Chavara** Q-Grade Indian Rare Earths Ltd. Kerala, India [2)]	**OSCOM** OR-Grade Indian Rare Earths Ltd. Orissa, India [2)]	**Manavalakurichi** MK-Grade Indian Rare Earths Ltd. Tamil Nadu, India [2)]	**Green Cove Springs** Iluka Resources Ltd. Florida, USA [3)]	**Folkston** Humphreys Gold Corp. Georgia, USA [3)]	**Jacksonville** Humphreys Gold Corp. Florida, USA [3)]	**Sierra Leone** Sherbro Minerals [4)]
Mineralogical composition										
Rutile	99.0	82-97	98.1	91.71	97.1	~90	46.7	74.9	77.2	100.0
Anatase								3.1	2.8	
Brookite								0.2		
Leucoxene		1-17		6.30	n.d.	~8	46.6	0.7	16.0	
Ilmenite		<1	0.9	+	1.2	0.2	6.5	20.1	3.4	
Titanite								0.1		
Zircon	1.0	~ 1	1.0	1.80	1.0	~1.4		0.9	0.4	+
Monazite		<0.1		n.d.	0.2	0.2	0.2			
Sillimanite				0.10	0.1	+				
Kyanite		0.5				+				
Garnet				n.d.	0.1	n.d.				
Tourmaline			+							
Hornblende			+							
Quartz		<0.1		n.d.	0.1	0.2				
Others					0.2	n.d.				+
Physical parameters										
Apparent density (g/cm^3)	4.2-4.3	4.0-4.3	4.2-4.3	4.18-4.24	4.25	4.18-4.25				
Bulk density (t/m^3)	2.4-2.6	2.4-2.7	2.4-2.7	2.63-2.65	2.5-2.8	2.5-2.8				
Repose angle	30°									
Melting point °c		1825	1825	1800	1630	1630				
Ph			7.1-8.8	5.8-6.3	5.8-6.3	5.8-6.3				
AFS-No. [5)]		75-95								

1) Company data sheets 2) Company information 3) Elsner (1992) 4) BGR analysis 5) The AFS-number is a characteristic value developed by the AFS (American Foundrymen´s Society) for characterizing the grain refinement of a foundry sand. For calculating the AFS #. cf. Weiss (1984, S. 170 ff.). The following applies in general: a lower AFS # characterizes a coarse and a high one a fine-grained sand. + traces n.d. = not detectable

Table 3.7: Grain size distribution (% by mass, screen residue) of rutile concentrates.

µm	ASTM *mesh*	**Malyshev. Volnogorsk** VSMMP Dnepropetrovsk, Ukraine 3)	**Richards Bay** Richards Bay Minerals KwaZulu Natal, RSA 1)	**Pulmoddai** Ceylon Mineral Sands Corp. Sri Lanka 2)	**Green Cove Springs** Iluka Resources Ltd. Florida, USA 3)	**Folkston** Humphreys Gold Corp. Georgia, USA 3)	**Jacksonville** Humphreys Gold Corp. Florida, USA 3)	**Namakwa** Namakwa Sands Western Cape, RSA 4)
>710	>25						0.002	
600	30					0.001	0.003	
500	35					0.001	0.002	
425	40				0.005	0.003	0.004	
355	45	0.003			0.001	0.004	0.004	
300	50	0.003			0.001	0.008	0.013	
250	60	0.018	0.2		0.013	0.025	0.098	
212	70	0.129	0.4		0.124	0.263	0.623	
180	80	0.496	2.8		0.668	0.903	1.749	
150	100	5.970	17.1	13.56	2.769	2.005	3.606	14
125	120	31.154	26.7	48.87	13.705	5.047	14.225	47
106	140	40.248	35.8		33.204	21.236	32.858	23
90	170	17.106	10.6	33.95	35.336	33.653	32.750	9
75	200	4.332	5.0		12.277	26.655	12.088	6
63	230	0.426	1.4	3.60	1.586	9.254	1.809	1
53	270	0.087			0.076	0.671	0.069	
45	325	0.019			0.107	0.020	0.036	
<45	<325	0.010			0.120	0.060	0.050	
***mean* (µm)**		**118.2**			**106.1**	**95.5**	**108.2**	

1) Fockema (1986) 2) Clarke (1983) 3) Elsner (1992) 4) Company data

3.6 Size of deposits and resources

With the exception of the rutile deposits in Sierra Leone and Cameroon (cf. Table 3.9), other aspects in addition to the rutile concentrations are also important for assessing placers. Other accompanying valuable heavy minerals, mainly ilmenite/leucoxene and zircon, formerly also monazite/xenotime, provide a similar high added value per tonne (cf. Figure 2.3) and are therefore important for the economic viability of the mining of some deposits.

The reference values specified in Table 3.8 can be applied for the size of deposits that are also mined for rutile. Table 3.9 shows data for selected important placer deposits that contain rutile.

Table 3.8: Reference values for the assessment of rutile deposits

	All deposits 1) **Mineral content (incl. anatase)**	**Placers 2)** **Mineral content**
Small	<100,000-500,000 tonnes	100,000 – 250,000 tonnes
Medium	500,000-5 million tonnes	250,000 – 500,000 tonnes
Large	5 – >20 million tonnes	500,000 – 1 million tonnes
Very large		>1 million tonnes

1) Lorenz (1991) 2) this work

Table 3.9: Comparison of rutile carrying placers of global importance.

Country	Area of deposit	Occurrence	HM-content in the ore sand (% by mass)	Percentage of rutile in the HM-concentrate (% by mass)	Total resources and reserves of rutile as of: end of 2003 (kilotonnes)
being mined					
Australia	Western Australia	Capel	9.3	1	490
		Eneabba	6.2	7	3,090
		Cooljarloo	3.1	4.5	840
	Murray Basin	Douglas	8.4	5	1,750
		Gingko	3.2	12.1	680
		Snapper	5.4	15	780
	Queensland	N. Stradbroke Island	0.9	14	3,030
India	Orissa	OSCOM	20.2	3	1,400
	Tamil Nadu	coast	7-39	5	1,500
	Kerala	Chavara	9	7	6,700
Mozambique	coast	Moma	3.4-4.9	2.5	1,080
Sri Lanka	North-East coast	Pulmoddai	80	8	300
Rep. South Africa	KwaZulu Natal	Hillendale	6.8	3.3	250
		Richards Bay	13.8	4	2,300
	Western Cape	Brand-Se-Baai	10	4	1,240
USA	Florida	Trail Ridge	3.9	1.7	550
production planned					
	Western Australia	Dongara	10	7	510
	Murray Basin	WIM 150	4.0	8.7	3,400
		KWR	9.3	10	5,420
		Mindarie	3.99	6.6 [1)]	880
Cameroon	Central	Akonolinga	0.94-1.35	0.94-1.35	2,850
Kazakhstan	Northern Kasakhstan	Obukhovsky	9.4	4	130
Kenya	coast	Kwale	3.5-6.8	16	2,450
Malawi	Lake Malawi	Chipoka	33	3.2	12,800
Mozambique	Corridor Sands	West Block	7.47	0.3	390
Senegal	Grand Cote	total	1.8	8	600
Sierra Leone	Gbangbama Range	Rotifunk	1.46	40	1000
Rep. South Afr.	KwaZulu Natal	Fairbreeze	5.9	3.3	730
currently not mineable					
Germany	Cuxhaven	Midlum	9.9	5.1	290

[1)] HM concentrate also contains additional 1.5 % by mass of anatase

The global reserves and resources of rutile – defined as known and published quantities of currently mineable heavy minerals, not blocked by competing uses and extractable from placers – are listed in Table 3.10.

Table 3.10: Currently known worldwide reserves and resources of rutile.

Country	**Total reserves and resources of rutile** million tonnes	**Total reserves and resources of heavy minerals** million tonnes
Australia	39.9	465
Western Australia	*7.4*	*154*
Murray Basin	*29.0*	*282*
Eucla Basin	*0.5*	*8*
Queensland	*3.0*	*29*
India	>18	>632
Malawi	>13	>545
Sierra Leone	10.2	~18
Rep. of South Africa	4.4	133
Mozambique	3.2	372
Kenya	3.0	99
Cameroon	2.9	3
USA	2.4	58
China	0.7	23
Namibia	0.6	39
Senegal	0.6	31
Ukraine	0.5	~20
Sri Lanka	0.5	~18
Egypt	0.5	4
Kazakhstan	0.3	~5
Brazil	0.1	10
Rest	0	510
World	**100**	**3,000**

3.7 Important producing countries

Rutile was extracted for the first time in 1901 as a by-product from the anorthosite complex of Roseland in Virginia. In 1925, rutile was extracted - for the manufacture of white pigment - from the placers of Florida, and from 1934 onwards from the placers of New South Wales, Australia. Until the mid 1930s, however, the Indian placers covered almost the entire global rutile consumption. With the increase in Indian duties and the simultaneous discovery of further placers on the Australian East Coast in the initial years after World War II, Australia became the leading worldwide producer of rutile, but also of ilmenite, zircon and monazite in the 1950s. With the depletion or blocking of deposits on the Australian East Coast by competing uses, production increasingly moved to the Australian West Coast at the start of the 1980s.

The fluvial rutile placers of Sierra Leone discovered in 1954 had already gone into production in 1967. Before the civil war in Sierra Leone they supplied one fourth of the rutile produced worldwide. Because of the civil war they were closed between 1995 and April 2005.

Similar but smaller placers are known from Cameroon. In 1977, production was started in the first placers in South Africa. Currently, large reserves only discovered in the last two decades are being developed in the Murray Basin, Victoria, Australia and in East Africa (Mozambique, Malawi, Kenya).

Especially the former contain relatively large quantities of rutile. Since the demand for natural rutile significantly exceeds the supply, synthetic rutile is increasingly used as a substitute.

Finally, Figures 3.1 and 3.2 show a direct comparison of the percentage distribution of world production (2007) and the currently known world reserves and resources of natural rutile.

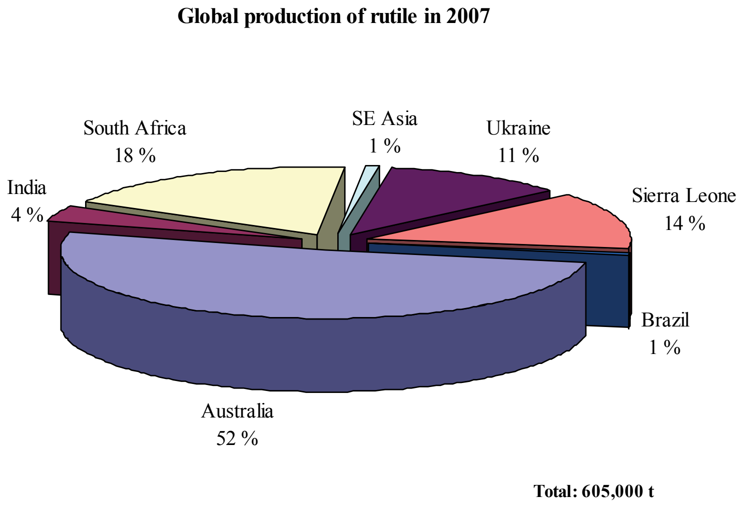

Figure 3.1: Percentage distribution of the world production of rutile in 2007.

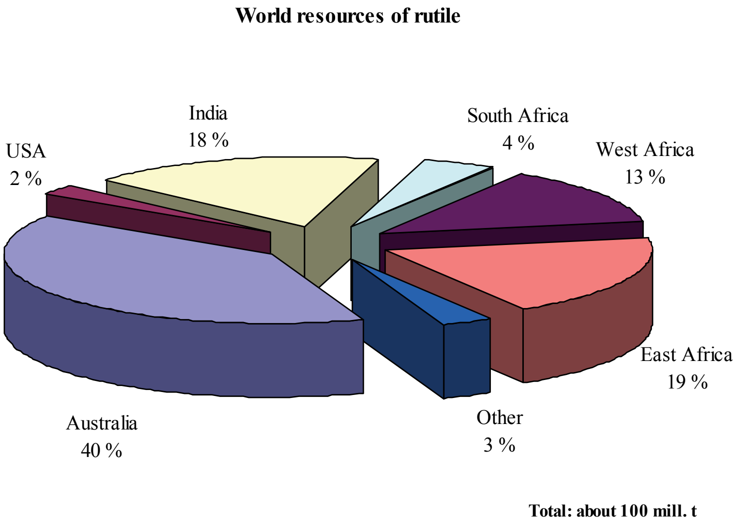

Figure 3.2: Percentage distribution of the currently known world reserves of rutile.

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4 Zircon

[German: *Zirkon*, Spanish: *circón*, French: *zircon*]

4.1 Mineralogy, Petrography, Chemistry

Pure **zircon** has the following characteristics:

Formula	$ZrSiO_4$
Chemistry	67.22 % by mass ZrO_2, 32.78 % by mass SiO_2
Density	4.68 g/cm^3
MOHS hardness	7 ½
Ccolor	colorless, yellowish, pink, red, brown, also green, blue, black
Magnetic property	non-magnetic
Electrostatic property	non-conducting

In addition to the element zirconium, Zr, the chemically very similar element hafnium, Hf, is always built into the crystal lattice of the mineral zircon. The content of HfO_2 in zircon averages 0.5-2.0 (4.0) % by mass. Zircons with increased contents of up to 24 % Hf are called alvites in mineralogical terms. Naegite, however, is a zircon with increased Y, Nb and Ta contents.

In addition to hafnium, zircon can also contain larger quantities of uranium and thorium. This renders zircon one of the main sources of radioactivity in granite rocks. This radioactivity can lead to the destruction of the lattice and therefore to “metamictization” of the mineral. U contents >1 % result in complete destruction of the lattice structure. The metamictization results from the α decay of ^{238}U, ^{235}U and ^{232}Th and their daughter isotopes. It is accompanied by hydration, a reduction in density, a reduction in hardness, a reduction in the refractive index, an increase in opacity, and a color change (cf. Table 4.1).

The effects of metamictization, particularly the color change, can be temporarily reversed by heating to more than 1,000 °C for 30 min (calcination). Calcination is a common processing step in the industry. It is used for dehydrating and burning organic coatings before zircon is used as casting sand (cf. below). If the zircons are covered by coatings containing Fe, these will take on a reddish-yellow color during calcination. Coatings containing Fe are therefore removed in acid baths before calcination.

Table 4.1: Selected properties of zircon with varying degrees of metamictization, supplemented according to GARNAR (1994).

	Common zircon	Modified zircon (hyacinth)	Highly modified zircon (malacon)
Density (g/cm^3)	4.6-4.7	4.2-4.6	3.6-4.2
MOHS hardness	7 ½	7	6-7
Color	white	violet	dark
Refractive index	1.92-1.96	1.90-1.92	1.76-1.90
LOI (% by mass)	0.1	0.5-1	10
Radioactivity	low	medium	high

According to ROZENDAAL & PHILANDER (2000):

- clear zircons contain: low levels of Fe, U and Th
- pink zircons: increased levels of rare earths (RE), U and Th
- yellow zircons: highly increased levels of RE, U, Th and increased levels of Fe, Al, P and Ca
- metamictic zircons: very highly increased levels of RE, U (up to the % range), Fe and Y

Very often, zircon contains inclusions of liquids and/or other minerals (rutile, spinel, feldspar, mica, silica, xenotime, monazite, Al silicates, cassiterite, magnetite and especially apatite).

Microcrystalline cracks are a result of metamictization (from the inside) or impacts (from the outside).

The zirconium mineral **baddeleyite** (ZrO_2), which up to now can only be extracted at an economic scale from solid rock deposits, for example Kovdor, Russia, is known as a placer mineral only from placers in Brazil and Sri Lanka. Due to its low concentration and its high radioactivity, it is however not extracted there.

4.2 Formation of deposits

Zircon develops exclusively through early liquid magmatic crystallization in albite-bearing acidic rocks, i.e. granites, diorites, syenites and their pegmatites. As zircon is ultra-stable in chemical and physical terms, all other reserves, such as in metamorphites, sediments and also volcanites, can be traced back to zircons initially crystallized in plutonites and later processed/transported.

Zircon is a typical placer mineral since it accumulates due to its weathering resistance and high apparent density. This does not apply to metamictic zircons that are unstable because of their physically disrupted crystal lattices. Therefore, these are rarely found in placers and are as a consequence also rare in commercial zircon concentrates.

4.3 Applications

The main application (approx. 53 % of the worldwide share) of zircon is in finely ground form in the **ceramics industry**. The very high refractive index of zircon enables opacification of melts and the white coloring of ceramic bodies. Typical areas of application are therefore the manufacture of porcelain melts for glazes, sanitary ceramics, wall and floor tiles, china, earthenware, special porcelains, glazed tiles and industrial tiles.

The proportion of zircon flour (d_{99} 45 µm) in enamel coats is approx. 7-12 %. The proportion of micronized zircon (d_{95} 5 µm) in raw glazes that are directly applied to the goods varies between 6-15 %. A typical glaze based on zircon requires grinding the zircon in a very narrow particle size band depending on the required opacifying effect. The products commercially available for ceramics applications include:

- zircon flour (opacifying enamels)
- 9 µm opacifiers (ceramic glazes)
- 6 µm opacifier (glazes, substitute for 5 µm opacifier in sanitary ceramics and densely fired unglazed tiles)
- 5 µm opacifier (limit value for sanitary ceramics and densely fired unglazed tiles)
- 3-1 µm opacifier (sanitary ceramics and special applications)

The good dielectric properties of zircon are used in the production of special ceramics.

If zircon is dissociated at high temperatures in a plasma arc furnace or if Zr sulfate or Zr hydroxide (cf. below) is calcinated, zirconium dioxide, **ZrO_2**, called **zirconia**, is produced, which has gained increasing significance over the last years, due to its:

- chemically high purity, great hardness and high apparent density,
- high melting point,
- high bending fracture and tensile strength,
- high fracture resistance,
- high wear resistance, corrosion resistance
- low thermal conductivity,
- thermal expansion similar to cast iron,
- Young's modulus similar to steel,
- onset of electrical conductivity at temperatures >600 °C,
- oxygen ion conductivity, and
- very good tribological properties, i.e. good properties in relation to friction, wear and lubrication.

Depending on the temperature, ZrO_2 occurs in monoclinic (<1.170 °C), tetragonal (1.170 – 2.370 °C) and cubic (2.370 – 2.680 °C (melting point)) crystal modification. Densely sintered components can be manufactured in cubic and/or tetragonal crystal types. In order to stabilize this cubic crystal modification, stabilizers in the form of MgO, CaO or Y_2O_3 must be added to the ZrO_2, occasionally CeO_2, Sc_2O_3 or Yb_2O_3 are also used as stabilizers.

In the case of fully stabilized zirconium dioxide (FSZ), the cubic high-temperature structure is maintained even after cooling because of the integration of foreign oxides into the crystal lattice. In the case of partial stabilization (PSZ), the amount of foreign ions compared to FSZ is reduced so much that in addition to the cubic phase there is also a proportion of convertible, tetragonal zirconium dioxide. ZrO_2 which is converted from the cubic into the tetragonal phase, but not converted further into the monoclinic phase due to its extremely fine structure (<100 nm), is called TZP (tetragonal zirconia polycrystal).

The very fine, tetragonal crystal phase in the PSZ and in the TZP exhibits a unique phenomenon in high-performance ceramics: the tetragonal crystallites are converted into the monoclinic crystal type under high mechanical stresses, undergoing a volume expansion – they can therefore react in a “pseudoelastic” manner, but at the same time this can also in part generate very fine micro fractures in their surrounding matrices. Cracks that start to run through the material under high tensile stress are stopped, slowed or branched by the volume expansion working against them or by the creation of micro fractures during this crystal conversion from the tetragonal to the monoclinic types. This leads to extremely high component strengths in the case of PSZ, and particularly in the case of TZP ceramics which can be utilized up to an application temperature of approx. 600 °C.

Because of the properties above, Zirconia is used for the manufacture of:

- Ceramics for mechanically highly stressed components (such as in pumps or for implants),
- Oxygen sensors in petrol engines, due to the oxygen ion conductivity of the ZrO_2 and therefore ability to measure oxygen partial pressures,
- Special glasses, because levels of up to 30 % ZrO_2 give rise to high refractive indices and long lifetimes,
- Color pigments in connection with Fe, V, Pr, Cd, S, Se because these exhibit the high temperature resistance required for glazes and enamels,
- Ammunition and explosives, in airbags and in professional flash technology because ZrO_2 powder is highly flammable,

- Grinding media, emery papers and special products that must be abrasion-proof and corrosion-resistant (coatings, textiles, printing inks, ceramics and others), since the yttrium stabilized ZrO_2 (YSZ) is ultra hard, tough and dense,
- synthetic zirconia gemstones that can easily be colored using other oxides.

Zircon has several properties that particularly distinguish it as a **refractory material** (approx. 12 % global share). These are:

- high melting point: >2,430 °C. The fire resistance of zircon sands corresponds to pyrometric cone 39/40, that is at temperatures around 1,885 °C.
- very low and regular thermal expansion,
- poor wettability by molten metal,
- excellent thermal conductivity,
- chemical stability.

Depending on the zircon content, quantity and type of the other aggregates, and the application temperature, zircon's properties result in potential uses in widely varying refractory applications. These are refractory mortar, firebricks or refractory linings for furnaces for different glass and metal melts.

The above refractory properties together with the characteristics:

- neutral to slightly acid pH,
- clean and round grains, which can be bonded at little cost and with little material,
- binding ability with all organic and inorganic molding sand binders,
- superior spatial and thermal stability at increased temperatures
- good recycling options

allow zircon to be used as a molding base material in the **casting industry** (approx. 12 % global share) in the form of zircon sand (steel) or zircon flour (casting paints, casing castings, super alloy and titanium castings) (cf. Table 4.2). Here, the fineness of the zircon flour improves the subsequent casting surface and reduces "burning").

Table 4.2: Comparison of the properties of important molding sands, according to KLOTZIN (1994).

	Zircon	**DuPont Zirclean** [2)]	**Quartz**	**Staurolite**	**Olivine**	**Chromite**
Color	white-brown	spotted	white	dark brown	greenish gray	black
MOHS hardness	7 - 7 ½	6 ½ - 7	6 - 7	6 ½ - 7	6 ½ - 7	5 ½ - 7
Bulk density dry (kg/m^3)	2,563-2,964	2,483-2,691	1,362-1,602	2,291-2,339	1,602-2,002	2,483-2,643
Apparent density (g/cm^3)	4.4-4.7	3.2-4.0	2.2-2.6	3.1-3.8	3.2-3.6	4.3-4.5
Grain shape	angular/ round	round	angular/ round	round	angular	angular
Thermal expansion (mm/°K)	0.003	0.005 [1)]	0.018	0.007 [1)]	0.0083	0.005
Heat conduction	high	high	average	high	low	very high
Melting point (°C)	2,038-2,204	1,815-1,982	1,427-1,760	1,371-1,538	1,538-1,760	1,760-1,982
High-temperature behavior	acidic	slightly acidic	acidic	slightly acidic	alkaline	alkaline
Wettability with molten metal	none	none	little	none	not generally	none
Chemical reaction	acidic-neutral	neutral	acidic-neutral	neutral	alkaline	neutral-alkaline
AFS #	95-160	~80	25-180	~70	40-160	50-90

[1)] sand mixtures bound in clay [2)] zircon blasting sand

Only a small part of the zircon mined worldwide (cf. Figure 4.1) is used for the extraction of the **metals zirconium and hafnium** or their further processing to produce **chemicals**. Zirconium and hafnium are highly reactive elements that form stable bonds with oxygen, sulfur, nitrogen and carbon. These again serve as base materials for further processing into Zr chemicals.

In **cathode ray tubes** of televisions and computer monitors, zircon is used as a screen against x-rays. The hardness of zircon is of additional advantage for the stabilization of the tube glass. Zircon is not used in TFT monitors because these have transistors instead of cathode ray tubes.

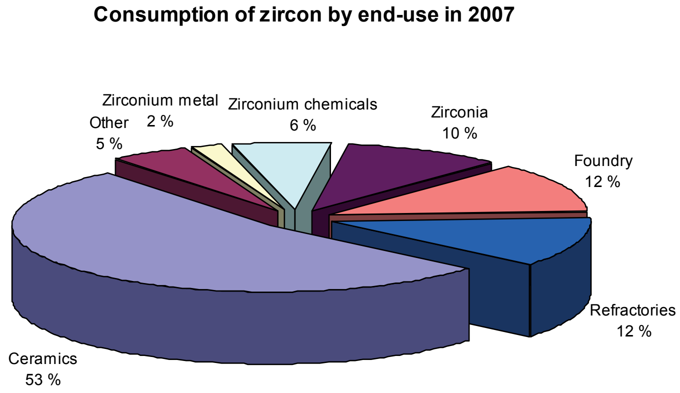

Figure 4.1: Consumption of zircon by end-use in 2007 (Baylis 2008).

Zirconium and hafnium are extracted using the Kroll process similar to titanium (cf. Chapter 2.3) via the intermediate product zircon tetrachloride, $ZrCl_4$. The main chemical steps here are:

$$ZrSiO_4 + 2\ C + 4\ Cl_2 \rightarrow ZrCl_4 + SiCl_4 + 2\ CO_2$$

$$ZrCl_4 + 2\ Mg \rightarrow Zr + 2\ MgCl_2$$

The zirconium produced is a hard, glossy, grey-white metal with an apparent density of 6.5 g/cm^3, good thermal stability (melting point 1,852 ^oC), low neutron capture cross-section and superior resistance to corrosion by most acids and caustic solutions, seawater and other substances. Its key area of application with approx. 90 % is therefore – absolutely free from hafnium! – in the linings and frames of nuclear reactors. Minor applications are in photography, in the manufacture of special steels and alloys, and high-density batteries.

In powder form, zirconium can be ignited by sparks, friction or low electrical discharge. It is therefore used as a heat source in ignition charges, as an igniter mechanism in airbags and flashcubes, and as an alloying aid.

Zr is alloyed with Fe, Si, Ni and also Sn, Cr, Cu and Mo. In steel manufacture, the affinity of Zr to O_2, S and N_2 is used to control sulfides and oxysulfides in inclusions, to bind N_2 and to stop crystal growth and strain ageing.

Melted zirconia or zirconia-mullite (pure Zr or with mullite heated to 3,000 ^oC and then quenched) is used after grinding in refractory and casting and molding applications as well as in high-tech ceramics.

The most important Zr chemicals include, in the order of their worldwide volume share:

- Zirconium oxychloride (ZOC), $ZrOCl_2$ x 8 H_2O, a white crystalline solid with a slightly acrid smell that can be dissolved with the addition of water and heating. The light yellow or colorless liquid produced in this way is used for applying white TiO_2 pigment and is an intermediate product for the manufacture of zirconium catalysts.

- Zirconium sulfate (ZOS), $Zr(SO_4)_2$, a moist, white, crumbly paste, which is used as an accelerator in adhesives, a gelatin hardener in photography, paper pigment, catalysis promoter and Cr substitute in leather tanning.
- Zirconium carbonate (ZBC), $ZrOCO_3$ x n H_2O, a moist, white solid. It is used as an aid in paint drying, as a thixotropic aid, as a deodorant, in photo catalysis and in paper manufacture.
- Ammonium zirconium carbonate (AZC), $(NH_4)_3ZrOH(CO_3)_3$ x 2 H_2O, is a clear or slightly opaque, water-soluble basic solution smelling of ammonia. It applications are catalysis, paint drying and/or as a thixotropic aid, for water-proof surface coatings for paper and packaging, printing inks, adhesion promoter for plastics and metals, bonding agent and accelerator in adhesives, molding material binder and for waterproof textiles.
- Organic compounds with zirconium, mainly acetates (ZAC), propionates, acetylacetonates. They are used in electrical and special ceramics, as a catalytic hardener for epoxy resins and silicones, in paint drying, as a water repellant for paper and non-wovens, as a printing ink adhesion promoter for plastics and metals, as a thixotropic agent in cements, as welding fluids and clay stabilizers, as a Cr substitute in the processing of Al canning metal, as molding material binder and a gelatin hardener in photography.
- Potassium zirconium hexafluoride (KFZ), K_2ZrF_6, is a white to light yellow crystalline powder whose uses are in Fe alloys, refractory, ceramics and glass and electrical materials for the nuclear industry.

Other, currently still insignificant Zr chemicals in terms of volume are:

- Zirconium phosphate, $Zr(HPO_4)_2$, and zirconium phosphate monohydrate, are both odorless white powders. They are used as catalysts in the synthesis of methyl-iso-butyl-ketones and in polymerization, hydrogenization, oxidation, hydration and dehydration reactions and in iron exchange (kidney dialysis, water treatment)
- Zirconium hydroxide, $Zr(OH)_4$ x n H_2O, is a moist white powder. It is used as high-purity Zr raw material in the production of catalysts and ceramics, in ion exchange, in paints and colorants, in absorbents, in deodorants and as an additive in plastics and glass.
- Zirconium oxynitrate, $ZrO(NO_3)_2$, is a clear to slightly turbid liquid. It is a high-purity Zr base material for the manufacture of Zr catalysts, chemicals and ceramics, is used as a white pigment and filler, a molding material binder, a bonding agent and accelerator in adhesives, and reacts with proteins in deodorants.
- Zirconium hydride, ZrH_2, is a grey-black, metallic, odorless powder that is used in various metallurgical and other special areas: oxidation promoter in pyrotechnics, gas binder in the manufacture of vacuum tubes, hardener and bronzer for carbides and in ceramics, reservoir for high-purity hydrogen and hydrogen source in the foaming of metals, additive in the application of ceramics onto metals, source for zirconium in powder alloys.
- Zirconium fluoride, ZrF4, is a white, odorless powder that is used in ceramic paints, optical fibers and special glasses, in gemstone processing, metal treatment and in textiles.

Hafnium, possessing very similar properties to zirconium, is used for the manufacture of control rods in nuclear reactors, for propulsion systems in nuclear submarines, as an additive for Ni based super alloys and in metal cutting for plasma cutters. HfC is the chemical compound with the best-known fireproof properties (melting point: 3,890 ^{o}C), similar to HfN with a melting point of 3,310 ^{o}C.

Despite its high price, zircon flour is used as a filler with functional effects to increase the thermal and electrical resistance in plastics, silicones, epoxies, resins and special paints, due to its chemical stability and its white color.

For the cleaning of highly sensitive turbine parts, zircon sand is also used as a blasting sand.

4.4 Substitutes

Depending on the area of application, zircon can be replaced by other mineral raw materials to a limited extent; some possibilities are as follows:

- refractory industry: andalusite, bauxite, chromite, kyanite, dolomite, graphite, magnesite, olivine, pyrophyllite, refractory clays, silica, sillimanite
- foundry purposes: bauxite and aluminum, chromite, clays (kaolin and bauxite), olivine, perlite, pyrophyllite, silica sand, vermiculite
- opacifier: tin oxide
- zirconium and chemicals: baddeleyite (ZrO_2), an accessory mineral in volcanic rocks that is currently only extracted in Kovdor near Murmansk, Russia (production: 6,700 tonnes in 2005)
- abrasives (YSZ): electrocorundum), corundum/emery, diamond, diatomite, feldspar, garnet, hematite, magnetite, nepheline syenite, olivine, perlite, pumice stone, silica sand, staurolite, tripoli, silicon carbide, ilmenite
- paint dryer: products based on Co, Pb and Mn

4.5 Demands on the raw materials (reference values)

In China there are specifications for zircon deposits or for zircon-bearing beach sands in Guangdong Province (cf. Table 4.3).

Table 4.3: Specifications for zircon deposits in China or for zircon-bearing beach sands in Guangdong Province, China (SHAODE & JIYE 1996).

Type	***Marginal Grade***			***Industrial Grade***		
	ZrO_2 (%)	**Zircon** (kg/m^3)	**Mineral content** (kg/m^3)	**ZrO_2** (%)	**Zircon** (kg/m^3)	**Mineral content** (kg/m^3)
beach sands	0.04-0.06	1-1.5		0.16-0.24	4-6	
- bearing zircon			1			2
- bearing monazite			0.25			0.50
- rich in hematite			20			30-40
- poor in hematite			10			15
weathering crust	0.3			0.8		
solid rock ore	3.0			8.0		

Physical properties of zircon important for various applications have been listed in Table 4.4.

Table 4.4: Important physical properties of zircon depending on the application, according to PIRKLE & PODMEYER (1992).

Physical properties	Application			
	Ceramics	Abrasives	Refractory	Foundry
AFS # [1]				x
Grain size distribution		x	x	x
Low LOI	x	x	x	x
pH	x		x	x
Apparent density			x	
Low demand for acid				x
Color	x			x
Grain shape		x	x	x
Calcination	x			x
High tensile strength				x
High melting point	x		x	x
Great hardness		x		

[1] The AFS number is a characteristic value developed by the AFS (American Foundrymen´s Society) for characterizing the grain fineness of foundry sands.

Green Cove Springs standard zircon: 121, Richards Bay prime zircon: 112, Yoganup standard zircon: 102, Trail Ridge standard zircon: 112, Georgia zircon sand: 166

GARNAR (1986) lists the specifications for zircon concentrates for different applications as follows:

- A zircon concentrate that is to be used as foundry sand must contain ≤3 % by mass kyanite and ≤0.1 % by mass staurolite. The corundum content (Al_2O_3) must also be low.
- For the purposes of the refractory and ceramics industry, the limits are ≤2 % by mass kyanite and ≤0.1 % by mass staurolite.
- For zircon that is used for casting aircraft parts, the following limits apply to trace elements: ≤25 ppm Pb, ≤75 ppm Zn, ≤1 ppm Bi, ≤25 ppm Sn and ≤160 ppm Ce. Here, Sn is often contained in the spinel gahnite, which can be separated electromagnetically however.
- Zircon for steel casting must be well rounded and calcinated and have a mean grain diameter of 110 – 150 µm. The concentrate must contain ≤0.1 % by mass accompanying minerals with low melting points.
- If zircon is to be ground wet or dry into zircon flour and then used as an opacifier, only zircon concentrates of *premium* or *intermediate grade* can be used as feedstock due to the specifications for the Fe content (≤0.04 % Fe).

Depending on the application and processing quality, zircon concentrates are put onto the market by the producers or commodities traders with the affix *premium (prime), intermediate, standard* or *ceramic* (cf. Table 4.5). DuPont has created further designations for special specifications (cf. Table 4.7): ZirconT is a zircon sand for foundries extended by Ti minerals. Zircore contains coarse Al silicates that allow gasses to escape in refractory applications. Zirclean is a blasting sand (cf. below).

Table 4.5: Guaranteed specifications (%) of zircon concentrates, supplemented according to ELSNER (1992) and SKILLEN (1993).

	$ZrO_2 + HfO_2$	TiO_2	Fe_2O_3
Traditional			
Standard	>65.0	<0.25	<0.15
Intermediate	>65.5	<0.03	<0.10
Premium	>66.0	<0.10	<0.05
USA			
Du Pont – Standard	>65.0	<0.35	<0.05
Du Pont – Premium	65.0 – 66.0	<0.15	<0.05
Iluka Resources Ltd.	>66.5		
Humphreys (Jacksonville)	>65.0	<0.35	<0.05
Humphreys (Folkston)	>65.0	<0.25	<0.10
Australia			
East Coast – Standard	>65.5	<0.30	<0.07
East Coast – Premium	>66.0	<0.10	<0.05
West Coast – Standard	>65.0	<0.25	<0.15
RZ-Mines – Premium	>66.5	<0.05	<0.10
Yoganup – Ceramic	>66.0	<0.10	<0.06
Yoganup – Standard „A“	>65.5	<0.15	<0.10
Yoganup – Standard „L“	>65.0	<0.25	<0.12
Yoganup – C.L.	>65.5	<0.25	<0.10
Yoganup – Coarse	>66.0	<0.25	<0.15
Allied Eneabba	>65.5	<0.15	<0.10
Rep. South Africa			
RBM – Refractory	>65.0	<0.50	<0.15
RBM – Standard	>65.0	<0.30	<0.25
RBM – Prime	>65.0	<0.15	<0.10
Namakwa – Premium	>66.0	<0.12	<0.06
Brazil			
Nuclemon – Standard	>64.5	<0.50	<0.30
Nuclemon – Premium	>65.5	<0.10	<0.05
India			
IRE – OR-*grade*	>64.8	<0.70	<0.30
IRE – MK-*grade*	>65.0	<0.25	<0.10
IRE – Q-*grade*	>65.0	<0.30	<0.12
South East Asia			
Thailand Sakorn Minerals	>66.25	<0.15	<0.08
Ceylon Mineral Sands Corp	>65.0	<0.50	<0.20
Malaysia Mining Corp.	>65.5	<0.30	<0.10
China	>63.0	<0.50	<0.50

Radioactivity

As a bearer of U and Th, zircon is slightly radioactive and therefore carcinogenic. In general, a global limit of 500 ppm U + Th or $U + (0.4 \times Th) \leq 100$ ppm applies. Different countries, however, have adopted differing limits.

Compliance with the above limits of U and Th in zircon concentrates has been one of the most important assessment criteria for its suitability for some years. The lower the level of U and Th, the higher its marketing potential (cf. Table 4.6). Moreover, according to current legislation, zircons with U and Th levels exceeding the legal limits do not constitute valuable heavy minerals, but radioactive waste material! Radioactive zircons (which are often weakly magnetic) must therefore be separated out during processing. This, however, leads to high production losses and to the storage of radioactive materials from zircon, xenotime and monazite, which is undesirable in ecological terms (cf. Chapter 5.5).

Table 4.6: Important chemical parameters of various zircon concentrates according to SKILLEN (1992) and other sources.

Area of deposit or producer	Zircon product	Fe_2O_3	TiO_2	Al_2O_3	U+Th
Western Australia-Eneabba	WTN-*grade*	0.08	0.12	0.35	410 ppm
Western Australia-Capel	WTC-*grade*	0.20	0.25	1.10	470 ppm
Western Australia-RZM Cable Sands	Premium	0.09	0.13	0.80	450 ppm
	Standard	0.20	0.20	1.00	450 ppm
Western Australia-Tiwest	Premium	0.06	0.13	0.42	410 ppm
Western Australia-Yoganup	Standard A	0.06	0.13	0.60	400 ppm
	unleached	0.12	0.15	0.60	445 ppm
Western Australia-ISK	Standard	0.12	0.15	0.43	370 ppm
Queensland-CRL	Premium	0.06	0.11	0.20	440 ppm
	Standard	0.15	0.24		
New South Wales-MDL	Ceramic	0.29	0.08	0.40	450 ppm
New South Wales-RZM	Premium	0.03	0.13	0.20	
R. South Africa-Richards Bay	Prime	0.08	0.12	0.14	450 ppm
	Intermediate	0.12	0.25	0.25	450 ppm
Rep. South Africa-Namakwa	Premium	0.05	0.11	0.24	410 ppm
Ukraine-Volngorsk	Standard	0.08	0.25	1.42	330 ppm
USA-Du Pont	Premium	0.03	0.13	0.30	350 ppm
	Standard	0.04	0.25	1.30	350 ppm
	Zircon T	0.20	1.20	1.00	450 ppm
USA-Iluka	Ceramic	0.04	0.13	0.35	350 ppm
	Standard	0.04	0.12	0.46	350 ppm
India-KM	Standard	0.86	0.70	2.51	
Mozambique-Congolone	Premium	0.06	0.05		
Senegal-MDL	Test	0.06	0.09/0.10	0.20/0.23	273/301 ppm

The radioactivity of zircon and its potential impact has been investigated and discussed in numerous studies and independent assessments (cf. Chapter 4.8). These reveal that there is no real hazard potential for persons coming into contact with the material.

When processing zircon, the potential for it containing free silica has to be taken into account though – as is the case for all heavy minerals. Here, the regulations regarding limits for silica dust (silicosis!) apply. The Zirclean product by DuPont is approved as blasting sand in the USA.

Tables 4.7 – 4.9 show the compositions and physical parameters of zircon concentrates produced globally from placers.

Table 4.7: Chemical composition (%) of zircon concentrates.

	Capel WTC-Grade RGC Mineral Sands Ltd. Western Australia 1)	**Eneabba** WTN-Grade RGC Mineral Sands Ltd. Western Australia 1)	**North Stradbroke Island** Cruzor Zircon Premium Grade Consolidated Rutile Ltd. Queensland, Australia 2)	**North Stradbroke Island** Ibis Ore Body Consolidated Rutile Ltd. Queensland, Australia 4)	**Tomago Sandbeds** RZM Pty Ltd. Newcastle, NSW, Australia 4)	**Pooncarie Project** Murray Basin NSW, Australia 11)	**Malyshev, Volnogorsk** VSMMP Dnepropetrovsk, Ukraine 6)	**OSCOM** OR-Grade Indian Rare Earths Ltd. Orissa, India 2)	**Manavalakurichi** MK-Grade Indian Rare Earths Ltd. Tamil Nadu, India 2)	**Chavara** Q-Grade Indian Rare Earths Ltd. Kerala, India 2)	**Kollam** Kerala Minerals and Metals Ltd. Kerala, India 2)	**Pulmoddai** Ceylon Mineral Sands Corp. Sri Lanka 3)
guaranteed												
$ZrO_2 + HfO_2$	≥65.0	≥66.0	≥66.0				≥65.0				≥64.0	≥65.0
Fe_2O_3	≤0.25	≤0.10	≤0.07				≤0.1					
Al_2O_3							≤2.0					
TiO_2	≤0.30	≤0.15	≤0.15				≤0.4					
U + Th												
typical												
$Zr(Hf)O_2$	65.5	66.5		66.30	65.06	66.8	65.7	64.50	65.8	65.30	64.81	66.46
HfO_2				1.07	1.05							
SiO_2	32.9	32.5	32.5-32.8	31.57	31.42	32.8	32	32.10	32.5	32.80	30.33	32.60
TiO_2	0.25	0.12		0.09	0.26	0.13	1.2	0.70	0.25	0.27	0.30	0.50
Fe_2O_3 (Fe Total)	0.20	0.07		<0.01	<0.01	0.04	0.09	0.30	0.1	0.12	0.86	0.11
Al_2O_3	1.1	0.35	0.20-0.40	0.43	0.28	0.27	1.2	n.d.	1.2	n.d.	2.51	0.2
Cr_2O_3	10 ppm	30 ppm		n.d.	n.d.		0.12	n.d.	0.001	n.d.	n.d.	
P_2O_5	0.10	0.09	0.11-0.14	0.20	0.20	0.12		0.10	0.05	n.d.	0.46	
U	250 ppm	210 ppm	265-330 ppm	232 ppm	198 ppm	269 ppm	320 ppm 5)	n.d.	500 ppm 5)	n.d.		
Th	220 ppm	200 ppm	140-175 ppm	<5 ppm	<5 ppm	145 ppm		n.d.				
Y				750 ppm	562 ppm							
LOI	0.04	0.15–0.25	~0.13	0.40	1.00	0.16	0.1	0.1	0.1	0.1		

Table 4.7: continued.

	Green Cove Springs Iluka Resources Ltd. Florida, USA 7)	**Folkston** Humphreys Gold Corp. Georgia, USA 7)	**Trail Ridge** Standard Zircon, Du Pont Florida, USA 7)	**Trail Ridge** Premium Zircon, Du Pont Florida, USA 7)	**Trail Ridge** Du Pont™ ZirconT® Florida, USA 7)	**Trail Ridge** Du Pont™ Zirclean ® Florida, USA 7)	**Trail Ridge** Du Pont™ Zircore ® Florida, USA 7)	**Kwale** Trial Product Tiomin Resources Inc. Kenya 10)	**Mambrui** Trial Product Tiomin Resources Inc. Kenya 10)	**Namakwa** Namakwa Sands Western Cape, RSA 2)	**Richards Bay** Standard Grade KwaZulu Natal, RSA 8)	**Richards Bay** Refractory Grade KwaZulu Natal, RSA 2)	**Athabasca** Oil Sands 9)
guaranteed													
$ZrO_2 + HfO_2$			≥65.00	≥66.50	≥64.0		≥27			≥66.0			
Fe_2O_3			≤0.05	≤0.05	≤0.5					≤0.06			
Al_2O_3			≤2.00	≤0.50	≤2.5								
TiO_2			≤0.35	≤0.15	≤2.0					≤0.12			
typical													
$Zr(Hf)O_2$	66.26	65.45	65.43	66.75	66.03	59.58	45.67	66.0	66.1	66.2	66.27	65.79	65.99
HfO_2	1.26	1.25	1.23	1.25	1.23	1.08	0.77			1.31		1.23	1.19
SiO_2	32.37	32.32	32.27	32.17	32.60	31.00	35.00	32.50	32.50	32.6	32.38	32.96	31.1
TiO_2	0.06	0.18	0.14	0.13	1.00	3.22	1.42	0.14	0.33	0.11	0.26	0.11	0.25
Fe_2O_3 (Fe Total)	0.05	0.09	0.07	0.06	0.11	0.98	0.55	0.049	<0.10	0.05	0.19	0.06	0.16
Al_2O_3	0.42	0.43	0.80	0.96	0.70	5.00	17.00	0.12	0.13	0.24	0.30	0.09	0.72
P_2O_5	n.d.	n.d.	0.11	0.12	0.12	0.17	0.06	0.09	0.09			0.11	0.40
CaO								0.01	<0.02		0.22		0.20
U	0.12	0.12	231 ppm	247 ppm	254 ppm	234 ppm	159 ppm	309 ppm	270 ppm	235 ppm		329 ppm	300 ppm
Th	210 ppm	203 ppm	193 ppm	174 ppm	200 ppm	290 ppm	129 ppm	143 ppm	170 ppm	165 ppm		141 ppm	100 ppm
Y	184 ppm	148 ppm	801 ppm	360 ppm	367 ppm	453 ppm	421 ppm						
Zn	288 ppm	743 ppm	143 ppm	84 ppm	362 ppm	1592 ppm	245 ppm						
LOI	0.90	0.48	0.50	1.40	1.27	2.23	1.53				0.31		

1) Company data sheets 2) Company information [Note: Iluka Resources Ltd. produced in 2004: Capel Zircon Premium Grade, Capel Zircon Coarse Grade, Eneabba Zircon Premium Grade, Eneabba Zircon Standard Grade, Eneabba Zircon Coarse Grade, Florida Zircon Premium Grade as well as Virginia Zircon Premium Grade] 3) CLARK (1983) 4) BGR analysis 5) incl. thorium 6) O`DRISCOLL 1998) 7) ELSNER (1992) [Note: DuPont produced in 2004: Premium Zircon, Standard Zircon, Low Alumina Zircon, Zircore, Zircon T as well as Zircon M] 8) SHIKANO et al. (1998) plus 0.05 % MgO 9) OXENFORD et al. (2003) plus 0.02 % Cr_2O_3 10) BALDERSON & ROSS (1998) 11) EVERETT et al. (2003) plus 0.03 % CaO n.d. = not detectable

Table 4.8: Mineralogical composition (% by mass) of zircon concentrates.

	Eneabba RGC Mineral Sands Ltd. Western Australia [2)]	**Capel** RGC Mineral Sands Ltd. Western Australia [2)]	**North Stradbroke Island** Ibis Ore Body Consolidated Rutile Ltd. Queensland, Australia [2)]	**Tomago Sandbeds** RZM Pty Ltd. Newcastle, NSW, Australia [2)]	**Brazil** Nuclemon [2)]	**Green Cove Springs** Iluka Resources Ltd. Florida, USA [1)]	**Folkston** Humphreys Gold Corp. Georgia, USA [1)]	**Trail Ridge** Standard Zircon, Du Pont Florida, USA [1)]	**Trail Ridge** Premium Zircon, Du Pont Florida, USA [1)]	**Trail Ridge** Du Pont™ ZirconT® Florida, USA [1)]	**Trail Ridge** Du Pont™ Zirclean ® Florida, USA [1)]	**Trail Ridge** Du Pont™ Zircore ® Florida, USA [1)]	**Lakehurst** Heritage Minerals Inc. New Jersey, USA [2)]
zircon	100.0	96.0	100.0	100.0	83.0	99.2	97.6	98.9	98.2	98.3	86.2	65.6	100.0
rutile					9.0			0.8	0.1	0.4	2.1	0.2	
anatase							0.3						
brookite						0.2							
leucoxene										0.2	0.4	0.6	
ilmenite											1.6	0.6	
titanite													
monazite	+												
andalusite		+										0.9	
sillimanite					3.0		0.6		+	0.2	0.1	6.0	+
kyanite	+	2.0			2.0	0.2		0.3	1.5	0.3	1.5	10.9	
garnet		+			3.0							0.3	
staurolite						0.2	0.4		0.1	0.5	7.2	3.5	
epidote						0.1							
topaz			+			0.1					0.1	1.2	
corundum							0.4		0.1		0.3	4.4	
tourmaline											0.1	1.3	
spinel											0.4		
quartz	+	2.0		+	+		0.4	+	+			4.5	

[1)] ELSNER (1992) [2)] BGR-Analyse + Spuren (< 0,1 %)

Table 4.9: Grain size distribution (% by mass, screen residue) and physical parameters of zircon concentrates.

		Eneabba Iluka Resources Ltd. Western Australia 1)	**Capel** Iluka Resources Ltd. Western Australia 1)	**Richards Bay** Richards Bay Minerals KwaZulu Natal, RSA 2)	**Namakwa** Namakwa Sands Western Cape, RSA 5)	**Pulmoddai** Ceylon Mineral Sands Corp. Sri Lanka 3)	**Trail Ridge** Standard Zircon, Du Pont Florida, USA 4)	**Trail Ridge** Premium Zircon, Du Pont Florida, USA 4)	**Trail Ridge** Zircon T^{TM}, Du Pont Florida, USA 4)	**Trail Ridge** Zirclean^{TM}, Du Pont Florida, USA 4)	**Trail Ridge** Zircore ^{TM}, Du Pont Florida, USA 4)	**Green Cove Springs** Iluka Resources Ltd. Florida, USA 4)	**Folkston** Humphreys Gold Corp. Georgia, USA 4)
Grain size distribution													
µm	ASTM m*esh*												
>700	>25									0.002	0.014		
600	30						0.001			0.000	0.024		
500	35						0.003		0.002	0.004	0.052	0.001	
420	40						0.002	0.001	0.005	0.025	0.190	0.001	0.001
355	45						0.002	0.004	0.013	0.070	0.683	0.002	0.003
300	50	+	1				0.009	0.009	0.138	0.337	2.296	0.003	0.006
250	60	14	3				0.012	0.129	0.910	1.235	4.307	0.005	0.006
210	70			0.1			0.046	1.051	3.843	4.196	9.819	0.005	0.016
180	80	46	30	0.9			0.540	3.359	7.168	6.188	11.850	0.012	0.253
150	100			6.5	14	0.10	2.843	8.778	11.913	10.292	13.771	0.025	1.115
125	120	30	52	18.4	47	5.28	18.879	21.286	23.916	19.486	17.521	2.396	3.768
105	140			42.9	23		36.025	40.040	34.466	32.208	23.115	23.158	11.379
90	170	9	13	18.1	9	35.10	29.685	20.505	14.535	18.620	12.834	42.163	36.417
75	200			11.0	6		9.421	4.332	2.651	6.063	3.140	24.684	32.168
63	230	1	1	2.1	1	38.40	1.847	0.340	0.227	0.955	0.240	6.468	13.376
53	270					0.08	0.291	0.047	0.070	0.099	0.027	0.542	1.061
45	325						0.171	0.016	0.017	0.051	0.009	0.192	0.362
<45	<325						0.220	0.010	0.120	0.160	0.100	0.110	0.060
mean (µm)		165	140	110 1) 148 6)	136 6)		108.7	119.2	129.0	124.8	146.6	94.5	89.9
Physical parameters													
apparent density (g/cm^3)		4.6-4.8	4.6-4.8	4.61	4.61		4.62-4.67				3.59-4.19		
bulk density (kg/m^3)		2,600-2,800	2,600-2,800				1,643-2,804				2,403-2,563		
melting point (^{o}C)		2,200	2,200				2,100-2,300				1,815-2,038		
linear extension (cm/cm ^{o}C)		2.5 x 10^{-6}	2.5 x 10^{-6}				7.2 x 10^{-6}				Ø10.8 x 10^{-6}		

1) Garnar (1986) 2) Fockema (1986) 3) Clark (1983) 4) Elsner (1992) 5) Company information 6) Aral & Macdonald (1999)

4.6 Size of deposits and resources

When assessing zircon deposits, the level of titanium minerals (ilmenite, leucoxene, rutile) is of greater importance than their zircon content. This means that zircon is always only a secondary, never a primary valuable heavy mineral when it is being extracted from placers.

As for the mineral rutile (cf. Chapter 3.6), which has a similar added value as zircon (cf. Figure 2.3) and occurs with similar incidence in placers, the reference values specified in Table 4.10 can be applied to the size of deposits where zircon is also mined.

Table 4.10: Reference values for the assessment of zircon deposits.

	All deposits [1] **ZrO_2-content**	**Placers** [2] **mineral content**
small	<50,000 – 100,000 tonnes	100,000 – 250,000 tonnes
medium	100,000 – 1 million tonnes	250,000 – 500,000 tonnes
large	1 –>10 million tonnes	500,000 – 1 million tonnes
very large		>1 million tonnes

[1] LORENZ (1991) [2] this work

Table 4.11 shows data for selected important placer deposits containing zircon.

The global reserves and resources of zircon – defined as known and published quantities of currently mineable heavy minerals, not blocked by competing uses and extractable from placers – are listed in Table 4.12.

Table 4.11: Comparison of zircon placers of global importance.

Country	Area of deposit	Occurrence	HM-content in the ore sand (% by mass)	Proportion zircon in the HM-concentrate (% by mass)	Total reserves and resources of zircon as of: end of 2003 (million tonnes)
being mined					
Australia	Western Australia	Capel	9.3	8	5.15
		Eneabba	6.2	14	8.15
		Cooljarloo	3.1	11.1	1.87
		Jurien	6.3	9	0.32
	Murray Basin	Douglas	8.4	8	2.25
		Gingko	3.2	10.1	0.67
		Snapper	5.4	11	0.59
	Queensland	North Stradbroke Island	0.9	11	2.21
India	Orissa	OSCOM	20.2	3	1.40
	Tamil Nadu	coast	7-39	9	2.66
	Kerala	Chavara	9	6	5.76
Mozambique	coast	Moma	3.4-4.9	5	2.7
Rep. South Africa	KwaZulu Natal	Hillendale	6.8	7.4	0.57
		Richards Bay	13.8	~8	~3.2
	Western Cape	Brand-Se-Baai	10	15	6.1
USA	Florida	Trail Ridge	3.9	15.0	4.8
	Virginia	Old Hickory	9.5	17	1.39
production planned					
Australia	South Australia	Jacinth	6	55	3.5
	Western Australia	Dongara	10	10	0.74
	Murray Basin	WIM 150	4.0	13.3	5.1
		KWR	9.3	10	5.44
		Mindarie	3.99	25.7	3.21
Gambia	coast	Sanyang et al.	5.2	14.6	0.12
Canada	Saskatchewan	Athabasca oil sands	0.25-0.50	21.0	35?
Kazakhstan	Northern Kazakhstan	Obukhovsky	9.4	26	0.5
Kenya	coast	Kwale	3.5-6.8	9	0.8
Malawi	Lake Malawi	Chipoka	33	4.3	17.2
Mozambique	Corridor Sands	West Block	7.47	2.0	2.64
Senegal	Grand Cote	total	1.8	9	2.8
Rep. S. Africa	KwaZulu Natal	Fairbreeze	5.9	8.1	1.81
currently not mineable					
Germany	Cuxhaven	Midlum	9.9	9.0	0.44

Table 4.12: Currently known worldwide reserves and resources of zircon.

Country	**Total reserves and resources of zircon in million tonnes**	**Total reserves and resources of heavy minerals million tonnes**
Australia	60.4	473
- *Western Australia*	*19.0*	*154*
- *Murray Basin*	*34.8*	*282*
- *Eucla Basin*	*4.4*	*8*
- *Queensland*	*2.2*	*29*
Canada[1)]	*35?*	310-505
India	>21	>632
Malawi	>18	>545
Rep. South Africa	14.4	133
Mozambique	9.9	372
USA	7.7	58
Kenya	3.0	99
Senegal	2.8	31
Brazil	2.2	10
China	1.8	13
Namibia	1.6	39
Sri Lanka	1.0	~18
Vietnam	0.9	9
Egypt	0.9	4
Kazakhstan	0.8	~5
Sierra Leone	0.2	~18
Ukraine	0.2	~20
Gambia	0.1	1.0
Malaysia	0.1	~15
Rest	0	60
World	180	3,000

[1)] from oil sands

4.7 Important producing countries

Zircon was first found in placers in 1895. Its first economic extraction, however, dates back to 1922 when it was extracted from beach placers in North East Florida until 1929. It was first used exclusively in the refractory industry.

In 1935, zircon was first extracted from Australian placers near Yamab in New South Wales. Ranges of use are mainly in the foundry sector and in the manufacture of firebricks for glass enamels. Since this time until well into the 1980s – with an interruption during World War II – Australia was easily the largest global producer of zircon with a share of 60 – 80 %. In the mid 1970s, the mining of heavy mineral placers in Australia moved increasingly from the East Coast to the West Coast. At the end of the 1970s, the first placer deposit in South Africa went into production in Richards Bay, which has since become the main source of zircon for the global market.

Worldwide, zircon is the mineral with the largest price fluctuations. Production historically fluctuates between oversupply and shortage. The main reason for this is that zircon has always been and still is only a by-product of titanium mineral extraction. If there is oversupply in the titanium mineral area, production is cut back, which immediately leads to a shortage in the zircon market. On the other hand, the increase in titanium mineral production has until now always resulted in oversupply and therefore a drop in zircon prices. Dramatic demand changes in the industry increased this price volatility in the past.

In the near future, more placer deposits in East Africa that only have relatively small proportions of zircon (<10 % by mass) will be developed. Since the demand from China, mainly from the ceramics industry located in the country, has already resulted in a significant shortage, zircon is not expected to be in oversupply in the foreseeable future. Due to the high price of zircon, most possible substitutions have already been exhausted. In the absence of new deposits that can be developed in the short term, the mining industry is currently working on improving the zircon production efficiency, as processing losses can be up to 25 %.

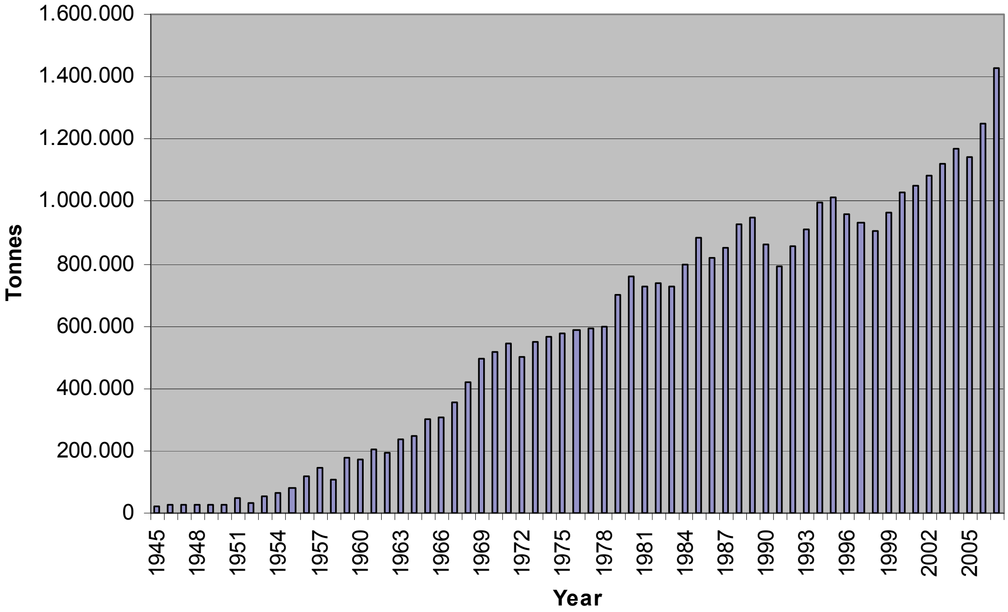

Figure 4.1: Global production of zircon in kilotonnes in the period between 1975 and 2003 (source: BGR database).

Finally, Figures 4.2 and 4.3 show a direct comparison of the percentage distribution of the world production (2007) and currently known world reserves and resources and of zircon.

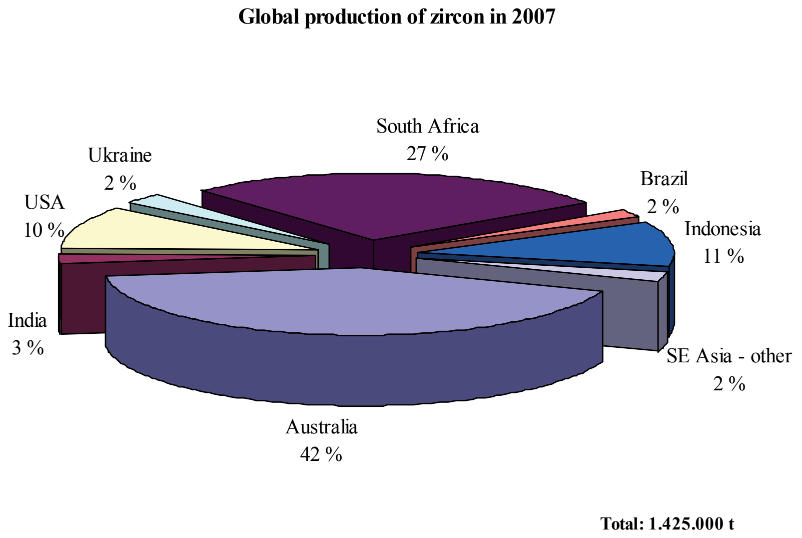

Figure 4.2: Percentage distribution of the global production of zircon in the year 2007.

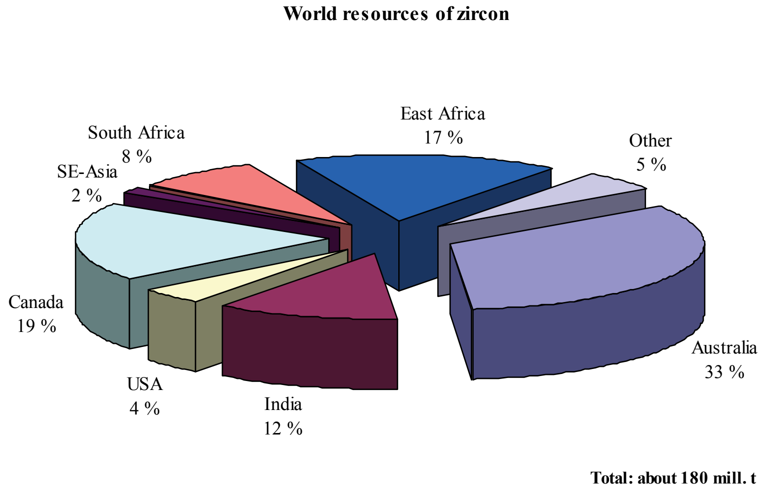

Figure 4.3: Percentage distribution of the currently known global reserves and resources of zircon.

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5 Monazite and Xenotime

[German: Monazit, Spanish: monacita, French: monazite]
[German: Xenotim, Spanish: xenotima, French: xénotime]

5.1 Mineralogy, Petrography, Chemistry

The heavy minerals monazite and xenotime are members of the rare earths minerals group. The term rare earths (RE) encompasses a group of elements that were originally deemed to be rare, but are by no means all rare in the Earth's crust. These elements, located between lanthanum and lutetium in the periodic table, are called lanthanides. Similar properties to the lanthanides are exhibited by the elements yttrium and scandium, whereas thorium (from the actinides group) is frequently associated with lanthanides in minerals.

Of rare earths minerals, the following occur as mineable heavy minerals:

allanite (orthite)	Formula:	$(Ca, Ce, Y)_2(Fe, Al)_3(SiO_4)_3(OH)$
(e.g. India, Sri Lanka,	MOHS hardness:	5 ½
Namibia)	Density:	3.0-4.2 g/cm^3
	Color:	black, brown, reddish brown, greenish, opaque

thorite, uranothorite	Formula:	$(Th, U)SiO_4$
(e.g. Sri Lanka,	MOHS hardness:	4 ½-5
Madagascar, New	Density:	4.1-7.2 g/cm^3
Zealand)	Color:	black

As well as in particular the two rare earths phosphates **monazite** and **xenotime** (cf. Table 5.1). Only the latter two have any major economic significance. Together with the mineral **bastnaesite**, $CeFCO_3$, which mainly occurs in carbonatites, they represent the resource base for the mining of rare earths.

Table 5.1: Mineralogical properties of monazite and xenotime.

	Monazite	Xenotime
Formula	$(Ce,La,Nd,Th)[PO]_4$	$Y(PO_4)$
Chemistry	often changing (cf. Table 5.2)	61.40 % by mass Y_2O_3, 38.60 % by mass P_2O_5
Density (g/cm^3)	4.8-5.5 $^{1)}$	4.4-5.1
MOHS hardness	5-5 ½	4-5
Color	light yellow, brown, orange brown, reddish, seldom black	yellowish, yellowish green, greenish brown
Magnetic properties	paramagnetic	
Electrostatic properties	non-conducting	

$^{1)}$ the higher the percentage of thorium, the higher the density

All rare earths minerals can incorporate different quantities of uranium and especially thorium into their crystal lattices, and are therefore radioactive to varying degrees. VAN EMDEN et al. (1997) were able to prove levels from 1.2-21.9 (on average 8.79) % ThO_2 (cf. Table 5.2) in individual grains from monazite concentrates from Western Australia. Similar to zircon, this radioactivity results in metamictization of the minerals and ultimately in their structural breakdown.

Table 5.2: Variation of the chemical composition (%) of individual monazite and xenotime grains from concentrates (Western Australia) according to Van Emden et al. (1997).

	Monazite			Xenotime		
	range	medium		range	medium	
		Mean	standard deviation		*Mean*	standard deviation
La_2O_3	8.9-21.0	14.53	2.13	-	-	-
Ce_2O_3	21.7-35.0	28.52	2.17	-	-	-
Pr_2O_3	1.8-3.2	2.53	0.26	-	-	-
Nd_2O_3	4.8-12.7	8.85	0.26	-	-	-
Sm_2O_3	0.36-2.89	1.53	0.45	<0.16[1]-1.82	0.47	0.22
Gd_2O_3	<0.16[1]-2.71	0.88	0.51	<0.16[1]-4.56	1.91	0.59
Dy_2O_3	<0.16[1]-1.28	0.26	0.30	2.4-7.5	5.11	0.72
Ho_2O_3	-	-	-	<0.16[1]-1.59	1.17	0.16
Er_2O_3	<0.16[1]-0.45	0.02	0.08	2.5-6.6	4.63	0.49
Tm_2O_3	-	-	-	<0.16[1]-0.70	0.70	0.14
Yb_2O_3	-	-	-	1.4-11.4	4.56	1.22
Lu_2O_3	-	-	-	<0.16[1]-1.95	0.54	0.24
Y_2O_3	<0.06[1]-6.25	1.19	0.66	40.2-53.2	46.82	1.91
ThO_2	1.2-21.9	8.79	0.08	<0.17[1]-8.44	0.46	0.68
UO_2	<0.17[1]-0.75	0.08	0.23	<0.17[1]-5.82	0.57	0.86
CaO	0.12-2.50	0.98	1.10	<0.02[1]-0.54	0.06	0.06
SiO_2	0.12-4.01	1.09	0.66	<0.02[1]-1.98	0.38	0.26
P_2O_5	25.1-32.6	30.33	1.24	29.7-36.4	34.55	0.73
Total	**92.5-103.1**	**99.58**	**2.10**	**96.0-105.2**	**101.93**	**1.17**

[1] = beneath the detection limit

Monazite:

In addition to Th and U, monazite can also carry Ca, Mg, Fe, Al, Zr, Mn, Be, Sn, Ti and Ta in its crystal lattice.

The light rare earths are enriched in monazite (and bastnaesite).

In mineralogical terms, a distinction is made between the following monazites depending on the predominant RE element:

- monazite-(Ce) – (Ce, La, Nd, Th)$[PO]_4$
- monazite-(La) – (La, Ce, Nd)$[PO]_4$
- monazite-(Nd) – (Nd, Ce, Sm) $[PO]_4$

where monazite-(Ce) occurs most frequently.

Frequently, monazite contains inclusions of foreign minerals (sillimanite, rutile, hematite, muscovite, biotite, silica, epidote, magnetite, galena, garnet and mainly apatite, zircon), more rarely of liquids and gases.

In individual deposits (such as *offshore* Taiwan) “black” monazite occurs. This has high Ce and Eu contents, as well as low Th contents. Furthermore, Si partially replaces P in the crystal lattice. The genesis of this black monazite is still disputed.

Xenotime:

In xenotime, apart from U, Th, Si, V, Zr, S and Ca, the yttrium in the crystal lattice can also mainly be replaced by high levels of other RE. Most common in xenotime, apart from yttrium, are the RE elements erbium, dysprosium and ytterbium. If the level of ytterbium exceeds that of yttrium, the mineral is called xenotime-(Yb).

The heavy rare earths are enriched in xenotime.

As zircon and xenotime are isotopic, these two minerals can become intergrown as they crystallize out of the magma.

5.2 Formation of deposits

Monazite has been detected in a large variety of rocks/deposits. The most important of these in order of their significance as potential source rocks for placers are:

- acidic magmatites (granites, granodiorites, monzonites)
- granite-pegmatites (large idiomorphic crystals)
- carbonatites (also as coarse ore)
- hydrothermal veins
- alpine crevasses
- pneumatolytic formations
- metamorphic slate and migmatites
- laterites by means of alkaline rock complexes rich in RE (so-called regoliths).

In general, there is an increase in light RE and a reduction in yttrium in the monazites in the series grading from granite-pegmatites, to granites to alkaline rocks and finally to carbonatites. The total content of REO in monazites increases from gneisses via granites to granite-pegmatites and finally to metamorphic black slates.

Due to its physical properties, monazite is a heavy mineral detectable in many placers, but mostly in very low concentrations. Monazite has been found in mineable concentrations in some metamorphic fossil placers, such as in South California in Precambrian gneisses, and in Wyoming in Cambrian conglomerates.

The relatively rare mineral **xenotime** is found:

- as early crystallisates in leucogranites, leucopegmatites and analogous gneisses
- in alpine fissures
- in hydrothermal precipitates.

For the most part, xenotime is a very rare mineral even in placers. Its distribution there is attributable to its slabby/tabular shape rather than its apparent density. This means that xenotime is more easily picked up by currents than other heavy minerals and can be relocated again.

5.3 Applications

Monazite was extracted for the first time in 1895 as a raw material for thorium. Thorium was used at the end of the 19th century in large quantities in the form of thorium nitrate (cf. below) for the impregnation of incandescent gas mantles. As the separation of lanthanides was not possible at that time, large dumps of RE oxides (REO) were created. Only a small part of this REO is used in pyrophoric alloys. These are highly flammable alloys of Al or Fe with “Mischmetal”, e.g. for lighter flints. Mischmetal, on the other hand, is the international designation for a mixture of RE after the separation of ThO_2.

Because the size of dumps for REO grew, a search for new application options started. Especially Cerium was soon used in arc electrodes, in pesticides and increasingly in various alloys. For other RE an application was found in the manufacture of special glasses, in ceramics, but also in beauty creams. Thorium was used for the production of radio and fluorescent tubes after the invention of electric light bulbs, but also for catalytic converters. From 1933 onwards, the value of monazite concentrates was not calculated according to its ThO_2 content, but according to its REO content.

In the meantime, the areas of application for RE have undergone a drastic change. Nowadays they are almost exclusively used in a very large spectrum of high technology applications after having undergone elementary and high-purity processing. Owing to technical advances, new areas of application continuously arise, while others decline in significance (cf. Figure 5.1).

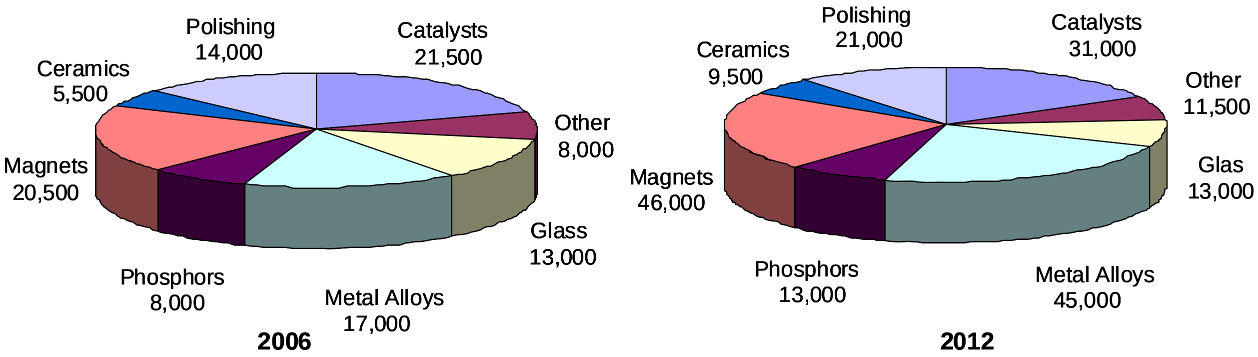

Figure 5.1: Use of rare earths (in tonnes) according to their areas of application from 2006 to 2012 (assumed), according to KINGSNORTH (2007).

RE were originally extracted from the various RE minerals by being dissolved in concentrated sulfuric acid after grinding, but today, a 70 % caustic soda solution is preferred. Due to the previous use of sulfuric acid, the results of the chemical analysis often refer to the proportion insoluble in H_2SO_4.

The addition of sulfuric acid leads to the formation of RE sulfates which are then precipitated as oxalates in ice water with oxalic acid, and transformed into the oxides by annealing. The separation of the REO occurs by ion exchange and the formation of complexes. With increasing atomic numbers from lanthanum to ytterbium, the tendency for complexes to form increases continuously. This property can be utilized in the separation process. By further reactions with acids (mainly HF) RE salts are produced that are then converted to the individual RE by fused-salt electrolysis or by reduction using Ca or MG.

Processing using caustic soda solution gives rise to RE hydroxides and, as a saleable by-product, trisodiumphosphate. The former are treated after filtration with hydrochloric acid or, less frequently, with nitric acid. The RE chlorides or RE nitrates produced accordingly are also converted into the individual RE by fused-salt electrolysis or by reduction.

Thorium compounds are dissolved in concentrated nitric acid using the Thorex process (= *Thorium recovery by extraction*). The thorium nitrate produced this way is isolated by extraction and converted into thorium oxide. Pure Th can then be extracted by reduction using Ca.

Due to the very similar chemical-physical properties, and the high reactivity and toxicity of most RE, their separation is very difficult, energy-intensive and extremely costly. The construction of corresponding factories is therefore only worthwhile in highly industrialized countries (mainly France, Japan, USA) or countries rich in reserves (Brazil, China, India, Malaysia).

Very different raw material prices result depending on the natural occurrences of the element, the time and expenditure required for its separation and, of course, current demand (cf. Figure 5.2).

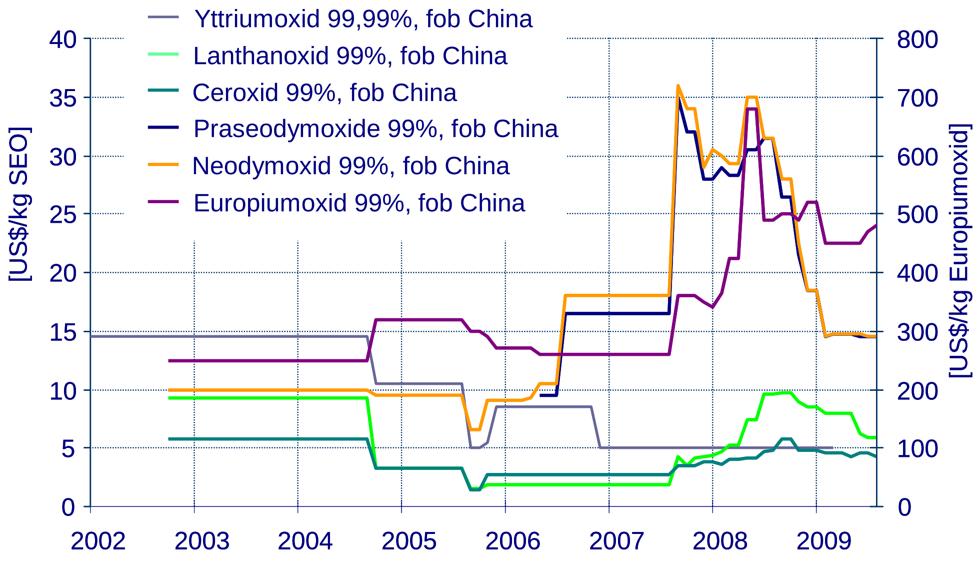

Figure 5.2: Prices for selected high-purity rare earth oxides (in US $/kg), source: LIEDTKE & ELSNER (2009)

REO not separated into their individual oxides are solely used in China as dyes, fertilizer and as insulating materials.

Mischmetal

Commercial-grade Mischmetal has an average composition of 51-53 % Ce, 22-25 % La, 15-17 % Nd, 3-4 % Pr, 2-3 % Sm, 3 % Tb, 3 % Y and 5 % Fe. It is used predominantly in the manufacture of lighter flints, low alloy steels with high-tensile strength, and Ni hydride batteries.

The areas of use for specific rare earths are as follows:

Lanthanum (La)

- Component in Mischmetal. Pyrophoric materials for flints contain 25-45 % lanthanum.
- "Impure" lanthanum-nickel $LaNi_5$ as a hydrogen store in nickel-metal hydride rechargeable batteries.
- Reducing agent in metallurgy.
- Cast iron additive. Promotes formation of nodular graphite.
- Alloy additive to improve oxidation resistance.
- Addition of lanthanum reduces the hardness and temperature sensitivity of molybdenum metal.
- High quality cathodes made from lanthanum boride LB_6 (substitute for tungsten wire) for the generation of free electrons.
- Cobalt lanthanum alloy $LaCo_5$ as a magnet material.
- Barium titanate doped with lanthanum for the manufacture of varistors (temperature-dependent resistors).
- Additive in carbon arc lamps for studio lighting and in film projection equipment.

Lanthanum oxide is used for:

- Manufacturing glass with a comparatively high refractive index that changes very little with the wavelength (low dispersion), for cameras, telescope lenses and for spectacle lenses.
- Manufacturing crystal glass and china glazes. It replaces more toxic lead compounds and simultaneously improves chemical resistance (dishwasher-safe).
- Manufacturing ceramic capacitor masses and glass without silicates.
- Component of glass polishing compounds.

- Catalyst for cracking petroleum and petrol.
- Manufacturing electron tubes (also lanthanum borides).

Cerium (Ce)

- Cerium dioxide, CeO_2, is used for stabilizing the ceramic catalyst substrate of Al_2O_3 for catalytic converters in cars.
- Mechanical-chemical polishing compound for computer chips.
- Cerium dioxide as polishing compound in glass processing.
- Component of some special glasses, for example UV filter and windscreens and de-opacifier in the manufacture of glass.
- In metallurgy, as an additive for Al alloys and high-temperature resistant Fe-based alloys. Part of the added Ce is used in the smelting process for separating sulfur and oxygen.
- Mischmetal as base material for flints for use in lighters and for the generation of showers of sparks in roller coasters and in film scenes (accident scenes).
- For coloration of enamel.
- Cerium-doped dyes in display tubes.
- Cerium sulfides as red dye in plastics.
- The coatings of self-cleaning ovens contain Cerium.
- Cerium(IV) sulfate as oxidant in quantitative analysis (cerimetry).
- Contrast agent for Nuclear Magnetic Resonance.
- Fluorescent material in gas discharge tubes.
- Coating for diesel particulate filters.

Praseodymium (Pr)

- Alloys with Mg for the manufacture of high-strength metal for aircraft engines.
- Alloys with Co and Fe are strong permanent magnets.
- Praseodymium compounds are used for tinting glass and enamel.
- These compounds also improve UV absorption and are used for goggles in welding applications.

Neodymium (Nd)

- Nd-Fe-B compounds for the manufacture of the most powerful magnets. They are used for Nuclear Magnetic Resonance imaging equipment and micro-motors, in MP3 players, in iPods and hard disks (positioning of reading/writing heads). They are substantially cheaper than Sm-Co magnets.
- Neodymium oxide for glass tinting. It produces very warm violet to burgundy and gray colors. Such glasses have sharp absorption bands and are used for calibration in astronomy.
- Neodymium salts for tinting enamel.
- Laser material Neodymium-YAG.
- UV-absorbing glasses (sun protection glass).
- Blue porcelain dye.
- Decolorizing of glass containing iron.
- Barium titanate doped with neodymium oxide for dielectric capacitor insulation.
- Due to its pyrophoric properties also as alloy combined with Cerium in firebricks.

Promethium (Pm)

Due to its short-lived isotopes and very low availability, this radioactive element is not used in technical applications.

Samarium (Sm)

- Sm-Co magnets:

  Permanent magnets made from $SmCo_5$ have a high resistance to demagnetizing and a coercive field strength of up to 2200 kA/m. The improved alloy Sm_2Co_{17} is more cost-intensive in manufacturing, but has higher magnetic properties and improved corrosion resistance. These alloys are used in step motors for digital watches, drive motors in miniature tape recorders/players (walkman, dictaphones), sensors for clutches, in agitators and hard disk drives. They are used in aerospace as weight-saving magnetic materials.
- Together with other RE, for carbon arc lamps for film projection equipment.
- Doping of calcium fluoride single crystals for masers and lasers.
- As a catalyst: samarium oxide catalyses the hydration and dehydration of ethanol (alcohol).
- Neutron absorber in nuclear applications due to its large effective cross-sectional area for thermal and epithermal neutrons.
- Samarium oxide is added to optical glass for the absorption of infrared light.
- Sm compounds are used to sensitize (lighting) fluorescent material during irradiation with infrared light.

Europium (Eu)

- Eu^{3+} doped yttrium oxide sulfide $Y_2O_2S:Eu^{3+}$ forms red fluorescent material (luminophor) in color cathode ray tubes.
- Solid-state materials doped with Eu^{3+} mostly show red luminescence, Eu^{2+} produces blue-violet colors.
- Doping agent for some light sources such as high intensity discharge mercury lamps and energy-saving light bulbs.
- Dopant in scintillation crystals (as activator).
- Organic compounds as shift reagent in NMR spectroscopy.
- Eu isotopes are good neutron absorbers and are used in nuclear power plants.

Gadolinium (Gd)

- Gd becomes superconductive at temperatures <810 °C. It is the only lanthanide to exhibit ferromagnetic properties, only however at temperatures <16 °C. Due to its Curie point close to room temperature, Gd could in principle be used for HCFC free refrigeration appliances using the magnetocaloric principle.
- Gd is used for the manufacture of Gd-Y garnet for microwave applications.
- Oxysulfides are used for the manufacture of green fluorescent material for photoluminescent displays (radar).
- Intravenously injected Gd^{3+} compounds are used as a contrast agent for examinations in Nuclear Magnetic Resonance imaging devices.
- Gd-Ga garnet was used for the manufacture of magnetic bubble memory devices.
- Additions of 1 % Gd increase the machinability and high temperature and oxidation resistance of Fe and Cr alloys.
- Manufacture of compact discs (CD-ROM)

Terbium (Tb)

- Terbium is used for doping calcium fluoride, calcium wolframate and strontium molybdate for use in semi-conductors.
- Used for molecular stabilization in high-temperature fuel cells together with ZrO_2.
- The oxide is added to green fluorescent material in cathode ray tubes and fluorescent lamps.
- Sodium terbium borate is used as a laser material for the generation of coherent light with a wavelength of 546 nm.

- Tb-Dy alloys show strong magnetostriction (change in length due to a magnetic field, or magnetic pulses in case of change of length). Such alloys are used in material testing. They increase coercivity in Nd-Fe-B magnets.
- Tb-Fe-Co or Tb-Gd-Fe-Co alloys are used as coatings in rewritable MO discs (magneto-optic).

Dysprosium (Dy)

- Used in different alloys
- In special magnets and alloyed with lead it is used as shielding material in nuclear reactors.
- Together with V and other elements, Dy is used for the manufacture of laser materials.
- Doping of calcium fluoride and calcium sulfate crystals for dosimeters.
- Alloys containing Tb and Dy show strong magnetostriction (change in length due to a magnetic field or magnetic pulses when length changed). Such alloys are used in material testing.
- In Nd-Fe-B magnets, Dy increases the coercivity and extends the usable temperature range.
- Dysprosium oxide improves the dielectric behavior of barium titanate (capacitors).
- Sporadically, Dy is used for the manufacture of control rods in nuclear engineering due to its large capture cross-section for thermal neutrons.
- Improving the emission ranges of high-intensity halogen lamps.
- Dy-Cd chalkogenes are used as a source of infrared light for the investigation of chemical reactions.

Holmium (Ho)

- Pole shoes for high-performance magnets for generating extremely strong magnetic fields
- Magnetic bubble memory devices use thin film alloys made from Ho-Fe, Ho-Ni and Ho-Co.
- Control rods in breeder reactors.
- Manufacture of Y-Fe garnet (YIG), Y-Al garnet (YAG) and Y-La fluoride (YFL) for solid-state lasers for microwave components in medical technology.
- Holmium oxide for production of yellow glass.

Erbium (Er)

- Er doped optical fibers are used for optical repeaters that are capable of repeating light signals transmitted via glass fibers without prior conversion into an electrical signal.
- Gold as host material doped with a few hundred ppm of erbium is used as a sensor material in magnetic calorimeters for the high-resolution detection of particles in physics and technology.

Thulium (Tm)

- Minor use in televisions (for activating fluorescent material on the display surface).
- ^{169}Tm removed from nuclear reactors is used as an x-ray source (gamma ray source in materials testing).
- X-ray intensifying screens made from thulium tantalate.

Ytterbium (Yb)

- Ytterbium can be used to reduce grain size and improve the mechanical properties of stainless steels.
- The radioactive isotope ^{169}Yb (half-life 32 days) is used occasionally as a γ-ray source in nuclear medicine.
- Ytterbium fluoride, YbF_3, can be used as an ingredient in high-quality polymer dental filling material and dental inlay cement. It produces a high contrast on x-ray films and provides caries protection by continuously releasing fluoride.

- Yb-Co-Fe-Mn alloys are suitable for particularly high-quality permanent magnets.
- Ytterbium-doped material is increasingly used as a laser material.

Lutetium (Lu)

- Lutetium is of practically no importance except occasionally in Cerium Mischmetals.

Scandium (Sc)

- Main use as scandium iodide in high-pressure high-intensity mercury discharge lamps, for example for stadium lighting. Produces a light intensity similar to daylight when combined with Ho and Dy.
- Manufacture of laser crystals.
- Sc_2O_3 is added to magnetic data storage devices to increase the remagnetization speed.
- As an alloy additive, scandium stabilizes the molecular structure and improves the grain size fineness. An Al-Li alloy with low amounts of added scandium is used for the manufacture of a few components in Russian fighter jets.

Yttrium (Y)

- Metallic yttrium is used for pipes in reactor engineering.
- A Y-Co alloy can be used as a permanent magnet.
- In metallurgy, minor amounts of yttrium additive are used to improve grain fineness, for example in Fe-Cr-Al heating element alloys, and Cr, Mo, Ti and Zr alloys. It improves the strength of Al and Mg alloys.
- As catalyst in ethylene polymerization.
- Yttrium aluminum garnet (YAG) is used as a laser crystal.
- Yttrium iron garnet (YIG) is used as a microwave filter.
- A wide variety of applications for yttrium oxides and yttrium oxide sulfides as luminophores (fluorescent material) doped with trivalent Eu (red) and Tm (blue) in television cathode ray tubes, fluorescent lamps and radar tubes.
- Yttrium ceramic for oxygen sensors, superconductors, ODS alloys etc.

Thorium (Th)

- Thorium in its oxide form is used for the manufacture of incandescent gas mantles. Incandescent gas mantles are produced by impregnating woven fabrics with a solution made from 99 % thorium nitrate and 1 % Cerium nitrate and then igniting them. This leaves a fragile structure that emits a white light in the gas lamps.
- Thorium oxide and thorium carbide are used in combination with uranium as a nuclear fuel in the thorium high temperature reactor (THTR).
- Alloying element in other metals to improve heat resistance (jet and rocket engines). Alloys with Cu and W are suitable for the manufacture of welding electrodes, alloys with Cu and Ag for electrical contacts.
- Pure Th binds the last remaining traces of undesirable gases in cathode ray tubes (e.g. television tubes).

5.4 Substitutes

As raw materials for the extraction of rare earths, monazite and xenotime can be substituted by a large variety of other minerals, mainly bastnaesite.

There are, however, no substitutes for most areas of application of the rare earths. And rare earths can also only substitute each other to a limited extent. Only in catalysts can rare earths be partially replaced by palladium and ultra stable zeolites.

5.5 Specifications for the raw materials (reference values)

According to the generally recognized guidelines, commercial concentrates of

- Monazite: must have $\geq$65 % REO + ThO_2

or

- Xenotime: must have >25 % or enriched >60 % Y_2O_3

There are no further specifications, not even regarding particle size distribution.

In the references, relatively few details can be found for chemical and mineralogical compositions and particle size analyses of monazite and xenotime concentrates. These have been compiled in Tables 5.3 to 5.7.

Table 5.3: Chemical composition (%) of monazite and xenotime concentrates.

Area of deposit or producer	REO	ThO_2	H_2SO_4-insoluble.	TiO_2	P_2O_5
WA-Eneabba	58	6.4			
WA-Capel	57	7			
WA-Yoganup (guaranteed)	$\geq$55	$\geq$6	$\leq$10		
WA-Yoganup (typical)	56-58	6.5-7.0	7.0-8.5	0.3-0.6	
USA-Green Cove Springs	57	7			
India-KMML	57.5	7.96	5.05		28.2
Malaysia – Monazite average		6			27
Malaysia – Xenotime average		0.7			29

Table 5.4: Chemical composition (%) of monazite concentrates.

	Manavalakurichi MK-Grade Indian Rare Earths Ltd. Tamil Nadu, India 1)	**Beihai Processing Plant** Guangxi Province China 4), 7)	**Folkston (I)** Humphreys Gold Corp. Georgia, USA 3), 8)	**Folkston (II)** Humphreys Gold Corp. Georgia, USA 3)	**Green Cove Springs (I)** Iluka Resources Ltd. Florida, USA 3)	**Green Cove Springs (II)** Iluka Resources Ltd. Florida, USA 3)	**Capel** Western Titanium N.L. Western Australia 2)	**Eneabba** RGC Mineral Sands Ltd. Western Australia 9)	**Yoganup** Westralian Sands Ltd. Western Australia 5)	**Indonesia** 9)	**Black Monazite** Taiwan 1)	**Brazil** 6)
REO total		61.86	av. 58.9	60.53	58.57	55.04			56.0-58.0			59.2
La_2O_3	15.7			11.99	11.98	10.03	16.20	14.82	13.5	14.29	25.41	8.64
CeO_2	30.6		av. 25.4	26.45	26.49	27.12	26.70	27.60	26.0	30.25	23.18	26.94
Pr_6O_{11}	2.9			3.07	2.99	2.55	2.60	2.93	2.85	3.35	1.27	3.55
Nd_2O_3	10.5			10.60	9.99	8.72	11.00	9.44	9.82	10.77	7.95	14.50
Sm_2O_3				2.09	2.09	1.72	1.30	1.45	1.43	2.01		3.26
Eu_2O_3				0.16	0.14	0.12	0.02		0.03			
Gd_2O_3				1.38	1.40	1.41	0.30		0.84			
Tb_4O_7				0.16	0.15	0.14			<0.02			
Dy_2O_3				0.77	0.63	0.53	0.20		0.39			
Ho_2O_3				0.14	0.107	0.087	+		<0.03			
Er_2O_3				0.312	0.168	0.139			0.12			
Tm_2O_3				0.038	0.018	0.014			<0.01			
Yb_2O_3				0.178	0.066	0.058			0.07			
Lu_2O_3				0.0200	0.0090	0.0068			<0.02			
Y_2O_3	0.4	2.22		3.16	2.35	2.39	0.60	1.42	1.36	2.51	1.07	
H_2SO_4-unsol.			av. 8.2			8.25	8.50		7.0-8.5		22.94	
TiO_2	0.4		av. 0.42			0.09		0.81	0.3-0.6	0.09		1.75
SiO_2	2.4	1.23	av. 2.6					2.55		2.17	18.08	2.2
ZrO_2	1.3	0.13	av. 3.8					2.05		0.20		
Al_2O_3	0.1	0.14	av. 1.7					0.81		0.37		
Fe_2O_3	0.9	0.62	av. 0.63					0.33		n.d.		0.51
P_2O_5	29.2	30.00					27.00	26.55		27.46	20.55	26.0
ThO_2	9.0	6.31	av. 4.2			4.24	6.80	6.40	6.5-7.0	4.67		6.5
U_3O_8								0.31		0.32		0.17
CaO		0.16	av. 1.1					0.95		0.18	+	
LOI	0.1							0.52		0.60		

1) Company information 2) Baker (1962) 3) Elsner (1992) 4) Ward & Towner (1985) 5) Company data sheet 6) Greinacher & Reinhardt (1970) 7) 90 ppm $(Ta,Nb)_2O_5$ 8) av. 0.111 % MnO, av. 0.16 % PbO 9) BGR analysis + = traces

Table 5.5: Chemical composition (%) of the rare earth fraction made from placer monazites and xenotimes.

	Monazite Eastern Australia 1)	**Monazite** Capel Iluka Resources Ltd. Western Australia 5)	**Monazite** North Stradbroke Island Queensland, Australia 1)	**Monazite** China 1) 4)	**Monazite (I)** Green Cove Springs Florida, USA 1), 2)	**Monazite (II)** Green Cove Springs Florida, USA 2)	**Monazite (III)** Green Cove Springs Florida, USA 2)	**Monazite** East Coast Brazil 5)	**Monazite (I)** Folkston Georgia, USA 2)	**Monazite (II)** Folkston Georgia, USA 3)	**Xenotime** Lahari, Perak Malaysia 5)	**Xenotime** Malaysia 1)	**Xenotime** Guangdong Province China 4), 5)
La_2O_3	20.20	23.8938	21.50	23.35	17.47	20.45	18.23	24.0	19.82	av. 17.7	1.24	0.50	1.20
CeO_2	45.30	46.0177	45.80	45.69	43.73	45.22	49.27	47.0	43.69	av. 42.0	3.13	5.00	3.00
$Pr6O_{11}$	5.40	5.0442	5.30	4.16	4.98	5.11	4.64	4.5	5.07	av. 5.4	0.49	0.70	0.60
Nd_2O_3	18.30	17.3805	18.60	15.74	17.47	17.07	15.84	18.5	17.52	av. 17.8	1.59	2.20	3.50
Sm_2O_3	4.60	2.5310	3.10	3.05	4.87	3.56	3.13	3.0	3.45	av. 3.6	1.14	1.90	2.20
Eu_2O_3	0.10	0.0531	0.80	0.10	0.16	0.234	0.222	0.055	0.266	av. 0.14	0.01	0.20	0.20
Gd_2O_3	2.00	1.4867	0.80	2.03	6.56	2.38	2.56	1.0	2.28	av. 2.4	3.47	4.00	5.00
Tb_4O_7	0.20	0.0354	0.30	0.10	0.26	0.261	0.246	0.1	0.272	av. 0.26	0.91	1.00	1.20
Dy_2O_3	1.15	0.6903	0.60	1.02	0.90	1.07	0.97	0.35	1.27	av. 0.94	8.32	8.70	9.10
Ho_2O_3	0.05	0.0531	0.10	0.10	0.11	0.182	0.158	0.035	0.232	n.a.	1.98	2.10	2.60
Er_2O_3	0.40	0.2124	0.20	0.51	0.04	0.287	0.253	0.07	0.516	n.a.	6.43	5.40	5.60
Tm_2O_3	+	0.0177	+	0.51	0.03	0.0307	0.0255	0.005	0.0623	n.a.	1.12	0.90	1.30
Yb_2O_3	0.20	0.1239	0.10	0.51	0.21	0.112	0.106	0.02	0.294	n.a.	6.77	6.20	6.00
Lu_2O_3	+	0.0354	0.01	0.10	0.03	0.0153	0.0123	n.a.	0.0323	n.a.	0.99	0.40	1.80
Y_2O_3	2.10	2.4071	2.50	3.05	3.18	4.02	4.35	1.4	5.22	av. 2.9	61.00	60.80	59.30
Sc_2O_3													
Total	**100.00**	**99.9823**	**100.00**	**100.02**	**100.00**	**100.0020**	**100.0028**	**100.035**	**99.9946**	**av. 93.14**	**98.59**	**100.00**	**102.60**

1) Hedrick (2004) 2) Elsner (1992) 3) Company data sheet 4) Kingsnorth & Harries-Rees (1993) 5) Harben (2002) + = traces

Table 5.6: **Typical mineralogical composition (% by mass) and physical parameters of amang (see below) and monazite and xenotime concentrates from placers.**

	Monazite Manavalakurichi MK-Grade Indian Rare Earths Ltd. Tamil Nadu, India 2)	**Monazite (I)** Green Cove Springs Associated Minerals (USA) Inc. Florida, USA 1)	**Monazite (II)** Green Cove Springs Associated Minerals (USA) Inc. Florida, USA 1)	**Monazite** Folkston Humphreys Gold Corp. Georgia, USA 1)	**Monazite** Lakehurst Nord Industries New Jersey, USA 3)	**Monazite** Eneabba Iluka Resources Ltd. Western Australia 3)	**Monazite** Indonesia 3)	**Amang** Tg. Malim, Perak Malaysia 3)	**Xenotime** Malaysia 3)	**Xenotime** Capel Iluka Resources Ltd. Western Australia 3)
Mineralogical composition										
Monazite	96.5	92.1	91.7	95.3	53.4	94.5	100.0			
Xenotime					2.8	0.6	+		91.2	82.8
Zircon	1.8	5.2	6.6	3.9	42.9	3.4		12.5	2.4	7.5
Rutile	0.7	0.2	+		+			0.7		6.9
Ilmenite	0.4	0.4	0.2	0.1	0.9	0.6		80.7	2.5	
Leucoxene	0.4		+							
Kyanite	+									
Staurolite		0.2		0.2	+	1.0				
Garnet		1.3	1.3	0.3		+			+	+
Epidote		+		0.1				+	+	
Tourmaline					+	+	+		3.9	
Spinel		0.5		0.1						2.8
Hornblende										+
Quartz	0.1	0.1	0.2	+	+	+		6.1		
Physical parameters										
Apparent density (g/cm^3)	5.2									
Bulk density (kg/m^3)	3200 – 3400									
Melting point °C	1900-2000									
Ph	6.2 – 6.8									

1) ELSNER (1992) 2) Company information 3) BGR analysis + = traces

Table 5.7: Particle size distribution (% by mass, screen residue) of placer monazite concentrates.

ASTM m*esh*	µm	**Green Cove Springs (I)** Associated Minerals (USA) Inc. Florida, USA 1)	**Green Cove Springs (II)** Associated Minerals (USA) Inc. Florida, USA 1)	**Folkston** Humphreys Gold Corp. Georgia, USA 1)	**Yoganup** Westralian Sands Ltd. Western Australia 2)
420	40		0.001		0.7
355	45	0.003	0.002		
300	50	0.002	0.002	0.001	
250	60	0.004	0.003	0.002	
210	70	0.004	0.002	0.001	
180	80	0.011	0.004	0.003	
150	100	0.032	0.025	0.006	11.7
125	120	0.501	0.512	0.125	19.7
105	140	2.627	6.049	1.052	34.6
90	170	16.852	31.718	5.330	33.0
75	200	45.473	41.002	31.158	
63	230	31.099	18.875	46.730	0.3
53	270	1.836	1.373	13.319	
45	325	1.476	0.369	1.907	
<45	<325	0.070	0.050	0.360	
mean (µm)		78.9	84.3	71.4	

1) Elsner (1992) 2) Company data sheet

5.6 Deposit size and reserves

Since the middle of the 20th century, the amount of titanium minerals (ilmenite, leucoxene, rutile) has almost always been more significant for the assessment of monazite and/or xenotime-bearing deposits than their actual monazite and/or xenotime content. This means that monazite and xenotime are almost always only secondary, not primary valuable heavy minerals. Concentration previously only took place if >500 tonnes could be produced annually.

In recent decades, this situation has changed considerably so that monazite (but not xenotime!) is now no longer considered to be a valuable heavy metal but only deemed to be an impurity because of its radioactivity and the worldwide much stricter radiation protection legislation and the good supply options for other RE minerals.

This means that potential reserves have to be assessed as to whether and in what quantities they bear monazite (refer to Table 5.8) and in what quantities it would be produced by processing. If the potential production of monazite concentrate is <10,000 tonnes/year, the effort involved in complying with radiation protection regulations is probably greater than the potential revenue!

Table 5.8: Comparison of monazite and xenotime placers.

Country	Region of deposit	Occurrence	HM-percentage in the ore sand (% by mass)	Percentage Monazite in the HM-concentrate (% by mass)	Total resources and reserves of monazite as of: end of 2003 (in kilotonnes)
being mined					
India	Orissa	OSCOM	20.2	4	1,860
	Tamil Nadu	coast	7-39	5	730
	Kerala	Chavara	9	1	960
formerly mined					
Australia	Western Australia	Capel	9.3	0.3	193
		Eneabba	6.2	0.05	29
		Cooljarloo	3.1	0.2	37
		Ludlow	0.8	0.3	28
Sri Lanka	North-East coast	Pulmoddai	80	0.3	11
Rep. of South Africa	KwaZulu Natal	Richards Bay	13.8	0.1	40
USA	NE-Florida	Green Cove Springs	6.05	0.7	1)
production of other heavy minerals planned					
Australia	Western Australia	Jangardup South	17.3	0.32 4)	13 4)
	Murray Basin	WIM 150	4.0	1.4	580 2)
Madagascar	Fort Dauphin	QMM	4.5-5.5	1.49	~1,200
Mozambique	coast	Congolone	3.25	0.21	11
not mineable					
Germany	Cuxhaven	Midlum	9.9	n.a.	n.a. 3)
Egypt	Eastern Rafah	El Arish & Rommana	4	0.96	27
Bangladesh	coast	Cox´s Bazaar	21.9	0.3	17
USA	NE-Florida	Amelia Island	4	0.2	2
		Yulee	3.12	2	90

1) End of mining 2004 2) plus 170,000 xenotime 3) plus 10,200 tonnes of xenotime 4) plus 0.14 % by mass or 5,500 tonnes of xenotime

The global reserves and resources of monazite and/or xenotime are generally a secret because monazite is considered by many countries to be a strategic mineral due to its ThO_2 and U_3O_8 contents. If data regarding reserves has been published by individual countries, these are listed in Table 5.9.

Table 5.9: Published reserves of placer monazite in million tonnes.

Country	Total reserves and resources placer monazite kilotonnes	Total reserves and resources heavy minerals million tonnes
India	>8,000	>632
Madagascar	~1,200	~80
Namibia	900	39
South Korea	141	1.5
Brazil	67	10
Malaysia	~60	~15
Bangladesh	17	3.5
Kazakhstan	10	~5

5.7 Important producing countries

Monazite was first extracted in 1885 from placers in Brazil. For many years, a German entrepreneur was the exclusive exporter of the mineral extracted in Brazil. At that time, the monazite was transported as ballast in merchant ships from Brazil to Germany. Today there are still fluvial placers in Brazil that are mainly mined for monazite.

From 1886 until 1917, monazite mining was extended to placers in Cleveland Co., North Carolina, USA. As with the processing of the Brazilian placer monazites in Germany, at that time only the thorium contained in the monazite was extracted and used for incandescent gas lamps (gas mantles).

In 1909, a German chemical engineer also discovered monazite in high-grade beach placers near Manavalakurichi, India. These were mined from 1911 onwards by a German-English company under German management.

Further high-grade monazite reserves were discovered from 1928 on the south-west coast of Sri Lanka and developed (KRUSCH 1938).

From the 1930s to 1965, the Australian placers, initially on the east coast, later also on the west coast, supplied large quantities of monazite as raw material for the worldwide demand for RE.

From 1965 to 2002, RE were extracted mainly from the Mountain Pass carbonatite deposit in the USA (California, bastnaesite with contents of 9.3 % REO) and since 1984 from Fe-Se-Nb mineralizations in dolomite from China (Bayan Obo, monazite and bastnaesite with contents of 3 % REO).

Until 1988, Malaysia was the largest supplier of yttrium, which was extracted predominantly from xenotime over a period of many years. Xenotime, together with other valuable heavy minerals, is a by-product of the cassiterite extraction in South East Asia (cf. Chapter 11).

The following approximate amounts can be extracted annually just from the residual heavy mineral concentrate (amang) generated by cassiterite extraction in Malaysia:

- 150,000 – 200,000 tonnes of ilmenite (cf. Chapter 2)
- 5,000 tonnes of zircon (cf. Chapter 4)
- 2,000 tonnes of monazite
- 150 tonnes of struverite (cf. Chapter 12)
- 100 tonnes of xenotime
- 50 tonnes of columbite tantalite (cf. Chapter 12)

After 1988, China also took over the leading role in yttrium extraction. The world's largest single reserves of xenotime were however detected in the "WIM 150" placer in the Murray Basin, Australia, with an estimated 170,000 tonnes of xenotime (and 580,000 tonnes of monazite).

Since mainly very large bastnaesite-monazite ore deposits have been developed in Inner Mongolia and the minerals there processed to RE in its own factories, China has taken over the globally dominating position in the extraction and processing of RE minerals. In 2000, only 1,500 tonnes of REO out of a total production of 75,000 tonnes of REO in the country were still extracted from placer monazites.

Table 5.10 lists the global production of monazite in recent years from reliable data sources, or at least reliable estimates.

Table 5.10: Worldwide production of monazite and xenotime from placers in tonnes.

Country / producer	2003	2004	2005	2006	2007
Australia [3)]	n.a.	n.a.	n.a.	n.a.	n.a.
Brazil [1)]	0	731	958	958	1,173
China	n.a.	n.a.	~200	n.a.	n.a.
India	2,891	n.a.	n.a.	n.a.	n.a.
Indonesia [2), 3)]	n.a.	n.a.	n.a.	n.a.	n.a.
Korea, North [2)]	n.a.	n.a.	n.a.	n.a.	n.a.
Korea, South [2)]	n.a.	n.a.	n.a.	n.a.	n.a.
Malaysia [3)]	795	1,683	320	894	682
Nigeria [2)]	n.a.	n.a.	n.a.	n.a.	n.a.
Rep. of South Africa	n.a.	n.a.	n.a.	n.a.	n.a.
Taiwan [2)]	n.a.	n.a.	n.a.	n.a.	n.a.
Thailand [3)]	n.a.	n.a.	n.a.	n.a.	n.a.
Vietnam [2)]	n.a.	n.a.	n.a.	n.a.	n.a.
DR Congo [2)]	n.a.	n.a.	n.a.	n.a.	n.a.
World (estimate USGS)	**5,800**	**7,410**	**6,280**	**6,850**	**6,970**

[1)] Production with stockpiling, but without processing [2)] extraction of very small quantities is assumed [3)] also xenotime
n.a.= production data not available

5.8 References

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6 Kyanite, Sillimanite and Andalusite

[German: Disthen, Spanish: cianita, French: disthène]
[German: Sillimanit, Spanish: Sillimanita, French: sillimanite]
[German: Andalusit, Spanish: andalucita, French: andalousite]

6.1 Mineralogy, petrography, chemistry

Disthene, sillimanite and andalusite belong to the anhydrous aluminum silicates, which are frequently grouped together as the sillimanite minerals or just called aluminosilicates. For reasons based on mining history, however, the USA uses the term “kyanite minerals”, while in the successor states of the former Soviet Union the term “andalusite minerals” is sometimes used. Important mineralogical properties of these minerals are listed in Table 6.1.

Table 6.1: Properties of the minerals kyanite, sillimanite and andalusite.

	Kyanite	**Sillimanite**	**Andalusite**
Formula	Al_2SiO_5		
Chemistry	62.92 % by mass Al_2O_3, 37.08 % by mass SiO_2		
Density (g/cm^{3}3)	3.56-3.67 (av. 3.61)	3.24	3.13-3.17 (av. 3.15)
MOHS hardness	4 ½ (longitudinal) 6-7 (transverse)	6-7	6 ½-7
Color	blue, white, pink, gray, green, black	colorless, gray, grayish green, yellowish gray, bluish	gray, brown, dark green, red, reddish gray
Magnetic properties	non-magnetic		
Electrostatic properties	non-conducting		

The stability of these minerals is temperature and pressure dependent (cf. Figure 6.1). At high temperatures and low pressures, these three minerals are converted to mullite ($3Al_2O_3 \cdot 2SiO_2$) and tridymite (SiO_2) (cf. Chapter 6.3).

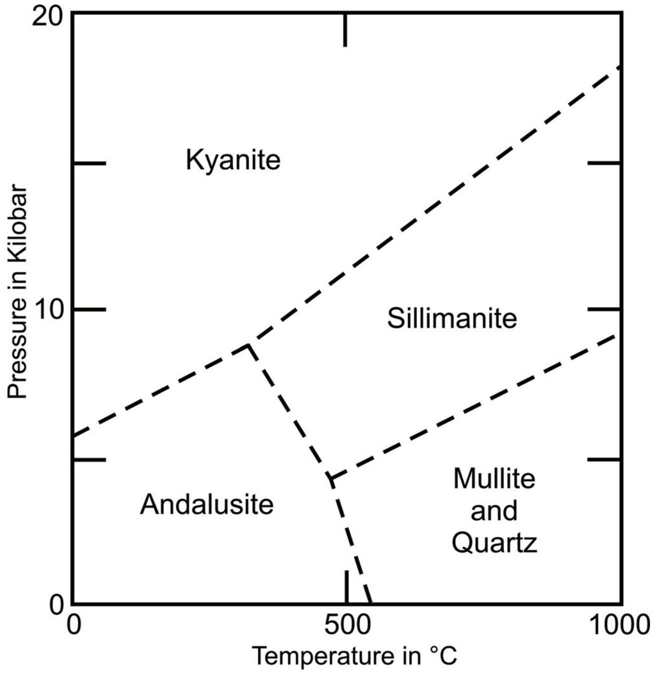

Figure 6.1: Mineral phases within the Al_2SiO_5 system, according to GROBBELAAR (1994).

Due to the crystal structure of the sillimanite minerals, the trace elements Fe, Mn, Ti and Cr which are harmful for its use (cf. below), are found only rarely and then mostly in kyanite and andalusite.

Chromium kyanite can contain up to 1.81 % Cr_2O_3 (KING 2003). Finely fibrous, felt-like aggregates of sillimanite are called fibrolite. Andalusite rich in manganese is called viridine.

Kyanite commonly contains inclusions of andalusite, calcite, zircon, monazite and rutile. Sillimanite can contain inclusions of corundum, rutile, Fe oxides, topaz, mica, clay minerals and silica. Andalusite with dark inclusions of graphite, rarely silicate or ilmenite, in a checkerboard pattern, is called chiastolite. Other typical mineral inclusions in andalusite are muscovite, biotite or chlorite.

Typical paragenesis minerals of kyanite and sillimanite are corundum, rutile, topaz, tourmaline and dumortierite, as well as Al phosphates like lazulite. Kyanite is also frequently combined with staurolite. Typical paragenesis minerals of andalusite are staurolite and almandine, which, although valuable heavy minerals in theory, are undesired in the andalusite concentrate (cf. Chapter 6.5).

6.2 Formation of deposits and occurrences

Sillimanite, kyanite and andalusite are typical minerals of the metamorphosis of Al-bearing rocks and their weathering products. All three minerals are frequently found in hornfels, shales and paragneisses with contents of 1- >30 % by mass. Large kyanite crystals also occur in pegmatites.

The most important, mineable deposits are formed by:

- Contact metamorphism:
  Andalusite deposits, such as Aktash/Uzbekistan, White Mountain/California, Groot Marico District/Rep. of South Africa (contact area of the Bushveld complex).
  Sillimanite deposits, such as Sona Pahar/Assam/India, Pipra/Madhya Pradesh/India, Cape Province/Rep. South Africa, Warmbad/Namibia, Thackaringa/New South Wales and Mount Crawford/South Australia.
- Regional metamorphism from rocks rich in Al, mainly clay or bauxite sediments:
  Kyanite deposits, such as Keiva/Kola Peninsula/Russia, Baker Mountain/Virginia, Celo Mountain/South Carolina, Graves Mountain/Georgia, Lapsa Buru/Orissa/India, Halway Kop/Botswana, N´cheu/Kapidirimba/Malawi, Grand Bassa County/Liberia.
  Sillimanite deposits, such as Hart County/Georgia and Bethanien District/Namibia
- Metasomatically: Examples of deposits are Semiz-Bugu/Kazakhstan and Lapsa Buru/Orissa/India.

Kyanite, sillimanite and andalusite as typical heavy minerals are found in many placers. In littoral and eolian placers, the sillimanite minerals are always very fine grained. Since, however, the demand for these fine grained sillimanite minerals is small, there is mostly no corresponding processing despite common large deposits.

The extraction of sillimanite minerals from placers is known in:

- **Australia, Western Australia**: Kyanite as a by-product of the extraction of Ti minerals and zircon from fossil beach placers near Eneabba since 1982, assumed production <10 kilotonnes/year.

- **Brazil, Minais Gerais**: Near Andrelandia, mining of a 2 m deep, eluvial placer with average contents of 25 % by mass kyanite, 20 % by mass garnet and 15 % by mass muscovite. The kyanite is found in the form of free, rectangular crystals up to 5 cm in length with a reddish brown to blue to transparent inherent color. Many of the crystals are contaminated by Fe coatings. The source rock is kyanite-bearing shale in the region.

  In the Jequitinhonha valley near Barra de Salinas: Boulders (5-15 cm diameter) of sillimanite as a mineable by-product in a fluvial gold diamond placer. Original reserves approx. 150 kilotonnes of sillimanite.
- **Ghana**: Near Abodum, alluvial andalusite placers of small thickness with staurolite.
- **India:** Sillimanite, with interruptions since 1936, as a by-product of beach placer mining for Ti minerals, zircon and monazite, average sillimanite contents in the HM fraction in the Federal State of Kerala: 4-8 % by mass, and the Federal States of Tamil Nadu and Orissa: 2-3 % by mass.

  Northwest of Midnapur in West Bengal: eluvial sillimanite placers (content in the raw sand: 0.8-1.0 % by mass sillimanite) with monazite, ilmenite and rutile, zircon, thickness: cm-3 m (on average: 1.2 m), reserves approx. 100 kilotonnes of sillimanite.

  Near Ghagidih in Bihar: alluvial kyanite placers with reserves of approx. 20 kilotonnes of kyanite.
- **Cameroon**: near Edea in the Nyiba River Basin, discovery of alluvial kyanite placers in 1960.
- **Peru**: Near Peipa, mining of alluvial andalusite placers is planned by Refractories Peruanos SA.
- **Russia, South-Yakutia**: 1933 discovery of high-grade corundum-kyanite placers (on average 63.9 % Al_2O_3, 33.15 % SiO_2) near Chainyt.
- **Zimbabwe**: Deposits of eluvial kyanite placers with small-scale mining of these in the Ky Mine and in Inyanga North. Further deposits at Madecheche Hill: 17 million tonnes of eluvial and residual placers (average content 8 % by mass kyanite) up to 3 m thick, as well as near Masterpiece northeast of Karoi: 440 kilotonnes of kyanite in eluvial placers.
- **Spain, La Coruña Province**: near El Pino and Touro: Extraction by floating dredge of the mineable upper 3-6 m of <28 m thick river gravel (original reserves 3 million tonnes with average content: 20 % by mass kyanite: 56-58 % Al_2O_3, 0.5-1.5 % Fe oxides). Mining until 1996 of 1,500-6,000 tonnes/year.
- **Rep. South Africa, Transvaal**: In the drainage basin of andalusite-bearing shales, mineable deposits of alluvial and eluvial andalusite placers known for a long time in the following regions: Groot Marico-Zeerust (average thickness 8 m, contents: 10-50 % by mass andalusite: 53 % Al_2O_3, reserves approx. 500 kilotonnes) and Northen Lydenburg (thickness up to 14 m, on average 1-2 m, content: 10-80 % (on average 15 %) by mass andalusite: 58 % Al_2O_3, reserves approx. 500 kilotonnes) (NN 1977, POWER 1986, IHLEN 2000).
- **Ukraine:** Kyanite and sillimanite as by-products of the extraction of Ti minerals and zircon near Volnogorsk, capacity approx. 60 kilotonnes/year, production approx. 25 kilotonnes/year.
- **USA**: 1932 until 1949 extraction of coarse kyanite rubble from residual placers (contents up to 24 kg kyanite/m^3 rubble) at Raper Creek, Georgia.

  1968 until 1973 from the Trail Ridge dune placer deposit in north-east Florida, extraction of the kyanite-sillimanite concentrate Kyasill®, which was used as special molding sand. After 1973 substitution of the Kyasill® by Zircore®, which is also used as special molding sand, and consists of zircon, kyanite, sillimanite, corundum, silica and staurolite (cf. Tables 4.8-4.10).

  In the case of the kyanite-bearing quartzites mined in Virginia at Willis Mountain and East Ridge by the Kyanite Mining Corporation, these are metamorphically strongly overprinted Ordovician quartz gravels and coarse sands of former eluvial placers.

In many tropical and subtropical countries there are also residual placers of varying thicknesses of sillimanite minerals in the form of talus, and in part blocks of up to m^3 size, which are worth mining on a small scale, and which have been exposed by weathering in the horizontal, still unweathered enclosing formations. Examples are the sillimanite deposits of Khasi Hills/Assam and the kyanite deposits of Singhbhum/Bihar, both India.

6.3 Applications

Sillimanite minerals were used for the first time in World War I for improving the quality of porcelain in spark plug insulators in aircraft engines. In the meantime, their main area of application is in the refractory industry with a share of approx. 90 %, and of this with a share of

- 55-65 % in the steel industry (lining of smelting furnaces in the form of bricks, which depending on the raw material are called andalusite bricks, kyanite bricks or sillimanite bricks, molds, plastic compounds, refractory concrete, ramming mix, refractory mortar (share of 10-40 % by mass, rest is refractory clay) etc.),
- 10-20 % in the non-ferrous industry (lining of electric smelting furnaces for the smelting of aluminum, copper-rich bronze, brass and Cu-Ni alloys, in zinc smelting and gold refining),
- 10 % in the glass industry (framework of glass mix tanks) and
- 10-15 % in the cement industry (lining of cement furnaces), for incineration plants and other industries.

In technical terms, the properties of sillimanite minerals result from their conversion into a mixture of silicic acid (tridymite alteration) and mullite at temperatures between 1,100 and 1,650 °C, where mullite, on the other hand, is stable until approx. 1,800 °C:

$$3Al_2SiO_5 + \text{heat} \rightarrow 3Al_2O_3 \cdot 2SiO_2 + SiO_2$$

$$\text{sillimanite mineral} + \text{heat} \rightarrow 88\ \%\ \text{mullite} + 12\ \%\ \text{tridymite}$$

The properties of mullite sought by the refractory industry, on the other hand, are that it forms well shaped, mostly finely felted crystals even after very fast quenching. Its other sought after properties are:

- highly refractory (1,790-1,830 °C),
- small coefficient of expansion,
- high resistance to abrasion and slag erosion,
- average conductivity,
- high pressure resistance,
- high resistance against corrosion at high temperatures.

Due to its properties, mullite is the mineral most sought after by the refractory industry, whereas sillimanite minerals are only required as “mullite raw material”.

The mullitization parameters specified in Table 6.2 are dependent on the base mineral and its purity. Due to the volume increase of kyanite during mullitization, calcination is often necessary before it can be used as a refractory material, but this is energy and cost intensive. On the other hand, kyanite is particularly sought after because it is the only mineral with intense expansion when heated and can therefore compensate for the shrinkage of other refractory materials.

Table 6.2: Mullitization and calcination parameters of sillimanite minerals, amended according to VARLEY (1965).

	Kyanite	**Sillimanite**	**Andalusite**
Mullitization start (°c)	1,100	1,550	(1,350, 1410)1,450
Mullitization end (°c)	1,410	1,625	(1,460)1,500
Temperature necessary for mullitization (commercial) (°C)	1,480	1,650	1,450
Bulking (% by volume) after complete mullitization	(15)16-18 [1)]	(5-8)7	(3)5-6
Density after calcination at 1,445 °C (g/cm^3)	3.05	3.10	3.04

[1)] Calcination required before mullitization

Approx. 10 % of the sillimanite minerals are used outside of the refractory industry:

- Ground andalusite and kyanite as mass additives (source for Al and Si) in the manufacture of sanitary and kitchen ceramics, tiles and electro-porcelain (high voltage insulators etc.) and brake shoes. Due to its volume increase, kyanite also counteracts shrinkage and cracking after firing.
- Due to its medium high density, medium hardness and its uneven and sharp fractures, sillimanite is used as a blasting sand and abrasive in mills. In addition, it can be used as a binder for other abrasives.
- Sillimanite is used for the manufacture of the Si-Al alloy "silumine" (87 % Al, 13 % Si), mainly in Russia. Due to its high strength and corrosion resistance as well as good thermal conductivity, this alloy is used in the manufacture of crankcases, cylinder heads and similar components in engine manufacturing.
- Fine grained kyanite-sillimanite-(zircon) mixtures) (Kyasill®, Zircore®), but also special kyanite concentrates, are used as molding sand in the foundry industry.
- Sillimanite for the production of ceramic fibers as a refractory material with low thermal conductivity.
- All sillimanite minerals as fillers, as additives for metallic fibers, and as raw materials for special Al oxides.

6.4 Substitutes

In its main area of application in the refractory industry, sillimanite minerals can easily be replaced by other minerals; some options are listed below:

- synthetic mullite (melt of bauxite or kaolin or Al and Si at 1,914 °C or sintering of Al and kaolin or bauxite and kaolin or Al, kaolin and kyanite at >1,763 °C or silicon-rich bauxite or a mixture of bauxite and kaolin at >1,561 °C)
- calcinated kaolin, refractory clay, fireclay (35-45 % Al_2O_3), pyrophylite (28-29 % Al_2O_3), zircon, chromite, silicon carbide, magnesite

6.5 Specifications for the raw materials (reference values)

In mineable solid rock deposits, sillimanite minerals should not be finely dispersed, but must occur in porphyroblasts, aggregated or free.

According to *Geological and Metallurgical Ministries of China* (GUANGHUAN 1990) kyanite deposits must contain >10 (15) % by mass kyanite, mineable ore bodies must have a thickness of >1.5 m, intermediate strata, however, of <1.5 m.

According to GWOSDZ & LORENZ (2005), placer deposits which are to be exclusively mined for sillimanite minerals contain >20 % by mass of this mineral in the raw material. To be mineable as a by-product in placers, their share in the HM fraction must be >15 % by mass. In the processed concentrate, a sillimanite mineral content of >90 % by mass must be achieved.

To produce high stabilities under load, >60 % by mass of the refractory compound must be coarse grained (>0.5 mm). Fine grained material, such as from placers, can also be added or must be mixed with refractory clays and homogenized. The worldwide demand for fine grained sillimanite minerals from placers is therefore small. Only fine grained material is used in the manufacture of sanitary ceramics or wall tiles and in the manufacture of precision castings, such as for engine blocks.

Due to their Fe content, garnet and staurolite belong to the undesired heavy minerals that also frequently occur in kyanite, sillimanite or andalusite bearing placers. For process engineering reasons, the smallest crystals or grains of these minerals must not be smaller than the smallest sillimanite minerals.

GWOSDZ & LORENZ (2005) also name muscovite, biotite, kaolin, silica, Fe minerals and rutile as harmful impurities in solid rock deposits of sillimanite minerals.

Chemical analyses of kyanite concentrates with Al_2O_3 contents that are higher than the stoichiometric content of 62.92 % Al_2O_3 in kyanite indicate the presence of corundum, which increases the fire resistance even more.

Crystals of andalusite to be used as reinforcing filler material must have a cross-section:length ratio of 1:10 to 1:50 (GWOSDZ & LORENZ 2005).

Improving the resistance of the mullite-silica compound formed during thermal conversion to high temperatures requires the sillimanite mineral concentrate to have

- an Al_2O_3 content as high as possible (>59-60 % by mass)
- an Fe_2O_3 content as low as possible (<1 % by mass)
- a TiO_2 content as low as possible (<2 % by mass) and
- alkali contents as low as possible, as these are used as flux.

More important than all the chemical-physical properties of the sillimanite minerals is, however, their price, which is also mainly influenced by the transportation costs. For this reason, only a single sillimanite mineral is used in the most important producing countries: this is andalusite in South Africa and France, kyanite in the USA, and sillimanite in India.

Tables 6.3-6.5 list raw material specifications for kyanite, sillimanite and andalusite concentrates for various uses, amended according to GWOSDZ & LORENZ (2005) and LEPEZIN & GORYUNOV (1988).

Tables 6.6 and 6.7 list the chemical compositions, physical parameters and particle size distributions of some kyanite, sillimanite and andalusite concentrates extracted from placers.

Table 6.3: Raw material specifications (reference values) for kyanite concentrates.

Application	Refractory industry							sanitary ware, wall tiles etc.	Al-Si alloy "silumin"[1]
	Bricks	Casting compound, spraying mixtures, ramming mass	Mortar	India		China			
				Grade I	*Grade II*	*Grade 55*	*Grade 58*		
Chemical composition (%)									
SiO_2	<39, <39[2], <42[3]					<42		39-44	
Al_2O_3	>59, >59[2], >56[3]			>58(>60)	>54	>55	>58	>54(>55)	≥57
Fe_2O_3	<1(<1.3), <2.00[2], < 1[3]			<1.5		<1.5	<0.8	<0.5(<1.0)	≤0.8
TiO_2	0.2-<1.5, <2.00[2], <1.2[3]					<2.0	<1.5	<0.2	
ZrO_2									≤1.5
Na_2O	<0.5, <0.3[3]					<0.5	<0.3	<0.2	≤0.5
K_2O									
MgO	0.2-<0.8, <0.2[3]					<2.0		<0.3	≤0.4
CaO									≤0.2
LOI	0.3-0.9								
Mineralogical composition (%)									
Kyanite	>90							>84-86	
Mica, rutile, pyrite	<2.0							<1.0	
Quartz	<2(<5)							<1.0	
Physical parameters									
Grain size (mm)[5]	>4.7, 0.5-4[4]	<1.0	0.3-0.4					0.07-0.15	
TBE float (% by mass)[6]	<0.5(<1)								
Refractability (Orton Cone)[7]		>36		>37	>36				

[1] from kyanite-sillimanite concentrate [2] in the UK [3] in the USA and Canada [4] 0.5-4 mm used in the groundmass [5] supplied grain sizes in the USA: 0.05-0.08 mm, 0.08-0.115 mm, 0.115-0.300 mm, 0.300-0.500 mm [6] proportion of light minerals that float on tetrabromethane [7] a comparison table for Orton/pyrometric cones can be found in DIN EN 993-13:1995

Table 6.4: Raw material specifications (reference values) for sillimanite concentrates.

Application	Refractory industry									Sanitary ceramics, wall tiles, etc.
				India			China			
	Bricks	Casting compound, spraying mixtures, ramming mass	Mortar	*Lump I*	*Lump II*	*Sand*	*Grade 52*	*Grade 55*	*Grade 58*	
Chemical composition (%)										
SiO_2	<39						<42			39-44
Al_2O_3	(>55)>59			>58	>54	>58	>52	>55	>58	>54
Fe_2O_3	<1(<1.3)		<2-<3.5	<1.5		<0.75	<2.0	<1.5	<1.0	<0.5
TiO_2	0.2-<1.5(<2)						<1.0			<0.2
Na_2O	<0.3(<0.5)						<1.2	<0.8	<0.5	<0.2
K_2O										
MgO	0.2-<0.8									<0.3
CaO										
LOI	0.3-0.9									
Mineralogical composition (%)										
Sillimanite	>90									>84-86
Mica, rutile, pyrite	<2.0									<1.0
Quartz	<2(<5)									<1.0
Physical parameters										
Grain size (mm)	4-8, 0.5-4 $^{1)}$	<1.0	0.3-0.4							<0.5
Refractability (Orton Cone) $^{4)}$		>36		>37 $^{2)}$	>36 $^{3)}$	>37 $^{2)}$				

$^{1)}$ 0.5-4 mm used in the base $^{2)}$ corresponds to >1,800 °C $^{3)}$ corresponds to > 1,820 °C $^{4)}$ a comparison table for Orton/pyrometric cones can be found in DIN EN 993-13:1995

Table 6.5: Raw material specifications (reference values) for andalusite concentrates.

Application	Refractory industry					Sanitary ceramics, wall tiles, etc.
	Bricks	Casting compound, spraying mixtures, ramming mass	Mortar	China		
				Grade 54	*Grade 58*	
Chemical composition (%)						
SiO_2	<37-39					39-44
Al_2O_3	(>53)57-60			>54	>58	54-57
Fe_2O_3	<1(<1.3)		<2-<3.5	<1.5	<1.0	<0.5
TiO_2	(<0.5)<1.0(<2.0)			<1.0	<1.0	<0.2
Na_2O	<0.3(<0.5)			<1.0	<0.5	<0.2
K_2O						
MgO	0.2-<0.5					<0.3
CaO						
LOI	0.3-0.9					
Mineralogical composition (%)						
Andalusite	>90					>84-90
Mica, rutile, pyrite	<2.0					<1.0
Quartz	<2.0					<1.0
Physical parameters						
Grain size (mm) [2]	5-8, 0.5-1.68 [1]	0.5-1.68	<1.0			<1.0
TBE float [3]	<0.75(<1.2)					

[1] 0.5-1.68 mm used in the base [2] supplied grain sizes in France 0.300-0.500 mm, Rep. of South Africa 1.00-5.00 mm, 5.00-8.00 mm [3] proportion of light minerals that float on tetrabromethane

Table 6.6: Chemical composition (%) and chracteristic values for kyanite, sillimanite and andalusite concentrates produced from placers.

	Ghagidih Bihar, India 5)	**La Coruna** Spain 6)	**Chavara** Q-Grade Indian Rare Earths Ltd. Kerala, India 1)	**Chapura (OSCOM)** OR-Grade Indian Rare Earths Ltd. Orissa, India 1)	**Kerala** India 5)	**Kollam** Kerala Minerals and Metals Ltd. Kerala, India 1)	**Trail Ridge** Kyasill Test Concentrate U.S. Bureau of Mines. Florida, USA 5)	**Folkston** Kyasill Test Concentrate Humphreys Gold Corp. Georgia, USA 3)	**Malyshev. Volnogorsk** VSMMP Dnepropetrovsk, Ukraine 4)	**Groot Marico-Zeerust** Western Transvaal Rep. South Africa 2)	**Abodum** Ghana 5)
Mineral	**Kyanite**		**Sillimanite**				**Kyanite-Sillimanite**			**Andalusite**	
Chemical composition (guaranteed)											
Al_2O_3			≥58.00	≥56.50		≥60			>57.0		
Fe_2O_3									<0.8		
TiO_2									<2.0		
Na_2O									<0.1		
MgO									<0.4		
CaO									<0.2		
humidity									<0.1		
Chemical composition (typical)											
Al_2O_3	66.47-68.4	58-63	59.30	56.60	61.15	61.62	63.6	59.50	58.0	53.81	51.60
Fe_2O_3	0.04-1.1	0.5-1.5	0.50	0.40	0.82	1.0	1.78	0.32	0.7	1.49	2.19
SiO_2	28.6-30.28		37.10	38.00	35.0	36.58	32.0	35.63		43.59	39.31
TiO_2	1.49	0.15-0.5	0.40	0.25	0.41	0.2	0.57	0.34	1.8	0.29	0.17
ZrO_2			1.50	2.20	2.13	0.18		2.59	0.3		
P_2O_5			0.05					n.d.			0.05
Na_2O		0.7						0.12	<0.1	0.01	2.02
K_2O			0.50					n.d.		0.31	1.32
MgO	0.2				+			0.03	0.2	0.02	0.30
CaO	1.3		0.60		0.06			0.05	0.1	0.13	0.39
LOI	1.02				0.38	0.47		1.63	7)	0.35	0.30
Physical parameters											
apparent density (g/cm^3)			3.20-3.25			3.27					
bulk density (kg/m^3)			1,950-2,050								

1) Company information 2) Carroll & Matthews (1983) 3) Elsner (1992) 4) O`Driscoll (1998) 5) Varley (1965) 6) Anonymous (1977) 7) 9 ppm U+Th, Moisture. 0.1 % by mass

Table 6.7: Particle size distribution and mineralogical composition for kyanite and kyanite-sillimanite concentrates produced from placers.

		Chapura (OSCOM) Sillimanite OR-Grade Indian Rare Earths Ltd. Orissa, India [1]	**Folkston** Kyasill Test Concentrate Humphreys Gold Corp. Georgia, USA [2]	**Malyshev, Volnogorsk** Kyasill VSMMP Dnepropetrovsk, Ukraine [3]
Mineralogical composition (% by mass)				
Sillimanite			58.9	51.0
Kyanite			27.7	46.0
Topaz			5.5	
Zircon			4.1	+
Andalusite			1.2	
Ilmenite			0.9	1.0
Leucoxene			0.4	
Rutile			0.4	+
Staurolite			0.3	+
Tourmaline				1.0
Epidote			0.2	
Quartz			0.2	1.0
Garnet			0.2	
Grain size distribution (screen residue % by mass)				
µm	Tyler mesh			
>355	+42	0.7	0.009	0.008
355	42		0.007	0.009
300	48		0.003	0.074
250	60	11.3	0.017	0.330
210	65		0.190	3.862
180	80	55.8	0.856	11.532
150	100		3.653	43.538
125	115	29.6	10.816	33.655
105	150		32.764	6.158
90	170	0.9	30.345	0.606
75	200	1.5	14.177	0.122
63	250	0.2	4.442	0.039
53	270		1.274	0.021
45	325		0.842	0.013
<45	-325		0.600	0.033
***mean* (µm)**			**102.6**	**154.3**

[1] Company information [2] ELSNER (1992) [3] BGR analysis

6.6 Deposit size and reserves

The following reference values can be applied according to LORENZ (1991) for the size assessment of sillimanite mineral deposits, also for placer deposits:

	all deposits **mineral content**
small	<50,000 – 500,000 tonnes
medium	500,000 – 5 million tonnes
large	5 – >20 million tonnes

The following reference values can be applied according to GUANGHUAN (1990) in China for the assessment of ore bodies of any type, also for sillimanite mineral deposits.

	Ore body mineral content
Very poor	<20 % by mass
Poor	20-30 % by mass
Medium	30-40 % by mass
Rich	>40 % by mass

The estimated global reserves and resources of the various sillimanite minerals are listed in Table 6.8 or shown in Figures 6.2-6.4.

Table 6.8: Reserves and resources of kyanite, sillimanite and andalusite in million tonnes, and percentage of worldwide reserves/resources of the three most important supply countries (various sources).

	Kyanite		**Sillimanite**		**Andalusite**	
	million tonnes	%	million tonnes	%	million tonnes	%
Australia	3					
Brazil	3.5					
Bulgaria	0.8					
Finland	0.3					
France					5	
Ghana					0.6	
India	>3.8		130	99.0		
Cameroon	0.1					
Canada	45	39.2				
Kenya	1.2					
Liberia	2.5					
Malawi	0.3					
Namibia	0.1					
Austria	4					
Russia	3.5				72	32.7
Sweden	4.5					
Somalia	0.1					
Rep. of South Africa	12	10.4	1.2		142	64.5
USA	>30	>26.1	0.1		0.6	
World- total	**>115**		**131**		**220**	

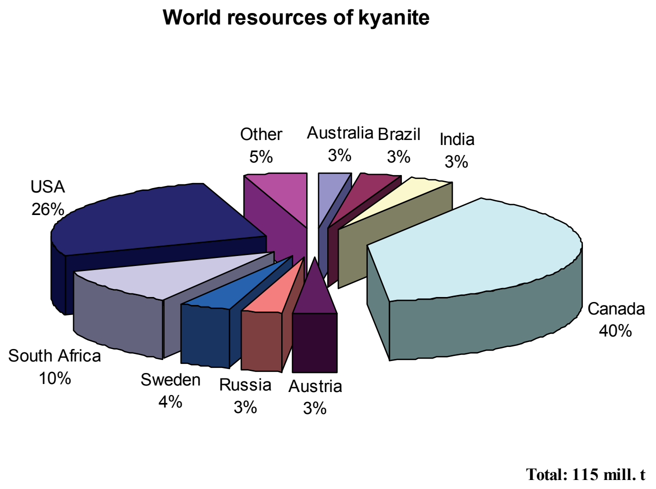

Figure 6.2: **Percentage distribution of the currently known worldwide reserves and resources of kyanite.**

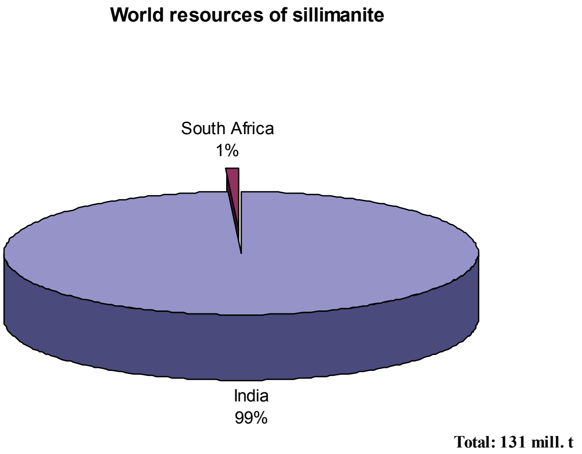

Figure 6.3: **Percentage distribution of the currently known worldwide reserves and resources of sillimanite.**

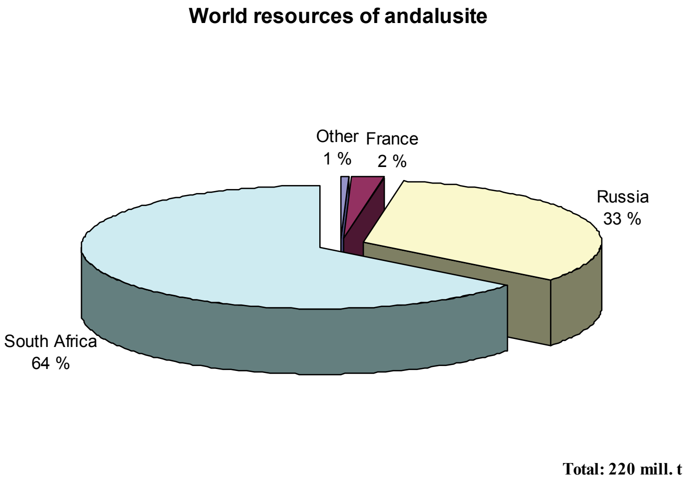

Figure 6.4: **Percentage distribution of the currently known worldwide reserves and resources of andalusite.**

6.7 Important producing countries

The global production of sillimanite minerals in the last decades is shown in Figure 6.5. In 1998, the worldwide production was divided into 2 % sillimanite, 74 % andalusite and 24 % kyanite (IHLEN 2000).

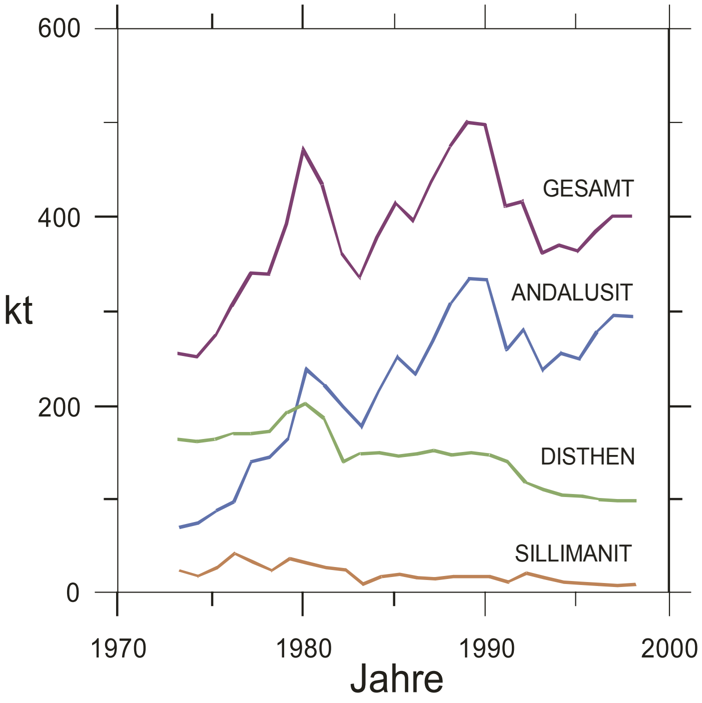

Figure 6.5: Global production of sillimanite minerals from 1973 – 1998 (IHLEN 2000).

The distribution of the global production of aluminum silicates in 2008 is shown in Figure 6.6.

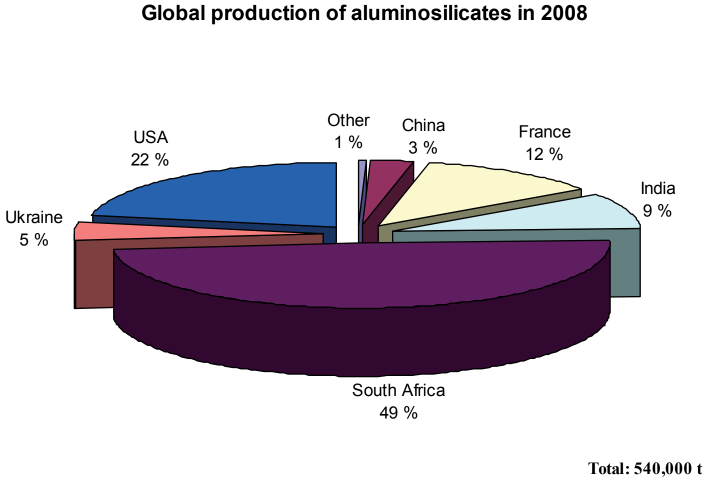

Figure 6.6: Percentage distribution of the global production of aluminum silicates in 2008.

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7 Staurolite

[German: *Staurolith*, Spanish: *estaurolita*, French: *staurolite*]

7.1 Mineralogy, petrography, chemistry

The mineral **staurolite** has the following properties:

Formula	$(Fe, Mg)_2(Al,Fe)_9O_6[SiO_4](OOH)$
Density	3.63 – 3.77 g/cm^3
MOHS hardness	7-7 ½
Color	yellowish brown, reddish brown, dark brown, brownish yellow
Magnetic properties	paramagnetic
eEectrostatic properties	non-conducting

Staurolite occurs as typical cruciform twins in larger crystals and in its host rock. This is also the origin of its name. In placer deposits it occurs as medium to very well rounded, usually coarse grains with differing yellowish brown natural colors. Inclusions of gases or minerals and other impurities are not uncommon.

7.2 Formation of deposits

Staurolite is a typical mineral of the mesozonal contact zone, and regional metamorphism. It is also only stable in this zone, and converts to almandine and kyanite and sillimanite in the katazone. The associated minerals are always the three Al_2SiO_5 versions: sillimanite-kyanite-andalusite (cf. Chapter 6) as well as frequently garnet and muscovite or biotite.

In placer deposits, derived from metamorphic host rocks, staurolite frequently occurs as an associated mineral.

7.3 Applications

Staurolite was first produced in 1952 by Du Pont from their Trail Ridge placer deposit in north-east Florida. Its first area of application was exclusively in the **cement industry** of Florida. In areas where no clay or argillaceous limestones were available as sources of Al and Fe, the cement industry was dependent on substitutes for Al and Fe. Because these elements are found in the placer minerals staurolite and tourmaline, Du Pont provided large amounts of the two minerals at low prices.

Approx. 200 tonnes of ore sand produced approx. seven tonnes of heavy mineral concentrate, which yielded approx. one tonne staurolite. For the production of one tonne of Portland cement the following materials were then used in Florida (EVANS 1955):

- 3.96 tonnes of untreated coquina and sand, which yielded after filtration and cleaning
- 1.32 tonnes of raw material. To this were added:
- 70 kg staurolite,
- 35 kg bed ash rich in iron, and after calcination of the resulting cement brick
- 29 kg gypsum.

Over the years, staurolite became more frequently used as an **abrasive**. These sand blasting abrasives are traded today under the name DuPont Starblast.

In the 1990s, Du Pont developed the even coarser blasting abrasive Starblast XL and Starblast ultra and separated them from the staurolite mineral fraction.

A coarse staurolite concentrate (DuPont Coarse Staurolite) is used for engraving and polishing marble tombstones and corner stones.

The advantages of staurolite as an abrasive are (cf. Table 7.1):

- greater blasting visibility due to coarse grains,
- fast cleaning and low depth of indentation in the surface to be cleaned, due to rounded and compact grains,
- non-hygroscopic (no freezing) and good flow characteristics (no agglutination),
- electrically non-conducting,
- low percentage of free quartz (guaranteed: <5 % by mass, typical: 3, TAB.
- good recyclability (cf. Table 7.2):

Table 7.1: Comparison of the physical properties of different abrasives (SKILLEN 1994).

Medium	Form	MOHS HARDNESS	Bulk density (g/cm^3)	Free quartz	Dust generation
Al-oxide	bulky	8	4.00	<1 % by mass	low
Blast-furnace slag	angular	7	2.80	none	high
Cinder coal	angular	7 ½	2.78	none	
Copper slag	angular	8	3.30	none	low
Flint(stone)	angular	6 ½-7	2.0-3.0	<90 % by mass	medium
Garnet	angular	7-8	3.9-4.2	none	medium
Nickel slag	angular	8	2.70	none	medium
Novaculite	angular	4	2.50	<90 % by mass	low
Olivine	angular	6 ½-7	3.2-3.6	none	low
Quartz sand	rounded	7	2.65	90-100 % by mass	high
SiC	angular	9	3.20	<1 % by mass	low
Staurolite	rounded	6 ½-7	3.66-3.83	<1 % by mass	low
Abrasive shot	rounded	6-7	4.80	none	low

Table 7.2: Blasting properties of staurolite in comparison to garnet, according to ELLIOTT & BENSON (2001).

Mineral	Grain size (µm)	Cleaning rate (m^2/Std.)	Depth of indentation (mm)	Recyclability (1 x / 3 x)[1)]
Staurolite	210	22	0.02	77 % / 45 %
Garnet	180	21	0.02	-
	250	18	0.02	61 % / 38 %

[1)] Percentage of the original amount that can be reused

Lead-based paint residues should not be sand-blasted using recyclable abrasives such as staurolite because the customary re-use of the blasting sand can result in the contamination of the operating personnel.

In Australia, staurolite for the blasting industry is also called *Black Garnet* to profit from the marketing success of garnet for the same purpose (cf. Chapter 8).

In the 1960s, Du Pont also developed Biasill (Bi-Iron-Aluminum-Silicate) as a special low-iron **foundry sand** because staurolite boasts:

- low quartz content (health and safety regulations),
- hardness and ductility of the individual grains,
- cleanness and round shape of the grains without fines,
- melting point (1,537 ^{o}C)
- low thermal expansion (7.8 x 10^{-6} cm/cm ^{o}C)

It is therefore particularly suitable for casting Al, brass and bronze, Mg and Cu.

The rather low melting point in comparison to other molding sands restricts the use of staurolite as a substitute for all types of molding.

Ground staurolite is also sometimes used as a **filler** with resistance to chemical and mechanical weathering. In the Ukraine, the local staurolite is said to be used by the local steel industry as a **slag liquefier** in blast furnace processes.

7.4 Substitutes

Depending on the usage, staurolite can easily be replaced by other minerals as follows:

- abrasive: bauxite and electrocorundum, corundum, emery, diamond, diatomite, feldspar, garnet, specular iron, magnetite, nepheline syenite, olivine, perlite, pumice, quartz sand, bed ash, tripoli, silicon carbide, ilmenite.

  Staurolite is more expensive than quartz sand, but less expensive than its main competitor garnet. Its usage is limited by the small number of producers.
- foundry sands: chromite, olivine, quartz sand, zircon

7.5 Specifications of the raw materials (reference values)

The specifications for staurolite for use as an abrasive are regulated in Germany by ISO 11126-9:1999 (cf. Table 7.3).

General specifications (ISO 11126-9:1999):

- staurolite must be free of corrosive impurities and contaminants affecting adhesion.
- SiO_2 may only be present in bonded siliceous form in staurolite.

Table 7.3: Specifications for staurolite for use as an abrasive in accordance with ISO 11126-9:1999.

Property	Unit	Requirement	Testing method
Grain size distribution		cf. below.	ISO 11127-2
Density	kg/m^3	(3.6-3.7) x 10^3	ISO 11127-3
	[kg/dm^3]	3.6-3.7	
MOHS hardness[1]		≥6	ISO 11127-4
Humidity	%	≤0.2	ISO 11127-5
Conductivity of the water extract	mS/m	≥25	ISO 11127-6
Chlorides soluble in water	%	≤0.0025	ISO 11127-7

Grain size[2]		mm	0.1-0.3	0.1-0.4	0.2-0.6
Oversized particle	screen set	mm	0.3	0.4	0.6
	residue	%	≤10	≤10	≤10
Nominal size	screen set	mm	0.1	0.1	0.2
	residue	%	≥85	≥85	≥85
Undersized particle	screen set	mm	0.1	0.1	0.2
	residue	%	≤5	≤5	≤5

[1] The parties can agree to use a different testing method for determining the hardness for different specifications. [2] The parties can agree that abrasives of different grain size can be mixed. Details of the ratio of oversized particles, nominal size and undersized particles have to be specified. The maximum grain size may not exceed 3.15 mm. The amount of undersized particles may not exceed 5 %.

In addition, staurolite concentrates generally have to contain ≤ 4 % by mass kyanite, ≤ 1 % by mass zircon and ≤ 5 % by mass free quartz. The warranted specifications of current staurolite producers are compiled in Table 7.4.

Table 7.4: Warranted chemical compositions (%) of staurolite concentrates.

Producer	E.I. du Pont de Nemours & Co	Volnogorsk State Mining and Metallurgical Plant	Tiwest Joint Venture
Occurrence, region	Trail Ridge, Florida	Malyshev, Ukraine	Cooljarloo, Western Australia
Al_2O_3	≥45.0	≥ 45.5	-
TiO_2	≤4.0		≤3
Fe_2O_3	≤18.0	-	-
SiO_2	-	≤29.0	-
ZrO_2	<3.0	0.9[1]	≤1
U + Th	-	<60 ppm[1]	≤60 ppm
H_20	-	≤0.5	-

[1] = typical values

Tables 7.5 and 7.6 show the compositions and physical parameters of staurolite concentrates produced from placer deposits.

Table 7.5: Granulometric composition (% by mass, screen residue of staurolite concentrates, according to Elsner (1992), Elliott & Benson (2001) and data sheets of several companies.

µm	ASTM *mesh*	Green Cove Springs "Staurolite" Associated Minerals USA. Florida, USA	Trail Ridge Du Pont Biasill Florida, USA	Trail Ridge Du Pont Starblast Florida, USA	Trail Ridge Du Pont Starblast XL Florida, USA	Trail Ridge Du Pont Starblast Ultra Florida, USA	Trail Ridge Du Pont Coarse Staurolite Florida, USA	Malyshev. Volnogorsk VSMMP Dnepropetrovsk, Ukraine
>850	>20		0.012		3	<1	0.048	
700	25		0.019	0.010		1	0.351	0.003
600	30		0.133	0.036			1.682	0.000
500	35	0.002	0.374	0.164		10	6.721	0.001
420	40	0.005	0.984	0.577			18.386	0.006
355	45	0.018	2.890	1.206	13	23	27.419	0.014
300	50	0.051	6.981	4.356			33.171	0.096
250	60	0.523	10.523	8.595	25	20	9.258	0.672
210	70	1.856	18.653	16.002			1.585	6.260
180	80	3.549	19.317	19.308	36	31	0.576	10.894
150	100	8.467	17.654	20.660			0.347	36.265
125	120	37.981	15.201	16.033	18	13	0.218	35.732
105	140	33.368	5.163	8.813			0.105	8.200
90	170	12.077	1.567	2.847	3	<2	0.040	1.433
75	200	1.759	0.359	0.919			0.016	0.362
63	230	0.225	0.061	0.252	<1		0.005	0.050
53	270	0.016	0.007	0.057			0.010	0.007
45	325	0.018	0.005	0.022	<1		0.006	0.004
<45	<325	0.080	0.090	0.140			0.050	0.002
***mean* (µm)**		**127.0**	**195.3**	**178.9**			**369.1**	**153.3**

Table 7.6: Chemical and mineralogical compositions as well as physical parameters of staurolite concentrates from Florida, according to ELSNER (1992) and data sheets of several companies.

	Green Cove Springs „Staurolite" Associated Minerals USA Florida, USA	Trail Ridge Du Pont Biasill Florida, USA	Trail Ridge Du Pont Starblast Florida, USA	Trail Ridge Du Pont Coarse Staurolite Florida, USA
Chemical composition (%)				
SiO_2	27.24	28.77	28.16	24.00
TiO_2	3.19	2.95	4.01	11.32
$Zr (Hf)O_2$	0.12	1.49	1.52	0.53
ZnO_2	0.42	0.51	0.54	0.34
Al_2O_3	46.08	47.26	47.05	42.87
Fe_2O_3	15.22	14.07	14.54	16.91
MnO	0.40	0.22	0.24	0.30
MgO	1.96	2.14	1.68	1.01
CaO	2.40	0.16	0.14	0.07
P_2O_5	0.07	0.04	0.06	0.02
Cr	199 ppm	199 ppm	219 ppm	230 ppm
Cu	195 ppm	n.a.	289 ppm	143 ppm
Th	83 ppm	29 ppm	79 ppm	<10 ppm
U	<5 ppm	<5 ppm	19 ppm	11 ppm
V	189 ppm	186 ppm	169 ppm	275 ppm
Zr	837 ppm	10481 ppm	10987 ppm	3833 ppm
LOI	1.76	1.40	1.60	1.86
Mineralogical composition (% by mass)				
Monazite/xenotime	0.5	0.1	0.1	
Zircon	0.4	2.8	2.5	0.7
Rutile/anatase	0.6	1.0	+	0.1
Ilmenite	6.7	4.4	6.4	28.2
Leucoxene	0.1	2.5	0.3	0.7
Kyanite		1.8	0.4	0.1
Staurolite	71.6	77.3	79.0	67.1
Hornblende	0.4			
Tourmaline	1.9	6.3	8.9	0.6
Sillimanite		1.3	0.1	0.1
Topaz		+	+	
Corundum		0.2		0.2
Garnet	2.2	+		0.3
Epidote	15.0	0.2		
Spinel (gahnite)	0.6	0.7	1.1	0.4
Quartz	+	1.4	1.2	1.5
Quartz-guaranteed		<5	<5	
Physical parameters				
AFS no$^{1)}$	103	73	67	
Apparent density (g/cm^3)		3.8-3.85	3.6–3.85	
Bulk density (kg/m^3)		2080	2080	
MOHS hardness		6.5-7.0	6.5-7.0	
Melting point (°c)		1370-1540		
Linear extension (cm/cm °c)		14.2×10^{-6}		

[1)] GARNAR (1989), The AFS-number is a metric developed by the AFS (American Foundrymen´s Society) for characterizing the grain refinement of foundry sand.

7.6 Size of deposits and resources

As staurolite is only produced as a by-product and is only economically produced from placer deposits in which it forms a large proportion of the mineral spectrum, deposits are not differentiated according to their sizes.

Please refer to Table 7.7 which compiles the small amount of data available on placer deposits containing higher percentages of staurolite.

The global reserves and resources of staurolite are not known. From a processing point of view, there are no restrictions to the extraction of staurolite from any placer deposits in which it is found.

Table 7.7: Deposit geological data of placers with high contents of staurolite.

Country	Region of deposit	Occurrence	HM-percentage in the ore sand (% by mass)	Percentage of staurolite in the HM-concentrate (% by mass)	Total reserves and resources of staurolite as of: end 2003 (kilotonnes)
Australia	Western Australia	Cooljarloo [3]	3.1	average 5	934
Ukraine	Dnepropetrovsk	Malyshev	10-19	average 20	~1,100?
USA	Florida	Trail Ridge	3.9	17.2	~5,500
		Green Cove Springs	6.1	10.3	[2]
		Yulee [1]	3.1	12.2	546
		Amelia Island [1]	average 4	6.9	~60
	Georgia	Altama	4.6	5.2	155
	N. Carolina/Virginia	various	average 6	8.5	~1,900

[1] not mineable because of competing usage [2] completely exploited [3] extraction since 1998

7.7 Important producing countries

Staurolite is currently only produced in three deposits (cf. Table 7.8):

Table 7.8: Producers of staurolite.

Country	USA	Ukraine	Australia
Region	Florida	Dnepropetrovsk	Western Australia
Occurrence	Trail Ridge	Malyshev	Cooljarloo
Company	E.I. du Pont de Nemours & Co	Volnogorsk State Mining and Metallurgical Plant	Tiwest Joint Venture
Volume	100,000 tonnes/year	100,000 tonnes/year	20,000 tonnes/year
Production	1990: ~50,000 tonnes 1994: ~68,000 tonnes	1990: ~50,000 tonnes 1994: ~68,000 tonnes 1998: ~15,000 tonnes 2003: ~25,000 tonnes	2001: 1,021 tonnes 2002: 2,120 tonnes 2003: 2,129 tonnes 2004: 739 tonnes 2005: 5,626 tonnes

According to ANONYMOUS (2000) the Hernic-Group planned to concentrate the staurolite accumulating when treating andalusite ore in its Hoogenoeg mine in South Africa and to market it as a blasting abrasive with an addition of 20 % by mass of garnet.

7.8 Literature

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8 Garnet

[Deutsch: *Granat*, Spanish: *granata*, French: *grenet*]

8.1 Mineralogy, petrography, chemistry

The garnet group comprises several minerals, which all constitute neso-silicates from a mineralogical point of view. All garnets are based on the general structural formula $X_3Y_2\ [ZO_4]_3$. In most cases in nature they are:

$X = Mg, Fe^{2+}, Mn^{2+}, Ca$
$Y = Al, Fe^{3+}, Cr^{3+}$, rarely Mn^{3+}, V^{3+}, Zr, Ti
$Z = Si$, more rarely Al, Fe^{3+}, Ti
or rarely instead of $[ZO_4]$ $(OH)_4$

The naturally occurring garnets and their properties are listed in Table 8.1.

Table 8.1: Naturally occurring garnets and their most important properties according to Weise (1995), revised according to Nickel & Nichols (2009).

Mineral	Chemical formula	Color	Mohs hardness	Density (g/cm^3)	Distribution
Almandine	$Fe^{2+}{}_3Al_2[SiO_4]_3$	brownish red, black-red	7-7.5	4.32	very frequent
Andradite	$Ca_3Fe^{3+}{}_2\ [SiO_4]_3$	brown, green-yellow, black	6.5-7	3.86	frequent
Calderite	$Mn^{2+}{}_3Fe^{3+}{}_2\ [SiO_4]_3$	dark yellow, reddish yellow	6-7	4.46	very rare
Goldmanite	$Ca_3V^{3+}{}_2\ [SiO_4]_3$	dark green, brownish green	6-7	3.74	very rare
Grossular	$Ca_3Al_2[SiO_4]_3$	colorless, yellow, brown, pinkish red	6.5-7	3.59	frequent
Henritermierite	$Ca_3(Mn^{3+})_2[(SiO_4)_2(OH)_4]$	orange brown	3-4	3.34	very rare
Hibschite	$Ca_3Al_2[(SiO_4)_{3-x}(OH)_{4x}]$ $(x=0.2-1.5)$	colorless, white	6-6.5	3.20	rare
Katoite	$Ca_3Al_2[(SiO_4)_{3-x}(OH)_{4x}]$ $(x=1.5-3.0)$	milky white, colorless	5-6	2.76	very rare
Kimzeyite	$Ca(Zr,Ti)_2[(Si,Al,Fe^{3+})O_4]_3$	dark brown	7	3.85	rare
Knorringite	$Mg_3Cr_2[SiO_4]_3$	green, blue green	6-7	3.83	very rare
Majorite	$Mg_3(Fe^{2+},Si)_2[SiO_4]_3$	magenta, yellow brown	7-7.5	3.76	very rare
Morimotoite	$Ca_3(Ti,Fe^{2+},Fe^{3+})_2$ $[(Si, Fe^{3+})O_4]_3$	black	7.5	3.75	very rare
Pyrope	$Mg_3Al_2[SiO_4]_3$	blood red, black red	7-7.5	3.58	relatively rare
Schorlomite	$Ca_3(Ti,Fe^{3+})_2[(Si,Fe^{3+})O_4]_3$	brown black, pitch black	7-7.5	3.76	rarely
Spessartine	$(Mn^{2+})_3Al_2[SiO_4]_3$	brown red, dark red	7-7.5	4.19	frequent
Uvarovite	$Ca_3Cr_2[SiO_4]_3$	emerald green	7-7.5	3.82	rare

All garnets crystallize in the cubic system, only henritermierite crystallizes tetragonally.

All garnets lack fissility. The fracture is usually conchiform up to splintery or brittle. There are major differences in the magnetic and electrostatic properties of garnets which are important for their processing. These properties reflect their chemical composition (cf. Table 8.2). Almandine, the most frequently occurring garnet, is paramagnetic.

All garnets form mixed compositions and/or mixed crystals with each other. Pure garnets are very rare in nature. 99 % of all garnets are mixed crystals of the five final members: grossular, andradite, pyrope, almandine and spessartine. Two series of garnets are completely mixable with each other:

- Mg-Fe-Mn-aluminum garnets: pyrope-almandine-spessartine, called: pyralspite
  as well as
- Calcium-Cr-Al-Fe garnets: uvarovite-grossular-andradite, called: ugrandite

Mixed garnet crystals are correctly designated, e. g. as pyrope-almandine-grossular mixed crystal or as grossular-bearing almandine-rich pyrope, with the proportion pyrope>almandine >grossular.

The most frequently occurring garnets form mixed crystals as follows:

- almandine in particular with pyrope and spessartine (pyralspite),
- andradite with grossular, uvarovite, the titaniferous garnets and hydro-andradite,
- grossular with andradite, uvarovite and katoite and frequently partly in metamorphic almandine and pyrope mixed crystals,
- pyrope preferably with almandine and knorringite, but also grossular,
- spessartine preferably with almandine, but also with grossular and secondarily also with andradite, pyrope and calderite,
- uvarovite with grossular, but also with andradite, pyrope, and knorringite.

Table 8.2: Chemical composition (%) of the six most frequent garnets.

	Almandine	Pyrope	Grossular	Spessartine	Andradite	Uvarovite
SiO_2	36.22	44.71	40.02	36.41	35.47	36.02
Al_2O_3	20.48	25.29	22.63	20.60		
Fe_2O_3					31.42	
Cr_2O_3						30.37
FeO	43.30					
CaO			37.35		33.11	33.61
MgO		30.00				
MnO				42.99		

The trace elements and inclusions most frequently occurring in garnets are listed in Table 8.3.

Table 8.3: Trace elements and inclusions in garnets according to WEISE (1995) and KOIVULA (1993).

Mineral	Trace elements	Inclusions
Almandine	Na, K, Cr, V, very rarely: Sc, Y, Eu, Yb, Hf, Th, U	rutile, zircon, also: apatite, biotite, monazite, chalcopyrite, mica, ilmenite, plagioclase and sphalerite
Andradite	Mn, V, Cr, Na, K, SE, Sn, F, Ti	byssolite, tremolite-actinolite
Grossular	Fe, Mn, Cr, V, Na, Ni, Sn, SE	actinolite, apatite, calcite, diopside, graphite, pyrite, scapolite
Pyrope	Cr, Fe, in eclogites also Na, K, P, V, Ni, Sc, Yb, Lu	diopside, forsterite, rutile, diamond
Spessartine	As, Cd, Co, Ga, Ge, Mo, Sc, V, Fe, Y (up to 2 % by mass Y_2O_3), Zn, Sn amongst others	mainly liquids and gases
Uvarovite	Fe, Ti, Mg, Na, Ni, K, Mn	

Due to their relative susceptibility to chemical weathering (e.g. humic acids), solution pits are frequently observed on garnet grains.

Additional designations of garnets, which frequently have jewelry quality, are:

- demantoide: an andradite colored yellow-green by chromium
- hessonite: a grossular colored yellow to deep red (opaque) by ferric iron
- melanite (name not officially recognized): a Ca-Fe-Ti-garnet of very dark color; Ti-rich variant of andradite.
- rhodolite: a mixed crystal consisting of pyrope-almandine. With increasing Mg/Fe-ratio its color changes from dark red via rose-colored to red-violet
- tsavorite: a nearly pure grossular, which is colored dark green to emerald green because of small percentages of vanadium and chromium

8.2 Formation of deposits

The occurrences of the garnets (cf. Table 8.4) in the order of their incidence are:

Almandine is a characteristic mineral of numerous metamorphic rocks such as amphibolites, granulites, eclogites and gneisses where it frequently occurs together with biotite as another Mg-Fe mineral. Like all pyralspites, almandine is formed in the epizonal, but particularly in the mesozonal to katazonal regional metamorphosis of Al-rich pelitic up to gabbroic parent rock material. Garnets rich in almandine can, however, also be found in magmatic rocks such as granites and granite pegmatites. The highest percentage of almandine ever measured in a garnet is 86.7 %.

Grossular is very common and occurs in many metamorphic rocks, e.g. lime-silicate rocks, marbles, garnet rocks and skarns. Like all ugrandites, grossular is also bound to basic to ultra-basic parent rock material rich in Ca, Si and Al. The highest percentage of grossular ever measured in a garnet is 97 %.

Andradite is very stable and relatively common. Garnets rich in andradite occur in chlorite schists, lime silicate rock, marbles, serpentinites and skarns. The highest percentage of andradite ever measured in a garnet is 100 %. Mixed crystals of andradite and uvarovite can be found in metamorphic chromite deposits and serpentinites.

Pyrope is only stable at pressures >11 kbar (corresponds to a depth of 36 km). It occurs globally only in rocks which were formed at high pressure, e.g. eclogites, peridotites and kimberlites. Garnets rich in pyrope from high grade metamorphic rocks typically contain 40-70 % pyrope with remaining contents of mostly almandine, sometimes also grossular. The highest percentage of pyrope ever measured in a garnet is 97 %.

Table 8.4: Average molar fractions (%) of the pure final elements of the five most frequently occurring garnets in different types of rocks according to WRIGHT (1938).

Type of rock	Almandine	Pyrope	Spessartine	Grossular	Andradite
Pegmatites	41.8		47.1		
Granites	56.8		36.0		
Siliceous contact rocks	56.4		30.7		
Biotite schists	73.0	13.8		6.0	
Amphibolite schists	53.6	20.3		20.7	
Eclogites	39.1	37.4		18.5	
Kimberlites and peridotites	13.4	72.3		9.0	
Different basic rocks	34.4	20.7		28.7	15.6
Calcareous contact rocks				51.5	40.8

Spessartine is not a common garnet and occurs mainly in gneisses, quarzites, schists and skarns. Garnets rich in spessartine also occur in granite pegmatites. The highest percentage of spessartine ever measured in a garnet is 97 %.

Uvarovite preferably occurs in metamorphic chromite deposits, more rarely also in metamorphic rocks such as marbles, skarns and lime silicate rocks. The purest uvarovites with a percentage of 91 % are found in the Outokumpu metamorphic chromite deposit in Finland.

Katoite is the garnet with the lowest thermal stability. It forms in aqueous solutions at room temperature. Grossular-katoite mixed crystals are very common and occur in metamorphic rocks, which have formed at low temperatures (hydrated lime silicate rock, garnet rocks and skarn).

The titanium garnets **melanite** and **schorlomite** number amongst the few garnets which can crystallize from magma and thus preferably occur in Si-undersaturated rocks (nepheline syenites, phonolites). Melanite, which occurs much more frequently than schorlomite, can also be found in metamorphic rocks, for instance in serpentinites and skarns.

Calderite is a rare component of garnets of metamorphic and highly oxidized rocks rich in manganese. Its proportion in garnet mixed crystals increases with increasing pressure. Pure calderite is only stable at pressures >30 kbar (corresponds to a depth of 100 km).

Goldmanite is a rare garnet of metamorphic rocks with high vanadium contents.

Henritermierite is a rare mineral which originates in manganese-rich rocks as a late hydrothermal product at low temperatures.

Kimzeyite also crystallizes directly from magma and thus occurs exclusively in silica-undersaturated magmatic rocks (nepheline syenites, carbonatites and phonolites).

Morimotoite is very rare and forms only in skarns of monzonites. Only identified in Japan to date.

Knorringite is only stable at pressures >80 kbar (corresponds to a depth of 270 km). In nature it thus only occurs in rocks which have formed under the high pressures of the Earth's upper mantle (kimberlites). Knorringite is thus an index mineral for diamond prospecting.

Majorite is only stable at pressures >135 kbar. Hitherto it has only been observed in meteorites and is generated by the high-pressure conversion of orthopyroxene and olivine, caused by collisions between larger cosmic bodies.

8.3 Applications

- The main application (80 %) of industrial garnets is sandblasting and related purposes (*abrasives*), reflecting their properties:
- relatively high apparent density (fast sedimentation = good visibility),
- roundish to semi-angular grain shape and/or wedge-shaped fractures,
- low to absent quartz content (in the concentrate),
- free of heavy metals,
- non hygroscopic (free influx of material),
- sufficiently high melting point (pure almandine: 1,313-1,318 ^{o}C),
- ecological compatibility and/or non-toxicity,
- recyclability (according to company information 3-10 times)
- relatively high chemical and physical resistance

For this purpose, almandine, followed by andradite, has the best ratio of hardness, density, dynamic viscosity and melting resistance. In the US in some cases the garnet grains are cleaned using calcination (quick firing).

Globally approx. 50-55 % of the traded industrial garnets are used as **abrasives** (*blasting agent*) for shot blasting or sand blasting of plane components, bridges, railroad cars and containers, on *offshore*-platforms and in industrial plant manufacturing (removal of rubber, paint, adhesives, bitumen and grease), in shipbuilding (removal of salt, rust, algae and shell incrustations), in the petrochemical industry for pipeline, tank and boiler cleaning (removal of incrustations of all kinds), in power station development as well as for finishing jeans (gentle removal of the dyestuff). To this end, garnet is the main substitute of quartz sand, which is used increasingly rarely for blasting because of the silicosis risk. Table 8.5 contains a general review of properties and prices of different abrasive traded in the market.

Table 8.5: **Properties and prices of different abrasives, source: Company information Kurt Freytag Handel GmbH, Hamburg-Rostock.**

Abrasive	Grain shape	Color	Mohs hardness	Available grain sizes	Apparent density (g/cm^3)	Bulk density ($tonnes/m^3$)	Price [12] (€ per ton)	Recyclability
Garnet[1]	angular	red	7.0	0.05-1.20 mm	4.1	2.38	175.-260	5-9-fold
Copper slag[1]	angular	black	7.0	0.20-2.80 mm	3.7	1.85	72.75-74.75	no
Al-silicate coal furnace slag[1]	angular	black-brownish	7.0	0.20-2.20 mm	2.5	1.30	56.25	no
Stainless steel blasting shot [2]	round	silver	62 HRC[13]	0.05-0.80 mm	7.4	4.70	165	100-fold
Limestone [3]	angular	cream	2.5-3	0.05-0.20 mm	2.8	0.70	220	no
Dolomite brick [4]	angular	white	3.5	0.30-0.60 mm	2.85	1.50	225	no
Glass bead shot[5]	angular	white	5-7	65-600 µm	2.45	1.30	680	no
Synthetic aluminum oxide abrasive [6]	angular	black-brownish	9.0	0.075-2.30 mm	4.0	1.70	560-600	10-30-fold
Synthetic special fused aluminum oxide abrasive [6]	angular	white	9.0	0.05-2.00 mm	3.94	1.70	1,000-1,120	10-30-fold
Ceramic beads[5]	round	white	9.0	0-850 µm	3.85	2.30	8,350	yes
Nutshells[7]	angular	brown	2.5	0.45-4.0 mm	0.95	0.72	885	yes
Carbamide resin granulate [8]	angular	multi-colored	3.5	0.15-1.68 mm	1.5	0.77	6,415	yes
Melamine resin granulate [8]	angular	multi-colored	4.0	0.15-1.68 mm	1.5	0.77	7,120	yes
Cast iron granulate[9]	angular	gray	61-65 HRC[13]	0.18-1.25 mm	8.0	3.80	460-585	150-fold
Steel blasting grains [9]	angular	gray	62-66 HRC[13]	0.10-1.20 mm	8.0	3.80	620-680	300-fold
Steel blasting shot [10]	round	gray	40-55 HRC[13]	0.20-2.00 mm	8.0	3.80	680	200-fold
Stainless steel blasting grains [11]	angular	silver	62 HRC[13]	0.05-3.00 mm	7.4	4.70	7,835-9,655	150-fold
Stainless steel blasting shot [2]	round	silver	62 HRC[13]	0.10-3.00 mm	7.4	4.70	4,310-4,800	100-fold

[1] For the removal of rust, scale and paint from steel structures, bridges, railroad cars, vessels, containers and machines, Foundry industry [2] For cleaning and surface treatment ("*shot peeling*") of stainless steel and base metals [3] For concrete repair and preservation of structures, in particular removal of graffiti [4] For the removal of weathering on sand-lime bricks [5] For the surface refinement of stainless steel and aluminum components [6] For the removal of rust, scale and paint in blasting cubicles, if non-ferrous abrasives are required [7] For gentle surface cleaning and for deburring plastic components [8] For gentle surface cleaning and for deburring parts made of Al, Zn and Mg [9] For the removal of thick rust, old paint coatings and for pre-treatment when metallizing in blasting halls [10] For use in centrifugal blasting machines for surface compaction, deburring and cleaning of steel sections, steel plates and cast iron [11] For cleaning stainless steel and base metals [12] As of: November 2004 [13] Rockwell hardness in accordance with DIN 10004

The blasting properties of garnet in comparison with other abrasives are listed in Table 8.6.

Table 8.6: Blasting properties of garnet in comparison with other abrasives (O`DRISCOLL 1993).

Abrasive	Grain size (µm)	Cleaning rate (m^2/hour)	Consumption (kg/hour)	Profile (mm)	Recyclability (1 x / 3 x)[1)]
Garnet	180	21	290	0.02	-
	250	18	238	0.02	0.61 / 0.38
Staurolite	210	22	272	0.02	0.77 / 0.45
Metal shot	180	14	318	0.04	-
		0.42	11	340	0.05
Slag	300	15	340	0.03	-
Fused alumina	600	16	302	0.02	0.80 / 0.61
	200/300	21	261	0.03	-
	150/180	23	245	0.02	-
Flint		11	236	0.03	0.58 / 0.32

[1)] Percentage of the original amount that can be re-used

A totally different area of application, used in the US in particular (proportion approx. 20 %), is **water filtration.** For this purpose garnet is used as a dense medium for stabilizing the up to 1 m thick filtration layer. An additional advantage is its physical and chemical resilience during filtration as well as during back-flushing.

A typical filtration layer in the US is built up as follows – from top to bottom:

Filtration medium	Apparent density (g/cm^3)	Grain size (mm)	Layer thickness (cm)
Anthracite	1.4	1.0-2.5	40-60
Quartz sand	2.65	0.4-1.0	20-30
Garnet	3.8-4.2	0.2-0.6 and 1.0-1.4	10-30
Gravel bed			

Approx. 52 tonnes of garnet are required for a 75 m^2 filtration tank. It only has to be replaced after approx. 20-25 years.

In Europe, filtration layers usually contain other materials (cf. Table 8.7) because garnet, which has to be imported, is too expensive. Activated carbon or diatomite is preferably used instead of anthracite.

Table 8.7: Properties of different filtration media, according to Carr & Herz (1989).

Mineral	Property	Bulk density (tonnes/m^3)	Specific surface area (m^2/g)	Flow rate (m^3/m^2 x h)
Garnet		1.6-2.0	-	5-50
Quartz sand	fine grained	1.0-1.3	0.10-0.02	5
	medium grained	1.0-1.3	0.01-0.02	12
	coarse grained	1.0-1.3	0.01-0.02	50
Diatomite	natural	0.25-0.37	10-30	0.16-2.0
	calcined	0.25-0.33	3-7	0.04-2.0
	melt calcined	0.29-0.37	0.5-5	0.04-4.9
Perlite	expanded	0.13-0.28	1	0.05-4.0
Asbestos	chrysotile	0.8-1.2	4-50	0.10-2.0

Approx. 16 % of industrial garnets are used as additives for *water-jet cutting* in the US. For this method, which is gaining in importance, water at pressures of up to >4,100 bar (410 Mpa) is forced through a small nozzle (diameter 0.07 – 0.4 mm) attaining exit velocities of 3,200 km/h. This process can be used to cut materials such as steel, titanium, aluminum, logs and boards, laminate, plastics, fabric, paper rolls, circuit boards, fiber optic cables, mixed materials, glass, stone, tiles and ceramics with average thicknesses of 0.5–5 (<30) cm. The cutting behavior can be improved by adding fine-grained garnet (mean grain size 0.125 – 0.180 mm (corresponding to *80 mesh*) at a constant rate of 1-10 kg/min to the water jet. It is either sucked in by negative pressure (*entrainment system*) or injected (*direct injection*). Water jet cutting can also be conducted under water.

The advantages of water jet cutting are:

- no dust generation,
- no heat generation,
- no sparking,
- high cutting speed,
- small cutting width (little cutting waste),
- any contour can be cut, from many directions,
- no mechanical stress on brittle material such as ceramics or marble.

On the other hand the disadvantages of water jet cutting are:

- high technical specifications (high pressure components) and investment costs
- conicity of the cutting edge (cf. laser and plasma arc cutting)
- grooving at the cutting edge at higher feed rates
- risk of corrosion of the components

Approx. 11 % of the industrial garnets in the US are used for the production of coated abrasives. This includes sand paper, grinding wheels, grinding rollers, abrasive bands, abrasive discs, abrasive sleeves and belts. Depending on accessibility and the surface, this allows the preprocessing and finishing of very different materials such as wood, leather, hard rubber, plastic, glass, aluminum, steel, etc.

In the US, sandpaper is categorized in accordance with its grit, (number of grains per square inch), in Europe in accordance with their grain size. The following applies: the smaller the value, the less aggregate per unit area, the coarser the abrasive. In addition, scatter density (substrate not visible) and open scatter density (spacing between the abrasive grains for accommodating swarf and loose abrasive) are differentiated.

Approx. 1 % of the garnet is processed in powdered form into a **polishing paste or powder** (15-25 µm) for lapping and polishing. This is mainly used for polishing special types of glass, such as TV screens. But car paint polishes and toothpaste may also contain micronized garnet.

Other, quantitatively insignificant uses of industrial garnet are:

- lapidary substrate for tumbling and polishing minerals,
- grit,
- weighting agent on oil platforms,
- playing ground surfacing materials,
- weighting additive for concrete for airport runways,
- filtration medium in waste incineration plants.

All garnet concentrates are subject to very strict grain size controls, and compete in a large, highly competitive market (cf. Chapter 8.4).

8.4 Substitutes

Due to its non-toxicity and its recyclability, and independent of its limited global availability and its relatively high price, garnet is mainly a substitute for quartz sand, which is increasingly shunned because of its silicosis hazard. But garnet can also be easily replaced by other minerals, as listed below:

- blasting abrasive: fused alumina, corundum, emery, feldspar, hematite spheres, magnetite, nepheline syenite, chopped pits and nutshells, olivine, perlite, pumice, quartz sand, different slags, steel shot, staurolite, silicon carbide, ilmenite.
- abrasive: fused alumina, silicon carbide, corundum, emery.
- jet cutting: no additive (for softer products), aluminum oxide, olivine, silicon carbide, different artificial products.
- polishes: ceroxide, diamond, fused alumina, silicon carbide, pumice, tripoli.
- filtration media: activated carbon /anthracite, asbestos, cellulose, diatomite, magnetite, olivine, perlite, pumice, quartz sand, ilmenite.
- grit: quartz sand.

8.5 Specifications for the raw materials (reference values)

The following specifications have been set for industrial garnet:

General:

- hardness as high as possible (ideal: almandine) and high dynamic viscosity, i.e. resistance to shattering (ideal: almandine, pyrope),
- in the concentrate >97 % by mass garnet and as little free quartz as possible. A higher concentration of staurolite is permissible as it has similar physical and chemical properties (cf. Chapter 7.3),
- grains without fractures and without inclusions,
- concentrates (of heavy mineral placers) without associated radioactive minerals,
- primary garnet (from bedrock) as pure and large as possible, to be able to produce different grain sizes of industrial garnet by crushing. The garnet should not be weathered. It must have a constant bulk density and hardness. The fracture behavior, the dynamic viscosity, the capillarity and the crystal size have to be determined.

Filtration media:

- clean grains,
- bulk density of the garnet $\geq$4.0 g/cm^3,
- angular to rounded grains,
- narrow grain size band of the concentrate.

Blasting abrasives:

- grains as idiomorphic-cubic as possible, not blunt or rounded,
- already cracked grains with long flat sides are unwanted,
- content of water-soluble chlorides <25 ppm.

The basis of the evaluation of blasting abrasives and reference results from the investigation of Greek dolomite brick with olivine and garnet listed by LABARKIS et al. (2002).

Jet cutting:

- constant grain size and a very narrow band of grain sizes of the concentrate.

Specifications for almandine when used as a blasting abrasive are regulated in Germany by ISO 11126-10:2000 (cf. Table 8.8).

General specifications (ISO 11126-10:2000):

- blasting abrasives of almandine garnet are naturally occurring mineral grains which may not absorb water, but which are wettable at their surface.
- the proportion of free quartz in the blasting abrasive must not exceed 1.0 % by mass, testing method: RDA.
- the blasting abrasive has to be free of corrosive impurities, and impurities which may influence adhesion.

Table 8.8: Specifications for almandine used as a blasting abrasive in accordance with ISO 11126-10:2000.

<table>
<tr><td colspan="3">Property</td><td colspan="3">Unit</td><td colspan="3">Requirement</td><td colspan="3">Testing method</td></tr>
<tr><td colspan="3">Grain size distribution</td><td colspan="3"></td><td colspan="3">cf. below</td><td colspan="3">ISO 11127-2</td></tr>
<tr><td colspan="3" rowspan="2">Density</td><td colspan="3">kg/m^3</td><td colspan="3">(4,0-4,2) x 10^3</td><td colspan="3">ISO 11127-3</td></tr>
<tr><td colspan="3">[kg/dm^3]</td><td colspan="3">4,0-4,2</td><td colspan="3"></td></tr>
<tr><td colspan="3">MOHS hardness1)</td><td colspan="3"></td><td colspan="3">≥6</td><td colspan="3">ISO 11127-4</td></tr>
<tr><td colspan="3">Humidity</td><td colspan="3">%</td><td colspan="3">≤0,2</td><td colspan="3">ISO 11127-5</td></tr>
<tr><td colspan="3">Conductivity of the water extract</td><td colspan="3">mS/m</td><td colspan="3">≥25</td><td colspan="3">ISO 11127-6</td></tr>
<tr><td colspan="3">Chlorides soluble in water</td><td colspan="3">%</td><td colspan="3">≤0,002</td><td colspan="3">ISO 11127-7</td></tr>
<tr><td colspan="2">Grain size2)</td><td>mm</td><td>0.2-0.5</td><td>0.2-1.0</td><td>0.2-1.4</td><td>0.2-2.0</td><td>0.2-2.8</td><td>0.5-1.0</td><td>0.5-1.4</td><td>1.0-2.0</td><td>1.4-2.8</td></tr>
<tr><td rowspan="2">Oversized particles</td><td>screen set</td><td>mm</td><td>0.5</td><td>1</td><td>1.4</td><td>2</td><td>2.8</td><td>1</td><td>1.4</td><td>2</td><td>2.8</td></tr>
<tr><td>residue</td><td>%</td><td>≤10</td><td>≤10</td><td>≤10</td><td>≤10</td><td>≤10</td><td>≤10</td><td>≤10</td><td>≤10</td><td>≤10</td></tr>
<tr><td rowspan="2">Nominal size</td><td>screen set</td><td>mm</td><td>0.2</td><td>0.2</td><td>0.2</td><td>0.2</td><td>0.2</td><td>0.5</td><td>0.5</td><td>1</td><td>1.4</td></tr>
<tr><td>residue</td><td>%</td><td>≥85</td><td>≥85</td><td>≥85</td><td>≥85</td><td>≥85</td><td>≥80</td><td>≥80</td><td>≥80</td><td>≥80</td></tr>
<tr><td rowspan="2">Undersized particles</td><td>screen set</td><td>mm</td><td>0.2</td><td>0.2</td><td>0.2</td><td>0.2</td><td>0.2</td><td>0.5</td><td>0.5</td><td>1</td><td>1.4</td></tr>
<tr><td>pass</td><td>%</td><td>≤5</td><td>≤5</td><td>≤5</td><td>≤5</td><td>≤5</td><td>≤10</td><td>≤10</td><td>≤10</td><td>≤10</td></tr>
</table>

1) The parties can agree to use a different testing method for determining the hardness of different specifications 2) The parties can agree that blasting abrasives of different grain size can be mixed. Details of the ratio of oversized particles, nominal size and undersized particles have to be specified. The maximum grain size may not exceed 3.15 mm. The amount of undersized particles may not exceed 5 %.

Tables 8.9-8.16 list the data on grain size distributions, mineralogical compositions and physical parameters of garnet-concentrates for different applications.

Table 8.9: Grain size distribution (% by mass, screen residue) of garnet for sand paper.

Gap (µm)	Tyler *mesh*	Barton Mines Company, L.L.C., New York									
		36	40	50	60	80	100	120	150	180	220
600	28	36	0								
500	32	53	12	0							
420	35	10	50	3							
355	42	1	34	40	2						
300	48	0	3	47	23						
250	60		1	9	46	10					
210	65			1	22	30	1				
180	80				6	30	6				
150	100					17	27	3			
125	115					9	39	18	1		
105	150					3	18	40	8	1	
90	170						8	29	50	13	1
75	200							8	33	48	14
63	250							1	7	27	46
53	270								1	8	24
45	325									2	11
38	400										4

Table 8.10: Grain size distribution (% by mass, screen residue) of garnet for different applications, source: company information.

Producer			V.V. Mineral, India								Wuxi Ding-Long Trading Co., Ltd., China [1]			
Application			water filtration		-		jet cutting				construction of playing grounds	sand blasting		
			-	sand blasting		-	sand blasting	-	sand blasting					
			product name											
Gap (mm)	ASTM *mesh*	Tyler *mesh*	A+	A	B	C+	C	D+	D	E	Synogarnet-GA	Synogarnet-1	Synogarnet-2	Synogarnet-3
2,360	8	8									0	0	0	0
2,000	10	9												
1,700	12	10	1.17											
1,400	14	12	11.58	0.12								<5		
1,180	16	14										>90		
1,000	18	16	74.21	19.58										
0,850	20	20	8.36	46.88	0.17	0.14					<15		<5	
0,700	25	24	4.68	33.10	31.25	12.70					>70	<5		
0,600	30	28					1.20					0	>90	<5
0,500	35	32		0.32	60.68	32.40	28.50	0.02						>90
0,420	40	35												
0,355	45	42			7.90	44.62	53.20	46.30	4.20				<5	
0,300	50	48												
0,250	60	60				7.54	14.60	37.70	48.00	1.53	<15		0	<5
0,210	70	65				2.60	2.50	15.64	44.00	51.87	0			0
0,180	80	80												
0,150	100	100						0.34	3.80	39.54				
0,125	120	115												
0,105	140	150								4.35				
0,090	170	170								2.71				

[1] guaranteed grain size composition

Table 8.11: Grain size distributions (% by mass, screen residue) of garnets for jet cutting, source: company information.

Producer			Barton Mines Company, L.L.C. New York									GMA garnet Pty Ltd. Port Gregory, Australia				Wuxi Ding-Long Trading Co., Ltd., China		Indian Ocean garnet Sands Co. Pvt. Ltd. India		
Trade name			Barton garnet[1]									GMA garnet				Sino garnet		POWER garnet		
			Product name																	
Gap (µm)	ASTM *mesh*	Tyler *mesh*	50 HPX	60 HPA	80 HPX	80 HPA	85 HPX	100 HPA	120 HPX	150 HPX	220 HPX	50#	60#	80#	100/120#	G 80	G 120	1	2	3
600	30	28														0		0.1		
500	35	32	1.0													0-0.5		33.7		
420	40	35	16.0									2-12				0-1.0				
355	45	42	37.0	10.0	3.0		3.0					60-80				10-25		56.3		
300	50	48	29.0	28.0	15.0	7.0	9.0						20-40	2-7	0-0.5				0.9	
250	60	60	15.0	38.0	31.0	38.0	15.0					8-20	20-40	25-45	0-0.5	20-40		9.8	27.5	
210	70	65	2.0	16.0	24.0	30.0	14.0	5.0	2.0			2-12	20-45	40-60	40-65	10-30	0-5	0.1	30.6	
180	80	80		7.0	17.0	20.0	15.0	50.0	1.0			0-0.5	0-5	2-10	20-50	8-20	10-20		29.5	0
150	100	100		7.0	7.0	5.0	21.0	35.0	30.0	1.0			0-1	0-1	6-14	5-15	25-40		11.5	66.0
125	120	115		5.0	3.0		15.0	8.0	28.0	14.0	5.0			0-1	1-4	0-5	25-40			30.0
105	140	150					6.0	2.0	16.0	38.0	8.0				0-1		0-10			4.0
90	170	170					2.0		7.0	27.0	24.0						0-5			
75	200	200							6.0	14.0	25.0									
63	230	250								4.0	18.0									
53	270	270								1.0	7.0									
45	325	325								1.0	3.0									

[1] HPX (High Performance Crystal) = garnet from bedrock, HPA (High Performance Alluvial) = garnet from placers

Table 8.12: Grain size distributions (% by mass, screen residue) and physical parameters of garnet for water filtration, source: company information.

Producer			Emerald Creek garnet Milling Co. Inc. Idaho, USA (HARBEN 2002)								African Pegmatite (Pty) Ltd. Rep. South Africa			
			Product name											
Gap (mm)	ASTM *mesh*	Tyler *mesh*	#8	#8/12	#12	#36	#30/40	#50X	#60	#100	0.4– 0.8 mm	0.6 – 1.0 mm	0.6 – 1.7 mm	3.0 – 5.0 mm
5.000											0.0	0.0	0.0	20.31
3.350	6	6	0-10		0-5									78.62
2.800	7	7	50-95		5-30									
2.360	8	8		0-10									0.04	0.97
2.000	10	9	0-20	15-25	20-30									
1.700	12	10	0-5	20-55	20-40									
1.400	14	12		20-50	20-50							0.17	38.91	
1.180	16	14		0-5	0-5	0-2								
1.000	18	16				60-95						0.74	46.48	
0.850	20	20										3.64	11.68	
0.700	25	24										20.12	2.47	
0.600	30	28					0-5	0-5	0-5			45.79	0.16	
0.500	35	32				0-10	20-40	10-20	5-25		0.4	23.21	0.01	
0.420	40	35					30-50	20-45	35-50			4.93	0.0	
0.355	45	42					0-35	15-25	40-50		99.86	1.29		
0.300	50	48					0-5	20-30	0-15					
0.250	60	60						10-20						
0.210	70	65						0-5						
0.180	80	80								0-20				
0.150	100	100								30-45				
0.125	120	115								30-55				
0.105	140	150								0-15				
Physical parameters														
Bulk density (kg/m^3)			2,419	2,387	2,403	2,099	2,003	1,954	1,922	1,746				
Effective grain size (mm)			2.05-2.45	1.40-1.55	1.40-1.70	0.55-0.60	0.35-0.45	0.25-0.30	0.21-0.28	0.10-0.15				
Uniformity coefficient			<1.4	<1.5	<1.5	<1.4	<1.6	<1.6	<1.8	<1.2				

Table 8.13: Grain size distributions (% by mass, screen residue) and mineralogical chemical composition (%) of garnet for sand blasting, source: company information.

Producer			Barnes Environmental Int. Ontario				Barton Mines Company, LLC New York, USA					Indian Ocean garnet Sands Co. Pvt. Ltd. India			
Trade name			Galaxy garnet				Barton garnet					POWER garnet			
			Product name												
Gap (mm)	ASTM *mesh*	Tyler *mesh*	10	30	50	80	Extra Coarse #16	Coarse #36	Medium 30x60	Fine 80 *Mesh*	Extra fine 100 *Mesh*	12 – 25	20 – 40	20 – 60	30 – 60
2.000	10	9	0.1												
1.700	12	10	12.0									1,0			
1.400	14	12	71.1									3,0			
1.180	16	14					4					19,0			
1.000	18	16	14.2				12					9,0			
0.850	20	20					32	1				34,0			
0.700	25	24	2.5				43	12				32,0	1,0	2,0	
0.600	30	28		9.7			8	36					21,0	8,5	
0.500	35	32	0.1	36.7	0.4		1	40	5				46,5	19,0	1,0
0.420	40	35		39.5	5.8	0.2		10	11				28,5	26,0	37,0
0.355	45	42		13.8	46.4	21.0		1	44				3,0	26,0	40,0
0.300	50	48								9				15,5	19,0
0.250	60	60		0.3	31.7	33.7			26	42				3,0	3,0
0.210	70	65		0.1	10.6	26.6			11	31	5				
0.180	80	80			5.0	18.5			3	16	50				
0.150	100	100								2	35				
0.125	120	115									8				
0.105	140	150									2				
Mineralogical composition															
Almandine			98.8	99.4	98.2	97.7									
Ilmenite			<0.1	<0.1	<0.7	<0.8									
Quartz			<0.4	<0.2	<0.5	<0.6									
Others			<0.7	<0.3	<0.6	<0.9									

Table 8.14: Grain size distribution (% by mass, screen residue) and bulk density of garnet for sand blasting (HARBEN 2002).

Gap (mm)	ASTM *mesh*	Emerald Creek Garnet Milling Co. Inc., Idaho, USA												
		#8	#8/12	#12	#16	#25	#36	#30/40	#50X	#60	#80	#100	#150	#250
Typical grain size distribution (% by mass), screen residue														
3.350	6	0-10		0-5										
2.360	8	50-95	0-10	5-30										
2.000	10	0-20												
1.700	12	0-5	35-80	40-70	0-2	0-2								
1.400	14		20-50	20-50	5-40	10-30								
1.180	16		0-5	0-5	30-70	20-30	0-2							
1.000	18				20-40	20-30	10-25							
0.850	20				0-5	5-20	20-35							
0.600	30					5-20	40-60	0-5	0-5					
0.420	40					0-5	0-10	50-90	30-65	0-5				
0.300	50							5-40			0-2			
0.250	60								30-55	80-100	0-20			
0.210	70								0-5	0-15				
0.180	80										45-90	0-20		
0.150	100											30-45		
0.125	120										0-30	30-55	0-20	
0.105	140											0-15	20-30	
0.063	230												50-70	0-15
0.045	325												0-10	15-80
	<325													20-75
Bulk density (kg/m^3)		2,419	2,387	2,403	2,211	2,211	2,163	2,003	1,938	1,922	1,874	1,746	1,666	1,586

Table 8.15: Chemical (%) and mineralogical compositions (%) as well as physical parameters of garnet concentrates, source: company information as well as HARBEN & CULVERT (1997).

	Bengal Bay Garnet Transworld Garnet India Pvt. Ltd. Tamil Nadu, India	**BMC Garnet** Beach Minerals Company India Ltd. Tamil Nadu, India	**IOGS Garnet / POWER Garnet** Indian Ocean Garnet Sands Co. Pvt. Ltd. Tamil Nadu, India	**Super Garnet** V.V. Mineral Tamil Nadu, India	**Sharpjet Garnet** Universal Minerals Inc.	**Granatsand Fastcut** Mädl GBT Tamil Nadu, India	**Sino Garnet** Liang Cheng, Inner Mongolia, China (hard rock)	**GMA Garnet** GMA Garnet Pty Ltd. Port Gregory, Western Australia	**Galaxy Garnet** Barnes Environmental International Rajasthan, India	**Barton Coarse Garnet** Barton Mines Company, LLC New York (hard rock)	**Barton Garnet** Barton Mines Company, LLC India (placers)
Chemical composition											
SiO_2	35		31.00	35.0	33	35	37.20	36.1	36.16	41.34	36
Al_2O_3	34		21.60	21.0	20	23	20.59	20.4	20.14	20.36	20
Fe_2O_3	33			31.0		33	3.73	1.7	29.68	12.55	2
FeO			37.00		36		29.49	29.8		9.72	30
TiO_2			0.55	1.0	3		0.25	1.8	1.45		2
MnO	1		0.53	0.5	2	1	0.64	1.05	0.42	0.85	1
CaO	1		1.84	1.5	2	1	2.02	1.55	7.03	2.97	2
MgO	7		7.40	8.0	4	7	6.09	6.0	5.05	12.35	6
Chloride (ppm)	25		<20	<50		<25	<25	10-15 (<25)	0.75	<50	10-15 (<25)
Mineralogical composition											
Type of garnet	almandine	almandine	almandine	almandine	almandine	almandine	almandine	almandine	almandine	almandine/ pyrope	almandine
Garnet content			97-99	97-98	96		>98	97-98	98.0	>98.0	>97.0
Free quartz	<0.5	<0.5	0	<0.5	<0.5	<0.5	0	<0.5	<0.50	<0.5	<0.1
Physical parameters											
Apparent density (g/cm^3)	4.0-4.1	4.10	4.10	4.10	4.2	4.0-4.1	4.052	4.1	4.0-4.1	4.0	4.1
MOHS hardness	7 ½-8		7 ½-8	8	7 ½-8	7 ½-8	7.96	7 ½-8	8	7 ½	7 ½
Conductance (µs/cm)			<15	10				10-15(<25)	55		0-15 (<25)
Bulk density			2,340	2,400	2,500	2,380	2,403	2,300	2,323	2,099-2,195	2,243-2,403

Table 8.15: continued.

	Garnet OR-Grade OSCOM Indian Rare Earths Ltd. Orissa, India	**Garnet MK-Grade** Manavalakurichi Indian Rare Earths Ltd. Tamil Nadu, India	**Sweetwater Garnet** Sweetwater Garnet Inc. Montana, USA	**Garnet** African Pegmatite (Pty) Ltd.	**Desert Garnet** Olympia Resources Ltd. Harts Range, Northern Territory, Australia	**Garnet** Patterson Materials Corp. Wingdale, NY, USA [1)]	Garnet Almeria, Spain [2)]	Garnet Almeria, Spain [3)]	Garnet Idaho Garnet Abrasive Co. Idaho, USA [4)]	**Luisenfeld Garnet** Newala-Lindi Area, Tanzania [5)]
Chemical composition										
SiO_2		40	36.9	36.9	38.1	39.6	37.06	37.82	39.60	33.94
Al_2O_3	19.8	21	15.5	19.7	19.9	19.9	26.92	19.34	23.55	22.87
Fe_2O_3	3.5	2.9	41.6	29.4	2.2	32.1				0.49
FeO	27.9	26			25.9		32.24	37.12	33.05	19.09
TiO_2	1.3	1.0		2.6	1.1			0.05		0.11
MnO				1.2	1.5		2.93	1.55	2.15	0.81
CaO				4.0	3.8	2.05	1.02	0.99	1.96	4.55
MgO	6.8		6.1	5.8	6.1		1.86	2.80	2.49	12.60
Chloride (ppm)					<25 ppm					
Mineralogical composition										
Type of garnet			almandine		almandine	almandine	almandine	almandine	almandine	almandine-pyrope
Garnet content	94.0	97.2	>92.0		95					
Free quartz	0.2	0.2	<1.0							
Physical parameters										
Apparent density(g/cm^3)	4.25	4.25	3.8-4.2		4.1					
MOHS hardness	6-7	6-7	7 ½		7 ½					
Conductance(µs/cm)					<150					
Bulk density (kg/m^3)	1,950-2,050	2,200-2,300			2,403					

[1)] ANONYMOUS (1994) [2)] LADOO & MYERS (1951) [3)] MUÑOZ-ESPADAS et al. (2000) [4)] ANONYMOUS (1971) [5)] OATES (1931)

Table 8.16: Chemical and mineralogical composition (%) of garnet concentrates.

	Green Cove Springs Titanium Enterprises Florida, USA 1)	Folkston Humphreys Gold Corp. Georgia, USA 1)	Liang Cheng City Sino Garnet Inner Mongolia, China 2)	Tomago Sandbeds RZM Pty Ltd. Newcastle, NSW, Australia 3)	Harts Range Olympia Resources NL Northern Territory, Australia 2)	GMI-Garnet GMA Garnet Pty Ltd. India 3)	GMA-Garnet GMA Garnet Pty Ltd. Port Gregory, Western Australia 3)
Chemical composition							
SiO_2	35.45	30.68	37.2	29.70	38.1	34.70	36.35
Al_2O_3	19.57	18.59	20.59	36.03	19.9	18.42	20.00
Fe_2O_3	32.57	15.97	3.73	13.09	2.2	32.42	34.35
FeO			29.49		25.9		
TiO_2	2.01	3.88	0.25	1.41	1.1	6.19	2.39
MnO	1.05	11.26	0.64	0.60	1.5	0.50	0.95
CaO	2.19	3.13	2.02	0.58	3.8	1.85	1.62
MgO	6.59	0.83	6.09	6.89	6.1	6.35	5.79
Cr_2O_3	298 ppm	189 ppm	438 ppm	2.38		274 ppm	231 ppm
P_2O_5	0.35	4.89	0.0	0.21	0.1	0.06	0.07
Ce	4053 ppm	13618 ppm	<1000 ppm	667 ppm		79 ppm	163 ppm
Ni	9 ppm	706 ppm	100 ppm	541 ppm		13 ppm	< 3 ppm
Pb	59 ppm	121 ppm	10 ppm	60 ppm		15 ppm	6 ppm
Sn	57 ppm	6 ppm	<10 ppm	24 ppm		2 ppm	< 2 ppm
Th	1095 ppm	2144 ppm		219 ppm		47 ppm	63 ppm
U	13 ppm	1102 ppm		74 ppm	2.3 ppm	7 ppm	7 ppm
V	203 ppm	108 ppm	100 ppm	287 ppm		242 ppm	208 ppm
Y	555 ppm	31171 ppm	40 ppm	755 ppm		217 ppm	331 ppm
Zn	277 ppm	1013 ppm	250 ppm	3759 ppm		284 ppm	189 ppm
Zr + Hf	0.10	3.32	100 ppm	3.97		0.05	0.28
LOI	-1.02	1.14		1.31		-1.08	-2.19
Mineralogical composition							
Garnet	85.8	63.4		28.2		82.8	93.9
Almandine	xxx	xxx					
Pyrope	xx	(x)					
Spessartine	x	xx					
Monazite/xenotime	1.0	15.7					0.1
Zircon	0.2	6.9		7.9		+	1.2
Ilmenite/leucoxene	9.5	7.6		1.7		9.5	4.3
Rutile/anatase	0.4	0.2				+	0.4
Kyanite /sillimanite	+	+				0.5	+
Staurolite	0.2	4.2		4.4			0.1
Hornblende	1.1					+	
Tourmaline	0.2			57.7			
Andalusite	0.2						
Topaz	0.1						
Corundum		+					
Epidote	1.1	1.5					
Titanite	+						
Beryl	+						
Spinel	0.1	0.3					
Quartz	+	+		+		6.7	+

1) ELSNER (1992) 2) Company information 3) BGR-Analysis + = traces (x) = very little x = little xx = much xxx = very much

8.6 Size of deposits and resources

Industrial garnet is extracted from placer deposits (*alluvial garnet*) as well as bedrock deposits (*crushed garnet*). Mineable bedrock deposits have the advantage that the garnet is very coarse: which enables sufficient amounts of coarse garnet – for water filtration or sand blasting – to be produced even after crushing. Placers can be mined more easily and frequently carry other extractable valuable minerals, such as ilmenite (cf. Chapter 2), rutile (cf. Chapter 3) or zircon (cf. Chapter 4). There are no qualitative differences between the garnets of one grain size mined from two different types of deposit.

The following standard values apply to the size of placer deposits, where garnet is predominantly mined.

	Placers Mineral content
Small	500,000 – 1 million tonnes
Medium	1 million – 2 million tonnes
Large	2 million – 5 million tonnes
Very large	>5 million tonnes

According to AUSTIN (1994), placer deposits mined mainly for garnet have to contain at least 2 million tonnes of ore sand with a garnet content of >20 % by mass.

Table 8.17 compiles data from different garnet-bearing placer deposits.

Table 8.17: Comparison of garnet-bearing placers.

Country	**Region of deposit**	**Occurrence**	**HM-percentage in the ore sand (% by mass)**	**Percentage of garnet in the HM-concentrate (% by mass)**	**Total geological resources and reserves of garnet As of: end 2003 (in kilotonnes)**
being mined					
Australia	Western Australia	Port Gregory		23-35	~4,000
		Port Gregory II	19.5	~90	3,300
India	Orissa	OSCOM	20.2	6.8	3,170
	Tamil Nadu	Coast	7-39	9	2,660
USA	Montana	Gold placer mining tips		4-4.5	1,100
production planned					
Australia	Northern Territory	Harts Range	6.3		6,200
Canada	Labrador	Hutton		20-60	1,308
Rep. South Africa	Western Cape	Geelwal Karoo	42.3	52.7	2,580
not mineable					
Egypt	E` Rafah, Nile delta	El Arish & Rommana	4	4.8	140
Germany	Cuxhaven	Midlum	9.9	1.5	149
USA	NE-Florida	Amelia Island	4	0.6	5.4

Table 8.18 show the global reserves and resources of garnet – defined as known and published amounts of currently workable, mineable heavy minerals, not blocked by competitive usages, from placers and/or bedrock deposits, possibly after processing.

Table 8.18: Currently known global resources and reserves of garnet in million tonnes.

Country	**Total resources and reserves of garnet** **from placers million tonnes**	**from bedrock million tonnes**
India	>107	-
Canada	>35	>100
Australia	14.6	1)
- *Western Australia*	*8.4*	
- *Northern Territory*	*6.2*	
USA	>3	>25
Malawi	1)	-
Italy	2)	-
Rep. South Africa	2)	-
Mozambique	2)	-
China	-	>1
Ukraine	-	15.4
Norway	-	13.5
World	>160	>150

1) = Very large deposits exist, but currently they are not yet workable due to high costs of transportation 2) = Smaller deposits of unknown extent exist

8.7 Important producing countries and occurrences

USA

Industrial garnet was first produced in 1878 from almandine-bearing diorites (percentage of garnet: 5-20 (average 10) % by mass, chemical composition: 37-43 (average 43) % by mass pyrope, 40-49 (average 40) % by mass almandine, 13-16 (average 14) % by mass grossular, average 2 % by mass andradite, average 1 % by mass spessartine) in the Barton mine at Gore Mountain in the Adirondacks in the US State of New York. In the first year of production, approx. 100 tonnes of garnet were produced as a grinding abrasive for the booming timber industry (KELLY & HILL 1995). This mine was productive on a large scale until 1983 and provided up to 95 % of the annual global production of high quality industrial garnet for polishing purposes. Mining by Barton Mines Co. LLC has been continued since 1983 in Ruby Mountain, which is only a few miles away. Production capacity is 20 kilotonnes /year.

Since the end of the 1930s, industrial garnet has also been mined from 1-2 m thick river placers (provenance: Precambrian mica schist) in Idaho. Emerald Creek Garnet Co., a subsidiary of WGI Heavy Minerals, Inc., has a production capacity of ~50 kilotonnes /year.

From 1994 to 2002, Patterson Material Corp. annually produced up to 18,000 tonnes of almandine as a by-product from their gravel pits in the US State of New York.

In Montana, Sweetwater Garnet Inc. produced almandine from weathered bedrock and colluvial placers. The capacity was 20 kilotonnes /year. Between 1996 and 2003, waste rock piles of former production companies in Montana were worked over for stream gold, which contains an average of 8 % by mass almandine and pyrope. The annual capacity is 40 kilotonnes.

In addition to wollastonite, NYCO Minerals, Inc. produces garnet as a gangue product from a gneiss (percentage: average 30 – 40 % by mass) in the US State of New York. This andradite-grossular garnet is marketed by International Garnet.

Large occurrences of industrial garnet are known in several states, including mainly New Mexico (ore with an average of 85 % by mass andradite) and Arizona (placers with almandine). These deposits have not been developed so far due to the bad infrastructure.

India

The largest Indian producer of industrial garnets is V.V. Minerals (VVM) in Tamil Nadu with an annual production of approx. 150,000 tonnes of garnet. This garnet is traded under the name *Supergarnet*. In 2008, V.V. Minerals also took over Transworld Garnet India Pvt. Ltd. from the US company WGI Heavy Minerals Inc. The latter produced 63,000 tonnes of garnet in 2003 under the name *Bengal Bay Garnet,* and 91,000 tonnes of ilmenite as a by-product. Transworld Garnet India Pvt. is preparing to start the large-scale industrial extraction of garnet from coastal placers near Srikakulam in Andhra Pradesh (HM-percentage: average 34 % by mass, of these 18-20 % garnet).

Since 1982, Indian Ocean Garnet Sands Co. Pvt. Ltd. (IOGS) has been producing almandine from coastal placers in Tamil Nadu. Its capacity is 36 kilotonnes /year. Garnet produced by IOGS is marketed in Europe as *POWERgarnet*.

Other producers of industrial garnet in India are Beach Mineral Sands Co. (BMC) and Indian Rare Earths Ltd. (IREL), from whose production site Manavalakurichi, Tamil Nadu, garnet has been extracted since 1936.

Australia

GMA Garnet Pty Ltd. has been the largest Australian producer of industrial garnet since 1981, it mines dune placers of an average of 23 (max. 35) % by mass almandine near Port Gregory in the state of Western Australia. Its capacity is 300 kilotonnes /year.

In mid 1995, Minerals Corp. Ltd. also began mining almandine from bedrock near Broken Hill in New South Wales. Its capacity there is 15 kilotonnes /year. Production data are not known.

Olympia Resources Ltd. is planning to extract garnet and a garnet-hornblende mix (*AMH* = Alumino-Magnesio-Hornblende) from river and dune placers in the Harts Range, Northern Territory, intended as a substitute for slag as a fine grained blasting abrasive (content of garnet in the ore sand: average 6.3 % by mass). The initial capacity is to be 80 kilotonnes/year, the final capacity 300 kilotonnes/year.

In a number of heavy mineral littoral placer deposits such as Capel, Western Australia, small amounts of garnet are produced as a by-product.

China

Near Liang Cheng in Inner Mongolia, almandine has been extracted from biotite-garnet shale (percentage: 45-70 % by mass) with an annual capacity of 20 kilotonnes, and marketed by WuXi Ding-Long Trading Co., Ltd. under the trade name *Sinogarnet*. According to MOORE (2006), the resources there are approx. 1 million tonnes. Other producers are Leshan Carborundum Natural Abrasives Co. in the province of Sichuan, and Inner Mongolia XL Abrasives Processing Co. Ltd.

Europe

In Ukraine, near Ivaniv 400 km to the south east of Kiev, a granite with almandine (percentage: average 27 % by mass) is to be produced and marketed by the Canadian company Black Sea Minerals Inc. (BSM).

In Almeria, Spain, high-quality industrial garnet occurs in eluvial placers. It was mined there in the 1950s. The remaining deposits are very small.

In Northern Italy, garnet, just like gold, is supposed to be extractable economically as a gangue product from gravel pits along the river Po.

Canada

In Headley near Penticton, British Columbia, garnet occurs at an average percentage of 80 % by mass in bedrock.

To the north-east of Sudbury, Ontario, occurrences of almandine-bearing gneisses (garnet content: 40 – 60 % by mass) are known, which are to be extracted there in three opencast mines.

Near Hutton, Labrador, high-quality almandine in workable amounts and concentrations >60 % by mass occurs in littoral and marine placers with thicknesses of 2-3 m. The infrastructure is very bad, however.

Africa

In Southern Malawi and at Lake Malawi, placers of different genesis with thicknesses of several tens of meters in part, with partly high contents of approx. 60 % by mass garnet in the ore sand, have been proven. High transportation costs have so far prevented economic production.

Figures 8.1-8.3 allow a direct comparison of the percentage distribution of the global production (2007) and the currently known global resources of industrial garnet.

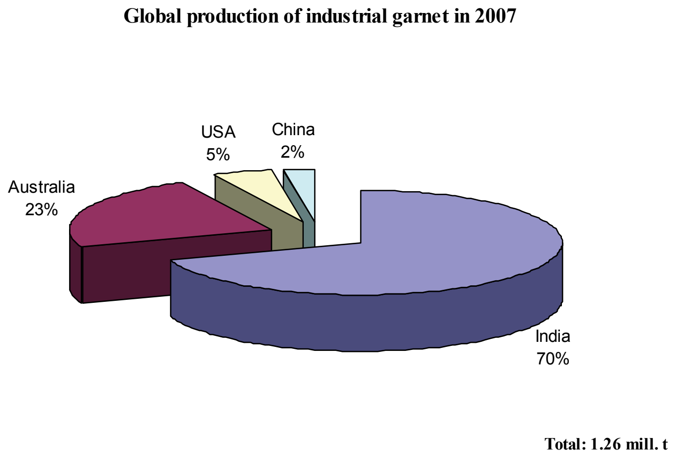

Figure 8.1: Percentage distribution of the global production of industrial garnet in 2007.

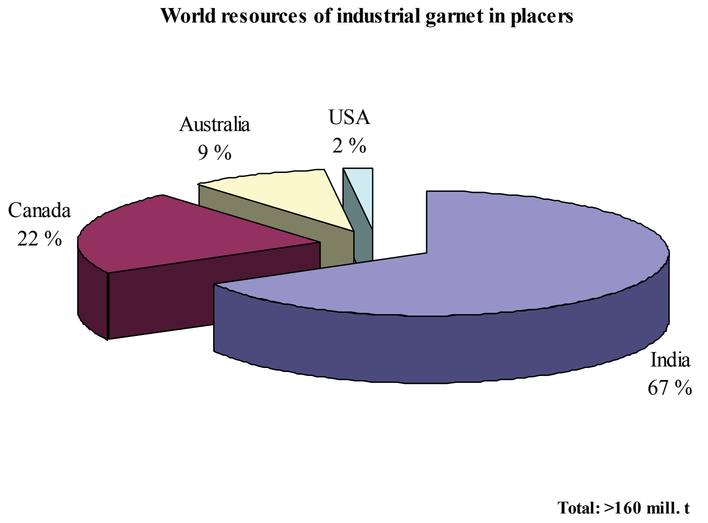

Figure 8.2: **Percentage distribution of the currently known global resources of industrial garnet from placers.**

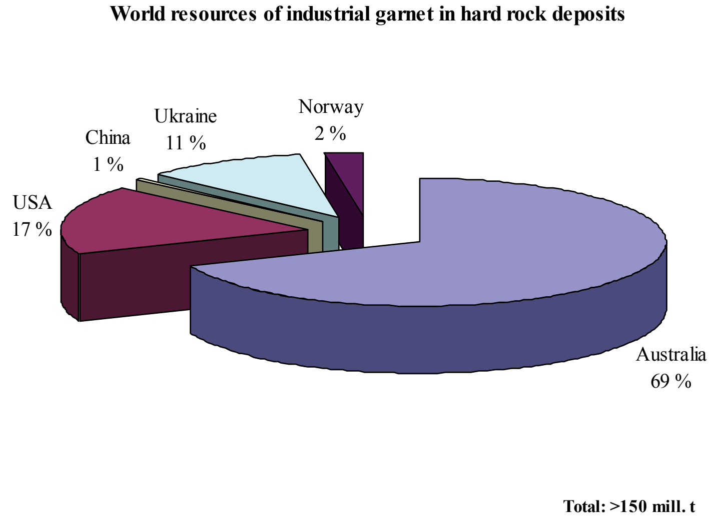

Figure 8.3: **Percentage distribution of the currently known global resources of industrial garnet from bedrock.**

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9 Chromite

[German: *Chromit*, Spanish: *cromita*, French: *cromite*]

9.1 Mineralogy, petrography, chemistry

The mineral chromite, colloquially called chrome iron ore, belongs to the spinel group, whose general formula is AB_2O_4. Their naturally occuring order of frequency is:

A = Mg, Fe^{2+}, Zn, Mn
B = Al, Fe^{3+}, Cr, Mn^{3+}, V, Ti

In accordance with the most common occupation of the B-position, the spinels are subdivided into aluminum spinels, iron (III) spinels and chrome spinels. Manganese(III), vanadium and titanium spinels are rarer. Chrome spinels in turn form a solid solution between $FeCr_2O_4$ (ferrochromite = chromite) frequently occurring in nature, and $MgCr_2O_4$ (magnesiochromite or picrochromite) rarely occurring in nature.

Chemically pure **chromite** has the following properties:

Formula	$FeCr_2O_4$
Chemistry	67.90 % by mass Cr_2O_3, 32.10 % by mass FeO
Density	5.09 g/cm^3
MOHS hardness	5 ½
Color	black to blackish brown
Melting point	2,180 °C (dimensionally stable up to 1,545-1,730 °C)
Magnetic properties	paramagnetic
Electrostatic properties	conductive

Due to their Cr_2O_3-content as well as their Cr/Fe-ratio, chromite can be subdivided into *high-chromium* chromites, *high-iron* chromites and *high-aluminum* chromites (cf. Table 9.1).

Table 9.1: Classification of chromite according to MALIOTIS (1996).

Type of chromite	Cr_2O_3-content [% by mass]	Cr/Fe-ratio	Al_2O_3-content [% by mass]	Main application
high-chromium chromite	46-55	>2.1		metal
high-iron chromite	40-46	1.5-2.0		metal and chemistry
high-aluminum chromite	33-38	2.0-2.5	22-34	fire proof

Typical trace elements in chromite, which can also be present in percentages up to 1 %, are Ti, V, Mn and Ni, and to a much lesser degree also Co and Zn.

9.2 Formation of deposits and occurrences

Chromite forms nearly without exception during the early-magmatic separation of ultrabasic magmas, i.e. it is liquid magmatic. Rocks rich in chromite with >50 % by mass chromite are called chromitites. Two types of primary chromite deposits are differentiated according to the structure of the ore bodies and the geological environment:

- **stratiform** or seam occurrence: long (50–100 km) "layered" deposit with thicknesses of several tens of meters, more rarely meters. Deposits of this type are characterized by uniform ore properties within the deposit. The most important deposits (Bushveld complex/Rep. South Africa, Great Dyke/Zimbabwe, Stillwater complex/USA) are very similar in composition, mineralogy and texture. Other extensive chromite occurrences of stratiform type are known from India (Orissa complex, Cuttack, Keonjhar and Dhenkanal District), Western Australia (Coobina), China (Gaosi, Maojia, Pinding, Tongyu, Shangnan, Xiaosong), Greenland (Fiskenaesset), Madagascar (Tsaratanana District), Finland (Kemi complex, Elijarvi District), Russia (Sarany, Perm region), Brazil (Campo Formoso) and Canada (Bird River).
- Chromite mineralizations of **podiform type** show different, in some cases merging forms, such as nuggets, streaks, bands, chimneys and “dykes”. Frequently they do not follow the magmatic layering and show significant variations in thickness, with maximum thicknesses of 15-35 m. The longitudinal extent varies from a few to several hundred meters. Mineable ore bodies contain between several thousand to a few million tonnes of chromite. The globally significant chromite deposits of podiform type, which contain approx. 4 % of the global resources and reserves of chromite, include Kempirsai/ Kazakhstan, Zambales District/Philippines and Selukwe/Zimbabwe. Other large chromite occurrences of podiform type exist in China (Luobosa, Sarthay, Donqiao, Yushi, Solun, Wudu, Hegenshan), south-eastern Europe (Albania, Northern Greece, Turkey), Iran and Pakistan (Muslimbagh area).

The weathering of chromite-bearing rocks in tropical areas produces chromite accumulates in laterites. The nickel-chrome laterites occurring for instance in Guinea, Cuba, Indonesia, Papua New Guinea, the Philippines and New Caledonia, contain on average 50 % Fe, 2-4 % Cr and 2-2.5 % Ni (cf. Table 9.2). The most important mineral is always nickel, however.

Table 9.2: Chemical composition (%) of limonitic laterite ore (SCHELLMANN 1983).

	Ora Banda Australia	Greenvale Australia	Prony New Caledonia	INCO	Nonoc Philippines	Mea New Caledonia	Pomalaa Indonesia	Gag Indonesia	Sukinda India
Fe	41.5	45.5	50.6	42.9	48.6	52.5	47.9	43.6	51.4
Fe^{2+}	0.04	0.04	0.04	0.04	0.04	0.04	1.20	0.04	
Al_2O3	5.89	5.10	4.57	6.59	8.21	2.55	8.50	13.6	2.60
Cr_2O_3	1.72	2.65	3.56	2.44	3.55	4.78	2.66	3.01	4.37
SiO_2	15.4	10.01	2.39	8.14	1.82	1.43	5.14	2.11	3.98
TiO_2	0.19	0.07	0.06	0.12	0.09	0.05	0.11	0.15	0.08
MgO	1.51	1.18	0.46	4.53	0.97	0.59	1.18	0.68	0.09
CaO	0.12	0.00	0.00	0.06	0.00	0.00	0.01		
K_2O	0.02	0.00	0.00	0.01	0.00	0.00	0.01		0.06
Mn	0.99	0.98	0.76	0.87	1.13	0.49	0.67	1.16	0.70
Co	0.111	0.261	0.095	0.16	0.191	0.050	0.18	0.20	0.06
Ni	1.62	1.70	1.22	1.49	1.51	0.91	1.00	1.21	0.70
H_2O^+	12.1	12.0	13.3	12.9	11.8	13.3	11.7	14.9	12.8

Due to its resistance and bulk density, chromite also occurs as a heavy mineral in **placers**. These are, however always connected to nearby primary chromite mineralizations. Important chromite placers, which contain approx. 2 % of the mineable global reserves and resource of chromite, are located in:

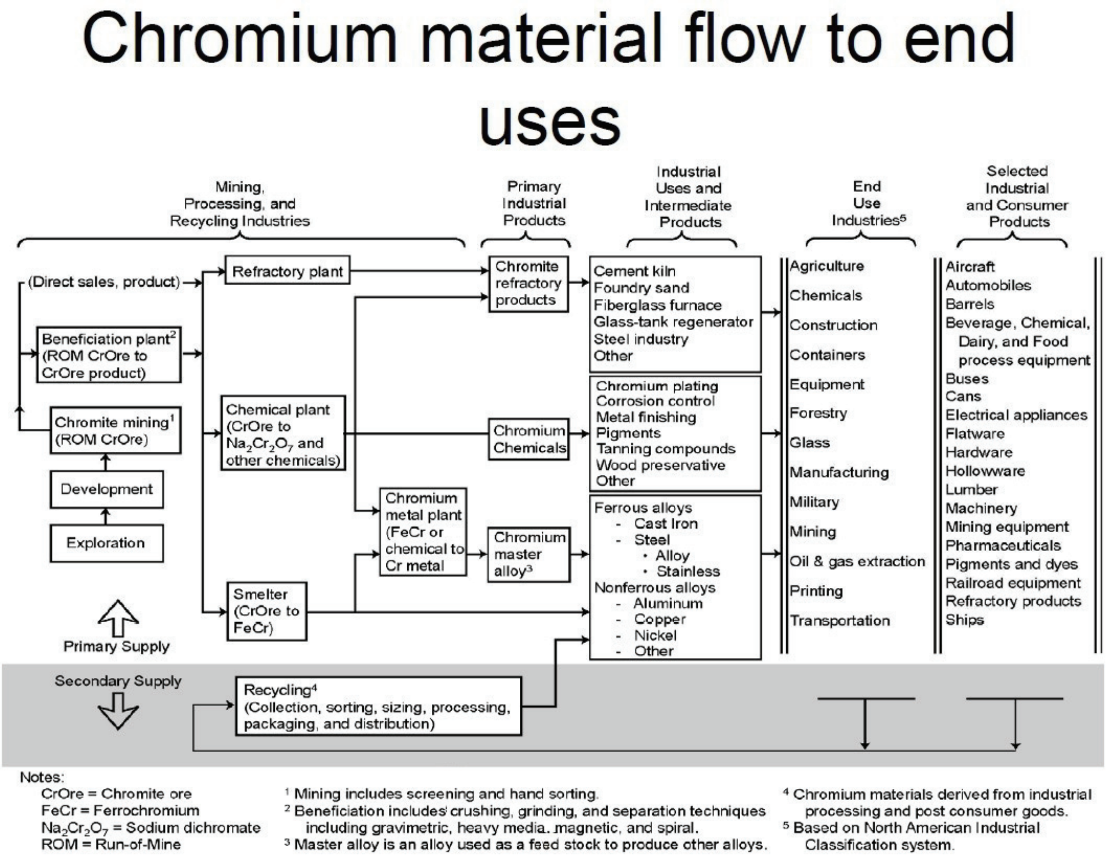
- **Australia, Murray Basin, Victoria:** chrome-spinels as a potential by-product of ilmenite production (FREEMAN et al. 2003), estimated resources approx. 1-2 million tonnes of Cr_2O_3, composition of the concentrate: 46.5 % Cr_2O_3, 0.50 % TiO_2, 35.9 % Fe_2O_3, 5.5 % MgO, 11.2 % Al_2O_3, 0.85 % SiO_2.
- **Australia, Tasmania:** 1) Barnes Hill: Tertiary quartzite gravel, resources: 240,000 tonnes with average contents of 5 % Cr_2O_3 in the gravel and an average of 56 % Cr_2O_3 in the concentrate, production until 1980, molding sand quality 2) Rifle Range: eluvial placers from serpentinites, resources 433,000 tonnes with average contents of 11.25 % Cr_2O_3 3) Adams Field near Andersons Creek: fluvial placer with contents of 2-16 % Cr_2O_3.
- **Indonesia, Sulawesi**: 1) East coast: resources of 1 million tonnes of chromite gravel with average contents in the concentrate of 43 % Cr_2O_3, <1 % SiO_2, production since 1988, since 2000, approx. 1,000 tonnes/year, fire proof and molding sand quality 2) South coast: at the end of the 1970s, successful exploration for chromite in beach placers by Japanese and Australian companies.
- **New Caledonia:** 1) Pirogue, N´go, Ouie, Mouea, SW Lagoon: Proven resources of 21 million tonnes of sediments with contents of 4 % Cr_2O_3 and 100 million tonnes of sediments with contents of 3.5 % Cr_2O_3, chemical and metallurgical qualities 2) Massif du Sud, Vercingetorix and Vercingetorix South: formerly extraction of 78,208 tonnes of chromite from eluvial placers 3) Kopeto-Boulinda mountain: fluvial placers at the foot of the mountain.
- **Papua New Guinea**: numerous, large chromite placer deposits with resources of up to 200 million tonnes of sediment, and contents of 1.5-2 % chromite. The Ramu-River area, 70 km from Madang has been investigated most thoroughly: Pleistocene fluvial placers averaging 3 m thickness intercalated with over-bank deposits, resources of 225 million tonnes of sediments with average contents of 9 % Cr_2O_3 in the ore and 45 % Cr_2O_3 in the concentrate, corresponding to 9.6 million tonnes of chromite, metallurgical quality, Cr/Fe-ratio = 1.6, underlain by 67 million tonnes of laterite with 4.9 million tonnes of chromite as well as contents of 1.14 % Ni and 0.16 % Co.
- **Philippines, Palawan Island**, Narra-Teresa: Beach placers with average contents of 6 % chromite, composition of the concentrate produced until 1986: 39.5-42.0 (average 41.0) % Cr_2O_3, 21.88-22.50 % FeO, 12.5-14.2 % MgO, 19.33-20.50 % Al_2O_3, 0.72-2.44 % SiO_2, Cr/Fe-ratio = 1.56-1.70, remaining resources: 5,019,000 tonnes of ore sand, fire proof and chemical qualities.
- **Philippines, Palawan Bay near Isabela on Luzon:** beach placers mined in the past with remaining 2,767,000 tonnes of ore sand with average contents of 6 % Cr_2O_3, composition of the concentrate: 34.05-44.0 (average 40.32) % Cr_2O_3, Cr/Fe-ratio = 1.0-1.65, metallurgical quality.
- **Zimbabwe, on both sides of the Great Dyke:** 500 km^2 area, thickness: on average 45 cm, resources of 54 million tonnes of ore sand (11 % of the total resources in Zimbabwe) with average contents of 15.0 % by mass chromite (corresponds to approx. 110,000 tonnes of chromite/km^2), until 1959, 40,000 tonnes of chromite mined by Rhodesian Mining Enterprises (Pvt) Ltd., 1970-1977 production by Rio Tinto (Zimbabwe) Ltd., contents in the concentrate: 53-55 % Cr_2O_3, Cr/Fe-ratio = 2.3-2.5, small-scale mining in the Feoch mine for eluvial placers in the 1950s, metallurgical quality.
- **USA, California**: resources of approx. 700 kilotonnes beach sands with average contents of 7.0 % Cr_2O_3.
- **USA, south-west Oregon:** low-grade beach placers, accompanying heavy minerals: ilmenite, rutile, zircon, garnet, magnetite, olivine, pyroxene, hornblende, epidote, production during World War II and during the Korean War (led to development of the Humphreys spirals, processing 1,844,800 tonnes of sand with contents of 3.8 % Cr_2O_3, in the concentrate: average (39.3) 42 % Cr_2O_3, Cr/Fe-ratio = 1.5), remaining resources: 8,068,700 tonnes [other sources: 5.8 million tonnes] of ore sand with contents of 4.77 % Cr_2O_3, corresponding to 384,500 tonnes of Cr_2O_3.

- **Vietnam**, Thanh-hoa area on Nul Nua mountain: Enrichments of chromite at the bottom of two gorges, contents of 1.5-5.0 [11.5-22.5] % Cr_2O_3, Fe/Cr-ratio = 2.2-2.4, resources of 1.7 million tonnes of chromite, periodic mining 1924/25, 1928-1932, again from 1978.

9.3 Applications

The areas of application of chromite are determined by the content of minor components, such as magnesium and aluminum, and the Cr/Fe-ratio(cf. Figure 9.1). Applications include:

- the steel industry for manufacturing ferrochromium. Ores with a high chrome-iron ratio (Cr/Fe>2.5) and a high magnesium content are required.
- the chemical industry. The content of Cr_2O_3 and Fe_2O_3 should be as high as possible, the content of aluminum, magnesium and silica as low as possible.
- the refractory industry, which requires a high content of Cr_2O_3 and Al_2O_3 and as much magnesium as possible but little iron.



Notes:
CrOre = Chromite ore
FeCr = Ferrochromium
$Na_2Cr_2O_7$ = Sodium dichromate
ROM = Run-of-Mine

[1] Mining includes screening and hand sorting.
[2] Beneficiation includes crushing, grinding, and separation techniques including gravimetric, heavy media, magnetic, and spiral.
[3] Master alloy is an alloy used as a feed stock to produce other alloys.
[4] Chromium materials derived from industrial processing and post consumer goods.
[5] Based on North American Industrial Classification system.

Figure 9.1: Material flow diagram of chromium (PAPP 2007)

The largest proportion of the produced chromite is used in the metallurgical industry. Of the approx. 24 million tonnes of chromite produced in 2008, about 95 % were used in the steel industry, 2 % in the chemical industry as well as in total 3 % in the molding sand industry (foundry sand) and in the refractory industry (INTERNATIONAL CHROMIUM DEVELOPMENT ASSOCIATION 2009).

Steel industry

Chrome is the most important alloy metal for the manufacture of stainless chrome steels (low C-proportion, Cr-proportion >11 %). Chrome also increases the hardness, strength, corrosion resistance and wear resistance of steels. There are numerous special alloys containing chromium. Their chromium content is usually approx. 18-30 % by mass. Due to its ubiquitous use in the metallurgical industry, and its occurrence in only a few countries, chrome is a classed as a strategic metal, and chromite as a strategic mineral.

Chemical industry

Chromite is a raw material for the manufacture of numerous chemicals containing chromium. The most important of these are:

- sodium chromate, Na_2CrO_4, an effective corrosion preventive agent because it causes the development of a protective film on metal surfaces (water cooling systems, piping, drilling fluids). Other uses as a catalyst, drilling mud additive, in the production of pigments, textile drying, water treatment, wood preservation, substitute for sodium dichromate in corrosion control and in alkaline pigments, a base for other chemical products
- sodium dichromate, $Na_2Cr_2O_7$, is used in batteries, bleaching wax and oils, in processing copper alloys, in metal working, a drilling mud additive, in leather tanning, in paints, pigments and colorants, for dyeing textiles, water treatment, wood preservation and as a base for other chemical products, in particular: chromium sulfate (37 %), chromic acid (32 %), chromium oxide (21 %), chromium pigments (10 %)
- After scrubbing, filtering, drying and grinding to 0.1-1 µm grain size, sodium dichromate is used to manufacture Cr pigments of good covering power and with additional corrosion retarding properties
- ammonium dichromate, $(NH_4)_2Cr_2O_7$, is a strong oxidant (staining agent for dyes, catalysts, oil cleaners, porcelain treatment, pyrotechnics, magnetic flux, lithography and photo printing, material for the manufacture of chromium oxide.)
- potassium dichromate, $K_2Cr_2O_7$, in contrast to sodium dichromate is non-hygroscopic and is thus used as a base for the manufacture of printing, photochemicals and lithographic chemicals, activator in pyrotechnics and in safety matches, furthermore for the manufacture of metallic salts, in metal work, in glass, for pigments and as an activator in alcohol testing devices
- lead chromate, $PbCrO_4$, pigment (light greenish yellow to orange-bright red)
- chromium sulfate, $Cr(OH)SO_4$, base material for leather tanning
- chromium (III)-oxide, Cr_2O_3, manufacture of magnetic tape
- chromic acid, H_2CrO_4, and “dehydrated” as flakes, chromium trioxide, CrO_3, use as ceramic colorants, additives in refractory mixes, in metallurgy, as fungicides, green pigments and in chromium plating metals (automotive and sanitary industry). In addition, chromic acid serves as the raw material for the manufacture of chromated copper arsenate (CCA), a mineral-based wood preservative used only in the US, with copper serving as the fungicide and arsenic as protection against termites, and chromium facilitates the bonding of the two substances in the wood.

Refractory industry

Chromite as an accessory in refractory substances brings about effective fire resistance, improved resistance against spalling/chipping, and excellent mechanical strength at increased temperatures. The structure of pure chromite decomposes at high temperatures however, which means that it always has to be mixed with other materials (magnesite, zircon etc.).

In different mixing ratios with MgO, mainly magnesite-chromium bricks (chromite percentage 30-40 %) or chromium-magnesite bricks (chromite percentage up to 70 % by mass) are used.

Refractive bricks based on chromite are used in particular in the cement, copper, aluminum, glass, nickel, noble metals and steel industries. For the manufacture of steel in blast furnaces, approx. 30 kg chromite per tonne of steel is required. In modern electric smelting furnaces, this value has decreased to 1-2 kg of chromite per tonne of steel.

For special refractory specifications, additional materials based on chromium have also recently been developed (cf. Table 9.3).

Table 9.3: Properties of newly developed refractory materials based on chromium (VELEZ 2004).

Name	Chemical formula	Main properties
Cr-Borides	Cr_4B, Cr_2B, Cr_5B_3, CrB, Cr_3B, CrB_2	• high melting point • high electrical conductivity • high chemical resistance
Cr-Carbides	$Cr_{23}C_6$, Cr_7C_3, Cr_3C_2	• high melting point • very hard
Cr-Silicates	Cr_3Si, Cr_2Si, Cr_5Si_3, Cr_3Si_2, CrSi, $CrSi_2$	• high melting point • hard and brittle • high acid resistance

Foundry industry

Molding sands from chromite:

- are fire proof and chemically stable,
- have good thermal conductivity and good cooling properties (resistance against thermal shock),
- withstand the penetration of metal (ballooning at approx. 600 ^{o}C, with FeO and Fe_2O_3 converting to Fe_2O_3 and Fe_2O_4, while expanding their volume and thus sealing the surface of the casting mold) and slag resistance,
- offer good permeability to the gases flowing from the melt,
- have an irregular and angular grain shape
- have a low thermal coefficient of expansion ($\sim 5 \cdot 10^{-3}$/K).

Its advantages in comparison to quartz sand, the most frequently used basic molding material, are:

- lower thermal coefficient of expansion,
- better thermal conductivity,
- better refractability,
- free of SiO_2 (silicosis hazard).

Its disadvantages in comparison to zircon, when used as a substitute, are:

- higher thermal coefficient of expansion,
- irregular and angular grain shape compared to the round zircon grains,
- higher acid requirement,
- occasional inclusions of aqueous impurities,
- different bonding properties with respect to different binding agents,
- occurrence of the “crazing effect” (formation of an irregular surface on the casting mold due to the discharge of Fe-oxides),
- inferior recyclability

Additional comparisons of the properties of chromite with other forming sands cf. Table 4.2 in Chapter 4.3.

Chromite molding sands are used in particular for casting oversize forms (>20-30 tonnes), for steels containing manganese, and copper workpieces. On average, 75-100 kg of chromite are used per tonne of cast steel. Approx. 30 % by mass of the chromite used in forms can be recycled. This secondary chromite in turn could meet 50 % by mass of the corresponding chromite demand (PAPP 1994), because approx. 50 % by mass "fresh chromite" has to be added to compensate for the impurities after casting.

Ground chromite is an additive of molding sands and acts as a natural colorant (glass, brick, ceramics).

9.4 Substitutes

There are no substitutes for chromite as a raw material of chromium for the production of ferrochromium. Some of the demand is satisfied by chromium-bearing scrap metal. Depending on the usage, chromite can be replaced by other minerals such as:

- steel industry: nickel for stainless steel.
- foundry purposes: quartz sand, staurolite, olivine, zircon.
- refractory industry: graphite, magnesite, zircon, quartz sand.
- chemical industry pigments on an organic basis or based on other metals (e.g. Mo, Cd).
- wood preservation: organic-based media.

9.5 Specifications for the raw materials (reference values)

The raw material specifications for chromite depend on the intended use as listed in Table 9.4.

Table 9.4: Specifications for chromite concentrates as raw materials (except for Cr:Fe in %) as a function of the intended use.

	Refractory industry		**Chemical industry**	**Steel industry** 3)
	refractory grade	***foundry grade***	***chemical grade***	***metallurgical grade***
Cr_2O_3	>30 (40)	>44	>40-46	≥(42)46(48)
FeO	≤(12)16	≤26(28)	<20	
Cr:Fe	2-2.5	2-2.5	1.5-2.0(2.1)	≥1.5(3)
SiO_2	≤1.5-(2.5)4	<(2.5)3.5(4)	2.5(<6)	≤3(2-8)
$Al_2O_3+Cr_2O_3$	≥57(58)(60)			
Al_2O_3	>20(25-32)	approx. 26-28	as low as possible	3-10
MgO	~15-20			as high as possible
CaO	≤0.5-1	≤0.5	≤3	
S				≤0.05(0.08)
P				<(0.2)0.04

1) as little Fe as possible and large amounts of Mg, chromite sand preferred, or needs to be ground

2) ≤0.5 % humidity, percentage of accompanying minerals as low as possible (quartz, olivine, serpentine), resulting in surface faults, ≥90 % by mass 390-75 µm and ≤0.5 % by mass <2 µm (finely grained molding sand), ≥95 % by mass 780-75 µm and ≤0.5 % by mass <2 µm (medium grain molding sand)

3) lump ore (25-150 mm grain size) preferred, fine grained ore (<10 mm) usable

4) fine grained ore preferred (easier production)

In China there is a standard for raw chromite ores (cf. Table 9.5).

Table 9.5: Chinese standard YB 4066-91 for raw chromite ores (WEN LU 1998).

	***Grade* (%)**									
	G-50A	G-50B	G-50C	G-45A	G-45B	G-45C	G-40A	G-40B	G-35	G-30
Cr_2O_3	≥50	≥50	≥50	≥45	≥45	≥45	>40	≥40	≥35	≥30
SiO_2	≤1.0	≤1.5	≤2.0	≤1.0	≤1.5	≤2.0	≤2.0	≤2.5	≤3.0	≤4.0

Unlike western industrialized countries, Chinese standards prescribe minimum and maximum contents for different chromite *grades*; the customer then chooses a product corresponding to the intended use.

Refractory purposes:

The Indian Sub-committee on Refractory Raw Material of the DGTD (Director General of Technical Development) has defined specifications for four types of raw chromite ores as well as of treated chromite for refractory purposes. Further specifications are contained in the Indian standard IS: 10189:1984 (cf. Table 9.6).

Table 9.6: Specifications (%) for chromite ores and treated chromite for refractory purposes in accordance with Sub-committee on Refractory Raw Material of the DGTD and Indian standard IS: 10189-1984.

	Standard IS:10819-1984 [1]		**DGTD [2]**				
	raw chromite ore						processed and dried
	Grade I	*Grade II*	*Special Grade*	*Grade I*	*Grade II*	*Grade III*	
Cr_2O_3	≥50	≥40	52-54	52-54	46-48	40-42	≥44
SiO_2	≤4		≤2	≤5	6-9	9-12	≤7
FeO (Fe total)	<18		≤20	≤20	≤20	≤20	<20
CaO	≤0.8		≤1	≤1	≤1	≤1	≤3
Al_2O_3	≤14						≤3
MgO	≤15						≤14
LOI	≤1.5						

Unlike western industrialized countries, Indian standards prescribe minimum and maximum contents for different chromite *grades*; the customer then chooses a product corresponding to the intended use.

[1] The ore must be hard, solid, fine-grained, free of serpentine and lumpy with a grain size of 50 – 150 mm. [2] the raw ore always has to be hard and lumpy. After crushing the ore, the fine fraction has to be (<1 mm) <30 % by mass.

Foundry purposes:

Specifications for chromite for intended use as molding sand have been established by the Verein Deutscher Gießereifachleute (VDG) issued in report R 92 (1997), by the Indian standard IS: 6788-1973, as well as the British Steel Casting Research and Trade Association (BSCRTA) by Specification No. 2: 1970 (cf. Table 9.7).

Table 9.7: Specifications for chromite concentrates when used as a molding sand.

	IS: 6788-1973 [4]	VDG	BSCRTA	
			medium grade	*fine grade*
Chemical composition (%)				
Cr_2O_3	≥44	≥44		
Fe_2O_3 (Fe total)		≤29	≤26	
FeO	≤20			
$Al_2O_3 + MgO$		Rest	Rest [1]	
SiO_2	≤7	≤2.0	≤4.0	
CaO	≤3	≤0.15	≤0.5	
LOI	≤1		≤0.5	
Humidity		≤0.1 [2]	≤0.2	
Physical parameters				
Ph	7-9		7-9	
Bulk density g/cm^3		~2.8 [3]		
A.F.S. proportion of clay			≤0.5	≤0.5
Grain size distribution(% by mass)				
710-75 µm			≥95	
355-75 µm				≥90
>500 µm		≤5		
<75 µm			≤5	≤8
<63 µm		≤1		
Residue at 355, 250, 212, 150 µm			individually>10 together >70	
Residue at 212, 150, 106, 75 µm				individually≥10 together>70

[1] plus trace elements [2] VDG-report P 26 [3] DIN 53468 [4] on dry base

Molding sand powder must have:

- approx. 40-44 % Cr_2O_3,
- low metallic impurities (V, Mn, Pt, Pd, Os, Ir).

Chemical purposes:

The Indian standard IS: 4737-1982 defines the following specifications for chromite concentrates for chemical purposes:

- ≥44.0 % Cr_2O_3
- ≤20.0 % FeO (Fe total)
- ≤14.0 % Al_2O_3
- ≤7.0 % SiO_2
- ≤3.0 % CaO
- ≤1.0 % MgO

Toxicity

Chromium - not chromite - is known to be toxic and carcinogenic. In detail, the following have to be differentiated:

- non-toxic: all Cr^{3+}-bonds, Cr-metal and $BaCr^{6+}O_4$
- slightly toxic: $Cr^{6+}{}_2O_3$, $Na_2Cr^{6+}{}_2O_7$
- toxic: all other Cr^{6+}-bonds

In most countries there are limits and thresholds for the different exposure paths of chromium products. Chromite raw material is not affected!

Tables 9.8-9.10 contain data on typical chemical and granulometric compositions of chromite concentrates for different applications. Table 9.4 provides a general comparison of the specifications for different applications.

Table 9.8: Chemical composition (except for Cr:Fe in %) and grain size distribution (% by mass, screen residue) of chromite concentrates for chemical industry applications (*chemical grade*).

	Villa Nova Brazil [1]	Henry Gould (Pty) Ltd. Elandsdrift Rep. South Africa [1]	Hernic (Pty) Ltd. Rep. South Africa [1]	Dilokong Lebowa Development Corp. Rep. South Africa [1]	Henry Gould (Pty) Ltd. Rand Mines Ltd. Rep. South Africa [1]	Winterveld Chrome Mines Ltd. Rand Mines Rep. South Africa [1]	Tweefontein Samancor Chrome Ltd. Rep. South Africa [1]	General Mining and Finance Corp. Groothoek Mine Rep. South Africa [3]	Chrome Chemicals (Pty) Ltd. Rep. South Africa [2]
Chemical composition									
Cr_2O_3	≥49	46.3	46.0	46.92	46.0	45.0	46.8	46.82	46.05
Al_2O_3	11-13	15.4	15.2	14.59	15.5	15.8	15.17	14.84	14.80
FeO	-	25.4	-	26.14	26.5	24.7	27.03	25.22	25.79
Fe	17-19	-	26.0	-	-	-	-	-	-
SiO_2	≤3	1.2	1.0	0.85	1.0	2.5	0.5	0.96	1.10
TiO_2	-	0.55	0.54	0.55	0.50	0.40	-	0.14	-
MgO	5-7.5	9.8	8.7	9.8	9.8	11.4	9.23	10.65	9.75
CaO	0.1	0.33	0.26	0.21	0.25	0.20	0.16	0.04	0.25
V_2O_5	-	0.36	0.43	-	0.40	0.30	-	-	-
Ni	-	0.08	-	-	-	-	-	-	-
P	-	0.005	0.002	-	0.003	0.005	-	0.007	0.003
S	-	0.000	0.003	-	0.002	0.002	-	0.006	0.001
Cr:Fe	≥1.7	-	1.55	1.58	1.53	1.60	1.52	-	-
Grain size distribution									
1.180	≤10	1.6	0.02		1.2	9.7			
0.850			0.06			11.3	0.3		
0.710			0.12		7.3	16.1	4.0		
0.600			0.124						
0.500			2.29	14.5	25.4	17.4	20.3		
0.425	≥80								
0.300		18.8	10.78		33.9	16.0	27.5		
0.250		30.0	20.36		23.5	11.9	24.4		
0.212				85.0					
0.180		26.1	30.96		6.1	6.8	14.2		
0.150		17.1			1.8				
0.125		4.6	17.32		0.5	4.7	7.3		
0.106	≤10								
0.075		1.4	13.80		0.3	2.8	2.0		
0.053		0.4	3.39			1.5	0.2		
<0.053			0.67			1.8	0.1		

[1] Papp (1994) [2] O'Driscoll (1998) [3] Dickson (1986)

Table 9.9: **Chemical composition (except for Cr:Fe in %) and grain size distribution (% by mass, screen residue) of chromite concentrates for foundry industry applications (*foundry grade*).**

	Henry Gould (Pty) Ltd. Elandsdrift Rep. South Africa 1)	Henry Gould (Pty) Ltd. Rand Mines Ltd. Rep. South Africa 1)	Millsell Chrome Mines (Pty) Ltd. Rand Mines Rep. South Africa 1)	Winterveld Chrome Mines Ltd. 1 Rand Mines Rep. South Africa 1)	Winterveld Chrome Mines Ltd. 2 Rand Mines Rep. South Africa 1)	Samancor Chrome Ltd. Rep. South Africa 1)	BEI Pecal Rep. South Africa 3)	Chrome Chemicals (Pty) Ltd. Rep. South Africa 2)
Chemical composition								
Cr_2O_3	45.9	46.2	46.0	46.6	46.3	47.05	46.21	46.5
Al_2O_3	15.4	15.5	14.7	15.2	15.2	14.84	14.8	15.5
FeO	25.4	26.5	25.2	25.0	25.0	25.77	27.2	25.8
SiO_2	1.3	1.0	1.0	0.8	0.9	0.7	0.95	0.5
TiO_2	0.55	0.50	0.60	0.50	0.50	0.69	0.67	-
MgO	9.8	9.8	10.2	11.2	11.2	10.75	10.0	10.1
CaO	0.33	0.25	0.20	0.23	0.23	0.05	0.22	0.2
V_2O_5	0.36	0.40	0.40	0.30	0.30	-	-	-
Ni	0.08	-	-	-	-	-	-	-
P	0.005	0.005	0.003	0.003	0.003	-	0.005	0.003
S	0.000	0.002	0.002	0.002	0.002	-	-	0.003
Cr:Fe	-	-	-	-	-	1.60	-	-
Grain size distribution								
2.000		0.4	0.1	0.1	0.1	0.1	0.6	
1.180					0.1			
0.850		2.1	1.0	0.4				
0.600		11.4	11.0	1.9	0.8	2.2	3.3	
0.425		29.6	34.1	8.5	4.7	15.4	16.2	
0.300		31.4	34.0	32.5	14.8	33.7	28.3	
0.212		17.6	14.4	34.6	24.0	27.1	27.2	
0.180						12.8	16.6	
0.150		5.5	4.2	15.6	26.6			
0.106		1.6	0.7	5.1	18.6	6.0	6.3	
0.075		0.3	0.3	1.1	8.4	1.6	1.4	
0.053		0.1	0.1	0.2	1.6	0.9	0.1	
<0.053					0.4	0.1		

1) Papp (1994) 2) O`Driscoll (1998) 3) Company information

Table 9.10: Chemical composition (except for Cr:Fe in %) and grain size distribution (% by mass, screen residue) of chromite concentrates for refractory industry applications (*refractory grade*). (Papp 1994).

	Marico Anglo American Rep. South Africa	Winterveld Chrome Mines Ltd. 1 Rand Mines Rep. South Africa	Winterveld Chrome Mines Ltd. 2 Rand Mines Rep. South Africa	Winterveld Chrome Mines Ltd. 3 Rand Mines Rep. South Africa	Samancor Chrome Ltd. Rep. South Africa	Masinloc 1 Benguet Corp. Zambales, Philippines	Masinloc 2 Benguet Corp. Zambales, Philippines	Masinloc 3 Benguet Corp. Zambales, Philippines	Masinloc 4 Benguet Corp. Zambales, Philippines
Chemical composition									
Cr_2O_3	48.3	46.6	46.5	46.94	47.07	31.55	32.18	33.88	35.73
Al_2O_3	17.2	15.4	15.6	15.6	14.84	-	-	-	-
FeO	20.7	24.9	24.5	24.5	25.77	-	-	-	-
Fe	-	-	-	-	-	11.34	10.83	10.79	12.45
SiO_2	0.94	0.70	0.75	0.30	0.56	5.84	5.42	3.30	1.69
TiO_2	0.39	0.50	0.50	0.50	0.69	-	-	-	-
MgO	12.4	11.5	11.5	11.5	10.75	-	-	-	-
CaO	0.01	0.25	0.25	0.25	0.25	-	-	-	-
V_2O_5	-	0.30	0.30	0.30	-	-	-	-	
P	-	0.003	0.003	0.003	-	-	-	-	-
S	-	0.002	0.002	0.002	-	-	-	-	-
Cr:Fe	2.05	-	-	-	1.60	-	-	-	-
Grain size distribution									
>4.750	0.2	6.2	0.1	1.2	8.2	17.57	22.86	1.3	
4.750						26.5	26.2		
3.350						19.93	22.81		
2.360						15.93	9.19		
2.000				14.6		6.7	12.37	7.1	
1.700	17.1								
1.400			1.3	30.0		3.71	2.18	7.8	
1.180	48.2								
0.850		14.8	4.8	21.7		5.50	2.09	12.3	
0.710		13.3	8.6	19.3	21.1			13.3	
0.600		13.4	8.3	4.8					
0.500		29.2	31.6	5.8	18.9			5.8	
0.425	29.5				15.3				
0.300		16.3	24.8	1.3	25.2			23.5	2.75
0.250		5.0	12.7	0.5	9.4	0.93	0.67	12.9	5.13
0.212	4.8								
0.180		1.1	5.2	0.3	1.6	3.25	1.63	6.3	18.5
0.150		0.3						3.4	
0.125		0.3	1.9	0.2	0.3			4.3	38.1
0.106	0.2								
0.075		0.1	0.5	0.1	0.1			1.3	24.69
0.053			0.1	0.1				0.7	8.68
<0.053			0.1	0.1					2.15

9.6 Size of deposits and resources

The reference values for the size classification of different chromite deposits are listed in Table 9.11.

Table 9.11: Reference values for the size evaluation of chromite deposits.

	All deposits 1) **Cr_2O_3 content**	**Placers2)** **Mineral content**
small	<10,000 – 50,000 tonnes	<50,000 tonnes
medium	50,000 – 500,000 tonnes	50,000 – 500,000 tonnes
large	500,000 – >5 million tonnes	500,000 – 1 million tonnes
very large		>1 million tonnes

1) LORENZ (1991) 2) this work

The global reserves and resources of chromite are shown in Table 9.12 along with a list of the different sources.

Table 9.12: Global reserves and resources of chromium and chromite in million tonnes.

Country	**Type of deposit 1)**	**Cr-content 1)**	**chromite 2)**
Rep. South Africa	stratiform	2,973.7	>6,000 2)
Kazakhstan	podiform	301.0	>1,000 2)
Zimbabwe	stratiform	285.4	>500 2)
USA	stratiform	35.0	240.623 2)
Greenland	stratiform	26.0	100.0 2)
India	stratiform	23.8	182.0 2)
Finland	stratiform	14.2	236.0 2)
Brazil	stratiform	9.0	21.5 2)
Turkey	podiform	6.8	25.931 2)
Albania	podiform	6.3	124.0 3)
Canada	stratiform	3.8	>8.0 2)
Papua New Guinea	lateritic	2.9	n.a.
Iran	podiform	2.8	25.4 2)
Philippines	podiform	2.3	36.7 2)
Madagascar	stratiform	2.1	3.88 2)
Cuba	podiform	2.0	4.5 3)
Russia	stratiform	1.2	>0.45 2)
Greece	podiform	0.8	n.a.
Oman	podiform	0.6	>2.0 2)
Australia	stratiform	0.5	0.124 2)
Sudan	podiform	0.5	>1.0 2)
Cyprus	podiform	0.3	n.a.
Indonesia	podiform	0.2	n.a.
China	podiform	n.a.	11.557 4)
Pakistan	podiform	n.a.	1.0 2)
World (total)		3,701.27	>12,000 2)

other countries with small chromite deposits: Indonesia, Japan, New Caledonia, Thailand, Sri Lanka, Vietnam

1) BOYLE et al. (1993) 2) Company information3) BGR-database 4) ZHU XUN (2002)

9.7 Important producing countries

Chromite was first found in 1799 in the Ural Mountains and was used soon after in the metal industry and as a colorant. In 1811, production was started in the first smallish chromite deposits in the US. In historical order, the countries listed below followed as important chromium producing countries, even if in some cases only for a limited time: Norway (1830), Turkey (1848), India (1849), Yugoslavia (1851), Canada (1861), New Caledonia (1875), Russia (1892), Australia (1894), Zimbabwe (1907), Cuba (1909), Brazil (1917), Rep. South Africa (1921), Cyprus (1924), Albania and Philippines (1937).

Global chromite production has doubled every 10 years since 1900.

Today, chromite ores are produced nearly exclusively from liquid magmatic deposits. The sedimentary deposits are of secondary economic importance. The mining of placers occurs exclusively in small-scale mining.

The most important chromite producing countries are South Africa with a proportion of about 40 % of the annual global production, as well as India (approx. 20 %) and Kazakhstan (approx. 18 %). Figure 9.2 shows the distribution of global chromite production in 2007.

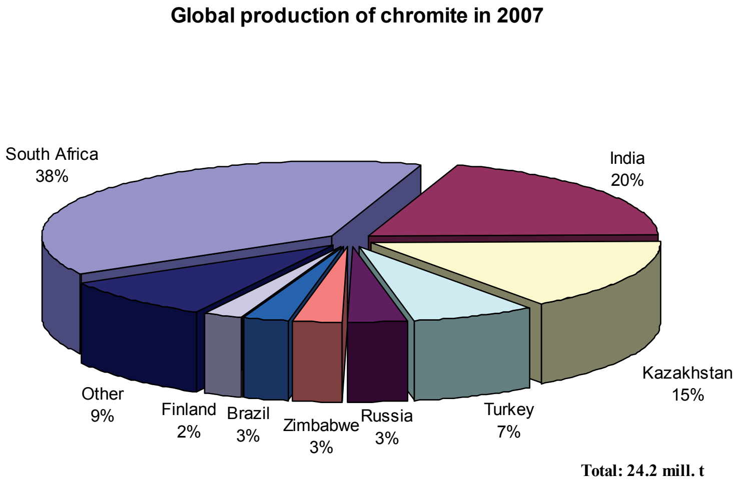


Figure 9.2: Percentage distribution of global chromite production in 2007.

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10 Magnetite

[German: *magnetite*, Spanish*: magnetita*, French: *magnétite*]

10.1 Mineralogy, petrography, chemistry

The mineral magnetite, colloquially magnetic iron ore, is a member of the spinel group with the general formula is AB_2O_4 – just as chromite described in Chapter 9.

The natural order of frequency is:

A = Mg, Fe^{2+}, Zn, Mn
B = Al, Fe^{3+}, Cr, Mn^{3+}, V, Ti

In accordance with the most common occupation of the B-position, the spinels are subdivided into aluminum spinels, iron (III) spinels and chrome spinels. Manganese(III), vanadium and titanium spinels are rarer. Magnetite is the most common iron (III)-spinel and at the same time the most frequent natural spinel of all.

Chemically pure **magnetite** has the following properties:

Formula	Fe_3O_4
Chemistry	31.03 % by mass FeO, 68.97 % by mass Fe_2O_3 and 72.36 % by mass Fe, 27.64 % by mass O
Density	5.16 (5.18) g/cm^3
MOHS hardness	5 ½
Color	iron black
Melting point	1,594 °C
Magnetic properties	ferromagnetic
Electrostatic properties	conductive

Due to the preferred incorporation of the elements Mg, Mn, Zn, Ni, Cr, Ti, Al, V in the spinel lattice, naturally occurring magnetite nearly always has varying percentages of these elements. Co is rarely found.

Magnetite is an important mineral in the mixing triangle $FeO-Fe_2O_3-TiO_2$ (cf. Figure 2.1). This explains why magnetite frequently occurs in magmatic and metamorphic rocks in conjunction with ulvite (Fe_2TiO_4) and titanomagnetite (solid solution between magnetite and ulvite) as well as ilmenite ($FeTiO_3$) and goethite (α-FeOOH). Depending on the crystallization temperature, the cooling rate, availability of oxygen, magma composition and rock pressure, these minerals occur either separately from each other or in homogenous fixed compounds or as inclusions within each other (MÜCKE 2003).

Titanomagnetite contains up to 13 % TiO_2 (cf. Table 10.1), vanadium magnetite (coulsonite) up to 5 % V_2O_5, and also Cr, Al and Mg.

Table 10.1: TiO_2 contents (%) of (titano-) magnetites in placers in Oceania (NOAKES 1977).

Country or region	Stratigraphy/host rock	TiO_2 content
Philippines, Taiwan, Japan	Tertiary volcanites	~7
Indonesia-Java	Quaternary volcanites	$\geq$10
New Zealand, Mount Egmont	Quaternary andesitic lava	8-9
Papua New Guinea	Quaternary volcanites	~10
	Mesozoic- Tertiary rocks	~10
Philippines Manila region	Quaternary volcanites	~11
	“older rocks”	3.4-6.8

Magnetite has the strongest magnetism of all minerals. Magnetic iron ore was thus used as a “compass needle” in the middle ages. At temperatures >578 ^oC (the Curie temperature) magnetite converts to hematite and loses its magnetic properties. Below 578 ^oC, it can be re-magnetized.

Magnetite easily weathers to Fe_2O_3, in particular to α-Fe_2O_3 (hematite). The shape of the magnetite crystals frequently remains intact during this conversion. Aggregates of hematite or pseudomorphs of magnetite are called martite. Occasionally, the magnetite lattice remains intact during oxidation and γ-Fe_2O_3 (maghemite) forms. These two minerals, martite and maghemite, are also magnetic.

10.2 Formation of deposits and occurrences

Magnetite can form under magmatic, metamorphic, sedimentary and even biogenic conditions. The most important conditions for these formations and occurrences are:

- as early crystallisates from basic magmas in plutonites (diorite, gabbro etc.) as well as vulcanites (the dark appearance of basalt is due to finely dispersed magnetite)
- due to crystallization differentiation, i.e. gravitative precipitation of the heavy elements Fe and V in ultrabasic and basic magmas. Globally this process resulted in the formation of important intramagmatic magnetite and titanomagnetite deposits. The paragenetic ores mainly contain magnetite, titanomagnetite, coulsonite, ilmenite, spinel and corundum. Examples of important deposits are: Taberg/Sweden, Otanmäki/Finland and Bushveld/Rep. South Africa
- also in huge amounts in gravitatively enriched melts, no longer “in-situ”, but as “ore magma” intruded into adjacent geological structures. These occurrences (paragenetic ore magnetite, apatite) are amongst the largest concentrations of iron in the earth's crust. Examples of important deposits are: Kirunavaara, Gellivaara, Grängesberg and Luossavaara/Sweden as well as Lake Superior/Canada.
- contact pneumatolytic titanium-free and phosphorous-free paragenetic rocks with skarn minerals and sulfides. Examples of large occurrences are: Magnitogorsk (Name!) in the Ural mountains/Russia, Dannemora and Persberg/Sweden.
- in pegmatites occasionally in larger amounts, e.g. in the gabbro-pegmatites of the Kola Peninsula/Russia.

Magnetite is also present in:

- the products of volcanic exhalations, e.g. on the Aleutians/Alaska,
- marine-exhalative-hydrothermal-sedimentary rocks in iron ore deposits of Lahn-Dill type,
- hydrothermal-metasomatic rocks at the point of contact to alkaline rock,
- sedimentary rocks in the Precambrian banded iron formations (itabirites) of ancient shields,

- contact metamorphic rocks as a result of the metamorphosis of siderite, chamosite or thuringite,
- regional metamorphic rocks due to the reduction of hematite,
- alpine fissures,
- heavy mineral placers (cf. below)

as well as non deposit-forming, but still important

- biogenic form in bacteria (e.g. Aquaspirillum magnetotacticum) as well as in the brains of bees and some birds (and humans). In this case, magnetite serves as a magnetoreceptor, i.e. to sense the earth's magnetic field to help navigation.

(Titano)magnetite is a typical heavy mineral, whose enrichment in placers is linked to the proximity of large basalt bodies or young volcanites. Economically exploitable magnetite and titanomagnetite placers, frequently called "iron sand", occur in:

- **New Zealand, North Island**: New Zealand is by far the largest producer in the world of titanomagnetite from placers. On North Island there are 24 individual deposits with total resources of >850 million tonnes of concentrate with an average content of 55-56 % Fe, 7-9 % TiO_2 and 0.3-0.4 % V_2O_5. Mining is active in the Waikato North Head deposit, and in the Taharoa deposit. The Waipipi deposit was mined between 1971 and 1987 producing a total of 15.7 million tonnes of concentrate with an average content of 56 % Fe and 7.8 % TiO_2 from 60 million tonnes of ore sand. All occurrences are Holocene placers as well as Pleistocene beach placers and above all dune placers. Host rocks are the very common andesite and rhyolite of the North Island. The data on the two deposits still being mined (both by BlueScope Steel Ltd.) are:
  - Waikato North Head: Since 1969, dune sands up to 120 m thickness are mined by bucket wheel excavators, to a lesser degree also beach sands, tephra and silts. The resources (as of 1989) were 780 million tonnes of raw sand at an average content of 18 % titanomagnetite, corresponding to 140 million tonnes of concentrate. The proven reserves (as of 1997) were 74 million tonnes of ore sand with an average content of 33.8 % by mass titanomagnetite, corresponding to 19.4 million tonnes of concentrate with an average content of 59 % Fe. The processed concentrate is used for the domestic manufacture of steel.
  - Taharoa: More than 120 m thick dune sands in a basin measuring 8 x 2 km have been mined since 1972 using cutting suction dredgers, i.e. wet (dredge) mining. The estimated total resources were (as of 1979) 2,560 million tonnes of ore sand, corresponding to 565 million tonnes of concentrate, of which only 593 million tonnes of ore sand with an average content of 35 % by mass titanomagnetite, corresponding to 208 million tonnes of concentrate were extractable, (as of: 1969). The proven reserves (as of 1997) were 11 million tonnes of ore sand with an average content of 55 % by mass titanomagnetite, corresponding to 5.3 million tonnes of concentrate with an average content of 57.5 % Fe and 8 % TiO_2. All mineral concentrates from Taharoa are exported for manufacturing steel, primarily to Japan, secondarily to South Korea and China.
- **Indonesia:** On the islands of Sumatra, Bali, Flores, and most of all in the south of Java, numerous occurrences of economically extractable (titano)magnetite deposits are known and also in some cases these have been mined for some time. The mid-Tertiary andesites of the islands are the host rocks. The most important occurrence (all in Java) are:
  - Cilacap: on average 3 m thick beach and dune placers with 20-50 % by mass (titano)magnetite, average contents of the concentrate: 57-59 (53-58) % Fe, 11 (6-8) % TiO_2, 4.5 % SiO_2, 5 % Al_2O_3, 0.05 % P and 0.03 % S, extraction of <400 kilotonnes concentrate/year from 1971 to 2003, deposit depleted, original content of the deposit: 6 million tonnes at a *cut-off grade* of 37 % Fe,

  - Kutoarjo: reserves of 11.6 million m^3 ore sand with 2.55 million tonnes of magnetite (average contents of the concentrate: 45.7-46.2 % Fe) at a *cut-off grade* of >45 % Fe (as of: 31.12.2003), mined, used in the local cement industry and for export to Japan,
  - Lumajang: reserves of 1.785 million tonnes of ore sand with 700,000 tonnes of magnetite (average contents of the concentrate: 48.6-50.2 % Fe) at a *cut-off grade* of >45 % Fe (as of: 31.12.2003), mined, used in the local cement industry and for export to Japan,
  - Yogyakarta: on average 2 m thick, elevated beach and dune placers (JACOB et al. 1979) with an average content of 12.25 % Fe, average contents of the concentrate: 59 % Fe, 7-10 % TiO_2, resources: 230 million tonnes of sand or 28 million tonnes of extractable concentrate,
  - Djambang Kulon: a) fossil (beach?) placer, average contents: 37 % Fe, 12 % TiO_2, content in the deposit 6.7 million tonnes at a *cut-off grade* of 37 % Fe, b) recent dune placers, average contents: 20 % Fe, 4 % TiO_2,
  - Cipatuja: beach and dune placers with an average of 19.8 (-31.5) % M. (titano)magnetite, average contents of the concentrate: 57 % Fe, 12.8 % TiO_2, 0.25-0.4 % V and 0.05-0.1 % P, contents of the deposit: 4.21 million tonnes at a *cut-off grade* of 7 % by mass (titano)magnetite,
  - Cadman: beach and dune placers with an average of 23.2 % by mass (titano)magnetite, average contents of the concentrate: 57.39 % Fe, 12.75 % TiO_2, contents in the deposit: 3.22 million tonnes,
  - Ciaos: beach and dune placers between the Ciaos and Cabaña Rivers with an average of 18.5 % by mass (titano)magnetite, average contents of the concentrate: 57.18 % Fe, 12.32 % TiO_2, resources: 25.0 million tonnes of sand or 4.65 million tonnes of extractable concentrate, in addition 0.46 million tonnes of concentrate offshore, completely protected as national iron ore reserve,
- **Philippines:** On the Philippines, and on the main island of Luzon in particular, (titano)magnetite is the main valuable mineral in numerous beach placers. The host rocks are andesites and other volcanites in the interior of the island. Mining of this mineral started in 1964 and was continued on a large scale until 1976. Approx. 8.5 million tonnes of ore sands were produced, whose contents were sold mainly to Japanese steel companies. A national mining prohibition because of ecological concerns was only eased in 1981. Currently no mining on a large scale takes place. The following is known about the individual islands:
  - Luzon: 22 individual deposits of titanomagnetite and/or magnetite with >1 million tonnes in each deposit, total reserves and resources approx. 45 million tonnes of (titano)magnetite, contents in the concentrate: 57-62 % Fe, 4.8-12.67 % TiO_2, 2.5-3.7 % SiO_2, 1.2-1.5 % Al_2O_3, 0.02-0.04 % P, 0.03 % S
  - Mindanao: 4 individual deposits of titanomagnetite with only small total reserves and resources of approx. 100,000 tonnes; chromium bearing, also chromite placers,
  - Leyte Island: 2 individual deposits of magnetite with total reserves and resources of approx. 5 million tonnes and contents of 4-55 % by mass in the sediment
  - Negros Island: 2 individual deposits of magnetite with total reserves and resources of approx. 1 million tonnes
- **Japan:** In Japan, magnetite sands were mined on all islands from ancient times until 1979. The iron used to be used for the manufacture of Samurai swords, and in World War II as a source of raw materials for the Japanese arms industry. Currently, only the severely restricted extraction of a few tonnes of iron sands for the manufacture of hand-forged kitchen knives is conducted. At first, fine-grained beach placers with an average content of 25.6 % by mass were mined, later only 10 % Fe in the ore sand. After these deposits had been depleted, the extraction was moved to older beach terraces, residual placers (TSUSUE & ISHIAHRA 1975) and coarse-grained fluvial placers with an average content of 20-30 % Fe and/or 30 – 40 % by mass magnetite in the sediment. In 1956, the production of offshore deposits started. A comparison of the chemical compositions of Japanese titanomagnetite concentrates is listed in Table 10.2. The remaining total geological resources in Japan have been estimated at 1,306 million tonnes of ore sand at an average content of 6.3 % Fe,

corresponding to 82.3 million tonnes of Fe. The economically extractable reserves and resources are estimated to be 67.5 million tonnes of ore sand with an average content of 14.5 % Fe, corresponding to 9.8 million tonnes of Fe. (WARD & TOWNER 1985b).

Table 10.2: Chemical composition (% by mass) of Japanese titanomagnetite concentrates (WARD & TOWNER 1985b).

	Onshore		**Offshore**
	recent beach	**older terraces**	
Fe	58.76	58.40	56.77
TiO_2	10.92	7.54	10.44
SiO_2	2.16	4.30	8.50
Al_2O_3	2.69	2.95	2.95
P	0.009	0.133	0.170

- **Canada, Quebec,** Natashquan River: resources of 22 million tonnes of magnetite in 1,659 million tonnes of sediment with an average heavy mineral content of 8.03 % by mass. Accompanying valuable minerals are ilmenite, garnet and zircon,
- **Chile,** La Barca and Duna Choapa Norte: magnetite, gold and garnierite $[(Ni,Mg)_6Si_4O_{10}(OH)_8]$ are gangue valuable minerals in the local dune placers. Ilmenite is the main valuable mineral. La Barca: resources of 100.56 million tonnes of ore sand with an average content of 9.71 % by mass of magnetite. Duna Choapa Norte: resources of 45.77 million tonnes of ore sand with an average content of 10.70 % by mass of magnetite.
- **India:** magnetite is enriched in the coastal placers of the Indian states of Andhra Pradesh and Maharashtra. Table 10.3 lists the known pertinent data.

Table 10.3: Magnetite bearing beach placers in India (according to RAJU et al. 2001).

State	**Coastal region**	**Content (% by mass)**		**Resources (million tonnes)**
		in the ore sand	**in the HM-fraction**	
Andhra Pradesh	northern		0.20	0.56
	central	11.66-36.68 (av. 16.50)	5.03	10.28
	southern	4.65-25.48	7.44	n.a.
Maharashtra	Ratnagiri			0.39

- **South Korea**: In South Korea, four smaller deposits with total resources of 285,000 tonnes of magnetite are known, accompanying valuable minerals are: ilmenite, monazite, zircon and in part gold,
- **Rep. of South Africa, KwaZulu Natal,** Richards Bay: magnetite and garnet are valuable gangue minerals in the local dune placers. Main valuable minerals are ilmenite, rutile and zircon,
- **Ecuador**, **Guayana**: small-scale mining of beach placers with titanomagnetite for the domestic cement industry, accompanying heavy minerals are ilmenite, pyroxene, amphibole, epidote, staurolite, as well as to a very small degree zircon and garnet,
- **Costa Rica, Guatemala**: Because of the predominance of volcanic source rocks, rock magnetite placers can be found along most of the pacific coast of Central America.

10.3 Applications

Magnetite is an important iron ore. The theoretical Fe-content of 72.4 % (the highest of all Fe-minerals) is only rarely attained because of the presence of isomorphous additions of Al, Ti, Mg and V. In particular Ti and V lower the value of the mineral as an iron ore, possibly turning Ti-V magnetites into ores of these two elements, however.

Because of its properties:

- high bulk density
- high physical and chemical resistance
- good thermal conductivity
- high magnetic sensitivity
- non-toxicity

Magnetite is used for the following purposes outside of the metallurgical sphere:

- as the raw material for the manufacture of high-purity iron oxide for audio/video tapes (decreasing use),
- as additive in toners for laser printers and copiers. The percentage of magnetite in toners differs significantly depending on the manufacturer and the exact application, and amounts to a few to 70 % by mass. Further important components of toners are synthetic resins, various polymers, polyolefin waxes and carbon,
- as an iron additive for the manufacture of cement. For producing cement in Indonesia a raw mix of ~82 % limestone, ~16.5 % sandy clay and ~1.5 % "iron sand" (= magnetite concentrate) is ground, homogenized and then baked in a rotary furnace.
- as a functional filling material in chemistry (e.g. for heavy polypropylenes for sound insulation in automotive applications and building construction),
- in physical water treatment for the removal of turbidity, algae and other impurities,
- as a dense medium for coal flotation. Finely ground magnetite (<45 µm) mixed with water produces a defined dense medium for the gravity separation of impurities in the introduced coal dust which sink together with the magnetite. The sunken magnetite is then siphoned off at the bottom with the impurities and can easily be recycled because of its magnetic properties. The clean coal dust floats and is collected. After drying it is ready for use.
- as a raw material in the manufacture of pigments for special colors. For this purpose, Fe_2O_3 manufactured by oxidation from Fe_3O_4 is consiederd to be of higher value than natural hematite.
- as a dense medium for radiation protection construction materials, heavy concrete (underwater concrete, coastal protection) and ballast (e. g. on oil platforms),
- as ballast (counterweights) for bridges, in excavators, ship loading devices, elevators and washing machines,
- as a blasting abrasive,
- as a molding sand for foundry purposes
- as an additive in fertilizers.

10.4 Substitutes

Depending on the usage, magnetite can easily be replaced by other mineral resources; some options are listed below:

- iron ore: all other, but usually lower grade Fe ore,
- cement industry: other iron bearing minerals, copper slag, used foundry sands and dusts,
- dense medium: barite, galenite, clay, quartz powder,

- ballast: barite, hematite, ilmenite, iron granulate,
- blasting abrasives: garnet, staurolite, emery, nepheline syenite, olivine, perlite, pumice, quartz sand, different slags, steel shot, silicon carbide, ilmenite.

10.5 Specifications for the raw materials (reference values)

The minimum content of (titano)magnetite in placers mined mainly for this mineral is 10 % by mass.

(Titano)magnetite for metallurgical purposes should have a low TiO_2-content and a high Fe-content. Contents of >65 % Fe and <7 % TiO_2 are best. The more unfavorable these values, the more high-quality iron ore has to be added.

Dense magnetite media for coal floatation must have a grain size distribution of 80 % by mass, optimally 90 % by mass <325 mesh (45 µm). The quartz content and the super fine contents should be low and the Fe-content should be high. These specifications ensure the good recyclability of the magnetite.

Tables 10.4 and 10.5 contain data on chemical compositions, grain size distributions as well as the physical parameters of natural and commercial (titano)magnetite concentrates.

Table 10.4: Chemical composition (%) of natural titanomagnetite and magnetite concentrates.

	Titanomagnetite Filmag Inc. La Union Province Luzon, Philippines [1]	Titanomagnetite Yogyarkarta Java, Indonesia [2]	Titanomagnetite BlueScope Steel Ltd. Waikato North Head North Island, New Zealand [3]	Titanomagnetite BlueScope Steel Ltd. Taharoa North Island, New Zealand [3]	magnetite "masa" black concentrate Hanaidani Mine Yokota, Shimane prefecture, Japan [4]	Magnetite "akome" reddish concentrate Zakka Mine Nita, Shimane prefecture, Japan [4]
Fe total	61.61		60.43	60.23	64.31	62.50
FeO	25.21	32.86	30.57	31.1	16.40	22.35
Fe_2O_3	59.44	54.34	52.47	51.6	73.72	64.53
TiO_2	6.17	6.07	8.00	7.74	1.95	5.20
SiO_2	2.34		1.00	0.01	3.84	3.14
Al_2O_3	3.03	2.83	3.51	3.1	0.72	1.42
Cr_2O_3	0.031		-	0.023	-	-
MgO	2.40	2.35	3.30	2.8	0.23	0.43
CaO	0.66		0.10	0.52	0.10	0.98
V_2O_5		0.56	0.36	0.57	0.11	0.35
P_2O_5			0.15	-	0.16	0.11
MnO	0.75	0.60	0.59	0.71	-	-
Zn	0.081					
Ni	0.006					
Cu	0.011					
Bi	0.004					
Pb	+					
S	0.098				0.019	0.008

[1] Ward & Towner (1985c) [2] Mücke (2003) [3] Williams (1974) [4] Tsusue & Ishihara (1975)

Table 10.5: Chemical composition (%) and physical parameters of commercial magnetite-concentrates according to company information.

	65 Grade Mmagnetite Universal Minerals	*UMI 90 Grade Magnetite* Universal Minerals	*7 Mesh Grade Natural Iron Oxide* Universal Minerals	*UMI Superfine Magnetite* Universal Minerals	*UMI Magnetite 96 Grade (A)* Universal Minerals	Magnetite Dal Logistics	Magnetite Cleveland-Cliffs Inc.
Chemical composition							
Fe total	70.00	68.2	67.0	68.8	68.0	69.0	67.0
FeO	29.4		26.63				
TiO_2				0.38	0.38		
SiO_2	1.65	2.26	3.03	1.844	2.50	2.3	4.5
Al_2O_3	0.31	0.87	0.62	0.40	0.60	0.78	0.3
MgO	0.58	0.42	1.07	0.565		0.55	0.5
CaO	0.20	0.61	0.57	0.637		0.65	0.9
Na_2O	0.018		0.132			0.04	
K_2O	0.049		0.143	0.080		0.08	
P	0.01		0.020	0.076	0.09		
Mn	0.02		0.019	0.83		0.12	
Zn	0.003					0.02	
Ni						0.02	
Cu	0.006		0.019	0.015	0.03	0.02	
As			+				
Pb	+					0.01	
S	0.138	0.29	0.315		0.05	0.3	
Typical grain size distribution							
<100 *mesh* (150 µm)	95.0		40.9				
<325 *mesh* (45 µm)	67.0		7.0			78-85	
>10 µm							
>6.35 µm							
>1.00 µm							
>0.15 µm							
<0.15 µm							
Guaranteed grain size distribution							
<100 *mesh* (150 µm)	90.0						
<325 *mesh* (45 µm)	63.0	90.0			96.0		90.0
<400 *mesh* (38 µm)		86.0					
<10 µm		21.0					
<5 µm				61.38			
Physical parameters							
Magnetic proportion	97.0	97.0		92.4	96.0	92.92	96.0
Humidity	8.0	9.0	4.9	1.0	0.04	9-10	9.5
Apparent density(g/cm^3)	5.07	4.95	4.85	5.0	4.95		5.0
Bulk density			2,900			2,770-2,810	
Spec. surface (cm^2/g)						1,500-1,700	

10.6 Size of deposits and resources

The exact proportion of magnetite in the total iron ore resources and reserves of approx. 330 billion tonnes is not known. The following standard values apply to the size of placer deposits, where solely (titano)magnetite is mined.

	Placers
	mineral content
Small	100,000 – 500,000 tonnes
Medium	500,000 – 1 million tonnes
Large	1 million – 5 million tonnes
Very large	>5 million tonnes

The distribution of the global deposits (reserves and resources) of (titano)magnetite in placers – defined as known and published amounts of currently workable, mineable heavy minerals, not blocked by competitive usages – is shown in Figure 10.2.

10.7 Important producing countries

Titanomagnetite from placers is currently only produced in New Zealand, Indonesia and Japan.

Figures 10.1-10.3 show the percentage distribution of global production (2007) and the currently known global resources of (titano)magnetite in direct comparison.

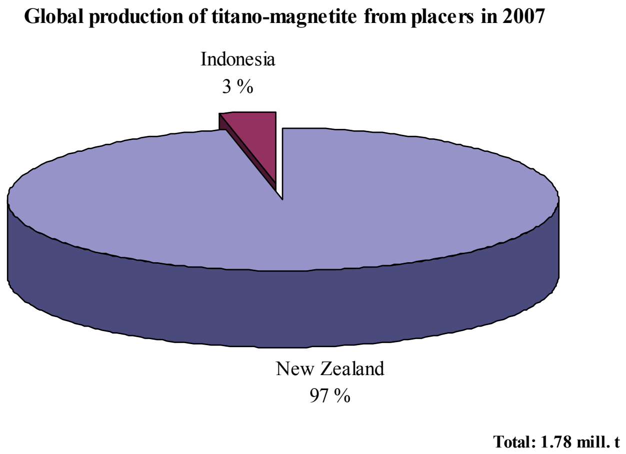

Figure 10.1: Percentage distribution of the global production (2007) of (titano)magnetite from placers.

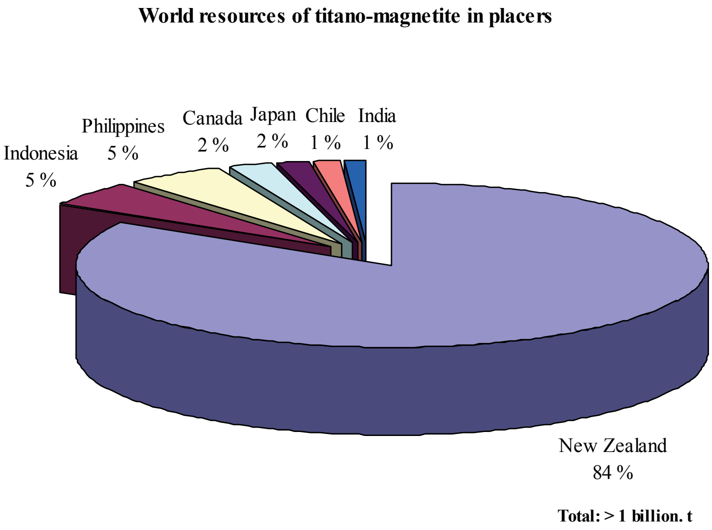

Figure 10.2: Percentage distribution of the currently known global reserves and resources of (titano)magnetite from placers.

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11 Cassiterite

[German: *Cassiterit*, Spanish*: cassiterita*, French: *cassiterite*]

11.1 Mineralogy, petrography, chemistry

Cassiterite, also called tinstone, is a heavy mineral of great economic importance. Pure cassiterite has the following properties:

Formula	SnO_2
Chemistry	78.8 % by mass Sn, 21.2 % by mass O_2
Density	7.02 g/cm^3
MOHS hardness	6-7
Color	black, brown-black, yellowish brown, reddish brown
Magnetic properties	nonmagnetic
Electrostatic properties	conductive

In cassiterite, Sn can be replaced by Fe at a ratio of 1:6 as well as by Nb and Ta to a ratio 1:30. Other frequently occurring trace elements are Ti, Li, Sc, Zn, Fe, W and Mn. Up to 1 % of oxygen can be substituted by $(OH)^-$groups. Correspondingly, rutile, lepidolite, columbite and tantalite are frequent accompanying minerals of cassiterite. Inclusions in cassiterite include rutile, wolframite, chalcopyrite and pyrite, to a lesser degree also ilmenite, zircon, columbite, sphalerite, pyrrhotine, magnetite and hematite depending on the genesis.

Submicroscopic inclusions of wolframite cause the dark color of the intrinsically transparent cassiterite. Inclusions of columbite in turn cause the strong pleochroism of some pegmatitic cassiterites (BINDE 1986).

11.2 Formation of deposits and occurrences

The element tin is mainly lithophile and is enriched in the residual melt of acid magmas. Many types of granite thus contain tin in the form of the mineral cassiterite. Cassiterite is mainly enriched in the “tin granites”, which contain approx. 15 – 50 g Sn/tonne. Cassiterite also occurs as “mine tin”:

- intra magmatic: in domes of granite intrusions (Saxony Erzgebirge), in feldspar topaz granites (Czech Republic, Saxony Erzgebirge), in rhyolites (Sierra Madre Occidental/Mexico) and titanomagnetite deposits (e.g. Grängesberg/Sweden with ~100 g SnO_2/ton). The more acidic the rock, the higher its Sn-content.
- pegmatitic: Besides cassiterite, Sn-W pegmatites contain the minerals wolframite, columbite, tantalite and lepidolite. Deposits of this type are Bikita/Zimbabwe, Manono-Kitotolo/DR Congo, Greenbushes/Western Australia and Phuket/Thailand.
- pneumatolytic: “greisenization” of granites and their adjacent rock. Known deposits of this type are Altenberg/Saxony Erzgebirge, East Kemptville/Nova Scotia/ Canada, Haad Som Pan/Thailand and Talushan and Chiu Lung Nao/South East China, Blue Tier/Tasmania as well as Zaaiplants and Rooiberg/Bushveld complex/Rep. South Africa. Contact metasomatic cassiterite mineralizations are known from the Erzgebirge and Namibia. One of the largest tin deposits in the world developed metasomatically – in dolomites: Renison Bell/Tasmania. Further examples are Cleveland and Mt. Bischoff/Tasmania as well as Dachang and Geiju/China.

- hydrothermally: Highly thermal veins are mineable in numerous cassiterite deposits. Primarily these are the tin ore veins in the Cornish, Saxony and Bohemian deposits (Zinnwald, Geyer, Ehrenfriedersdorf, Schlaggenwald etc.), Herberton/North Queensland/Australia, Aberfoyle/Tasmania/Australia, Sungei Lembing/Pahang/Malaysia as well as Billiton/Indonesia. The individual deposits are mostly small (<4.5 tonnes of ore), but high-grade (0.7-2.3 % Sn). In the Bolivian subvolcanic deposit province, mainly sulfidic tin lodes with the valuable minerals cylindrite ($Pb_3Sn_4FeSb_2S_{14}$), frankeite ($Pb_5Sn_3Sb_2S_{11}$), stannite (Cu_2FeSnS_4) and teallite ($PbSnS_2$) occur.

Because cassiterite is very resistant to all weathering influences, is it a typical placer mineral. “Placer tin” was produced a long time before “mine tin” and traded long distances. Important placer tin deposits include:

- **Bolivia**: Since 1924, mining of alluvial placers of the Lipez Huayco and Antequera for cassiterite, accompanying minerals are hematite, magnetite, ilmenite and tourmaline, average depths of the mineable areas are 27.5 m, and the overburden 3.5 m,
- **Brazil**: Small-scale mining of alluvial placers of the Rio Abaixo in Minais Gerais; fossil alluvial cassiterite placers in Rodonia, mineable thickness of the gravel sands 1-6 m, average content 0.3-1.2 kg Sn/m^3, Holocene fluvial placers have significantly smaller thicknesses, but higher contents,
- **Burma**: Fluvial placers of the Tenasserim range with cassiterite, wolframite, bismuthite, magnetite and pyrite,
- **China**: Province of Hunan, Changning region: placers near Baisha, Xiling and Zoujiaqiao with an average content of 650 g cassiterite /m^3; Province Guangxi, Hexian region: Shuiyanba placer currently being mined with 0.053 % Sn,
- **Mongolia:** Eluvial and in particular fluvial placers with cassiterite, wolframite and other heavy minerals (mainly garnet and zircon) in the Modot Valley and at Khujkhaan near Tsernhermandel, Khentii Aimag, in Eastern Mongolia. Production with interruptions since 1949. Up to now cassiterite concentrate with approx. 10,000 tonnes Sn capacity has been mined. The tin content of the placers varies between 170 g/m^3 and more than 700 g/m^3 (frequently up to 450 g/m^3),
- **Nigeria**: Tertiary to Holocene alluvial and eluvial placers on the Jos Plateau in the provinces of Bauchi, Benue, Kano and Zaria with cassiterite and columbite, secondary gangue mineral wolframite, tantalite and thorite (ANONYMOUS 1981), extractable reserves 1977: 140 kilotonnes cassiterite,
- **Russia:** North-eastern Yakutia and Chukotka, e.g. eluvial-alluvial placers on the Pyrkakaivaam river (contents up to 6 kg cassiterite /m^3) and Krutoi brook (up to 17.3 kg cassiterite /m^3). Accompanying minerals are wolframite, gold, magnetite, pyrite, arsenopyrite, hematite, garnet, topaz, zircon, fluorite and anatase. Only the cassiterite and the gold are economic.
- **South-East Asian tin belt**: nearly 3,000 km long from Moulmein District in Northern Burma via Thailand and Malaysia to the Indonesian island of Belitung. Mine tin in coarse-grained biotite granites and secondary fine to medium grained two-mica granite. Age: Carboniferous to Lower Tertiary. Tin placers of colluvial, eluvial origin (average thickness 1-2 m) and most of all alluvial placers (thickness dm->100 m) onshore (⅔), as well as offshore (⅓) in Western Malaysia, Thailand and Indonesia (cf. Table 11.1). Mining by gravel pump “dry mining” using high-pressure water jets), floating dredge (ladder dredger or suction dredger) and quarrying (e.g. Hong Fat mine in the Province of Selangor/Malaysia, 152 m depth) as well as secondary underground mining and artisanal mining. Estimated resources, 6 million tonnes Sn – more than the total resources of the rest of the world. The heavy-mineral concentrate from which cassiterite has already been separated is called “amang”, and is processed further to extract additional valuable minerals (cf. Chapter 11.6, Tables 5.6, 11.2-11.4).

Table 11.1: Tin contents of placers mined in Indonesia and Malaysia according to SCHMIDT (1976) and LAHNER (1982).

Country	Mining region	Range (g Sn/m^3 Sediment)	Average (g Sn/m^3 Sediment)	Comment
Indonesia	Bangka	400-1,400	750	
	Belitung	190-900	400	
	Singkep	-	250	cassiterite contains 1 % Nb/Ta
	Sumatra	-	260	
Malaysia	Kinta near Ipoh	150-350	-	
	Berjuntai	130-160	-	
	Sungei Besi	76 – 15,310	-	

Table 11.2: Distribution of valuable minerals (% by mass) in the raw sand in tin placers of Thailand according to PRADITWAN (1985, 1988b, c, 1989a).

Mineral	Phuket Island		Central Thailand		Southern Thailand		Northern Thailand	
	range	mean value	range	mean value	range	mean value	range	mean value
Cassiterite	15.24-89.15	62.16	1.4-93.7	66.7	6.1-90.8	52.7	24.6-81.9	71.52
Columbite-tantalite	0.08-0.83	0.24	0.1-3.4	0.9	0.2-2.5	1.1	-	
N-Ta rutile	0.01-6.09	0.34	+-3.3	0.4	0.1-5.0	1.0	-	
Wolframite	0.01-0.52	0.18	0.1-0.3	0.2	0.1-1.1	0.3	0.7-36.8	0.8
Scheelite	-		+-1.6	0.3	-		0.1	0.1
Monazite	0.32-5.01	1.5	+-11.8	0.9	0.1-3.4	0.6	0.9-20.4	9.5
Ilmenite	0.37-51.14	10.7	0.5-49.6	6.5	0.1-38.6	4.0	0.3-3.5	2.5
Leucoxene	-		+-41.0	0.1	-		-	
Rutile	-		+-5.6	0.3	-		0.1-0.6	0.3
Anatase	-		-		-		13.5	13.5
Zircon	-		-		0.1-3.5	0.7	0.1-3.2	1.0
Sphalerite	-		-		0.1	0.1	-	
Galenite	-		-		0.1	0.1	-	

+ = traces

Table 11.3: Mineralogical composition (% by mass) of heavy mineral pre-concentrates from the tin belt of South-East Asia.

	Indonesia			**Thailand** 2)				
	Banka, Muntok District 1)		**Belitung** 3)	**Chiang Mai**	**Phangnga**	**Phuket**	**Trang**	**Kanchanaburi**
	Mine # 4	Mine # 2	(avg. of n=4)	Omkoi (avg. of n=6)	Chaiyayuth Dredge	Tantikovit Mine	Loom Seng Mine	Patana Mine
Cassiterite	36	60	67.1	62.2	34.3	49.6	34.3	24.2
Columbite-tantalite				3.9	1.4	0.3	1.8	0.3
Struverite					0.9	+	1.8	0.1
Samarskite				0.1			0.1	
Nb-Ta rutile				0.3				
Rutile	+	+	0.4	0.3	0.4	+	0.8	0.7
Anatase	1	+		2.2	+		0.5	0.3
Brookite	+	1						
Ilmenite(+leucoxene)	31	11	0.6	1.8	23.0	0.4	9.2	23.3
Wolframite				0.3				
Scheelite				0.4	+			+
Zircon	3	3	4.9	1.0	1.6		0.7	2.2 5)
Monazite	19	22	0.6	8.5	7.7	0.1	0.7	0.8
Xenotime	5	1		+				
Magnetite			0.1		0.1			+
Martite			0.1					
Pyrite (+marcasite)			7.0	0.1	2.2	0.1	+	
Arsenopyrite						0.9	+	+
Fe-(Hydr)oxide 4)			4.6	0.9	8.8	1.0	2.3	13.0
Mn-oxides			+	0.4	0.1	13.1		0.5
Garnet			0.1	4.4	13.7	19.6	11.0	26.9
Tourmaline	4	2	0.1	1.1	0.3	1.9	20.6	3.6
Topaz			0.8		2.4			
Spinel					0.1		1.6	0.4
Beryl				0.1				
Corundum	+	-						
Ankerite	+	+						
Quartz	1	+	13.1	12.3	3.6	13.0	14.7	3.6

1) BODENHAUSEN (1954) 2) PRADITWAN (1988a) 3) PRADITWAN (1989b) 4) lepidocrocite, goethite, hematite, limonite 5) plus 0.2 % allanite + = traces

11.3 Applications

Cassiterite is mainly used for extracting the metal **tin** and is almost the only tin mineral of economic importance. Tin is silvery white, very inert because of the oxidation layer, and thus singularly suitable for protection against corrosion (tin coating of sheet metal = tinplate). Tin is also used for:

- alloys: bronze, bearing metals, type metal, German silver,
- tin casting (tin figures) consisting of 60-70 % Sn and 30 – 40 % Pb,
- soldering tin,
- opaque white glazes,
- organotin compounds (tributyltin) as toxic protective paints, e. g. in shipbuilding,
- catalytic converters,
- as a stabilizer in PVC,
- together with Ca for strengthening the Pb-electrodes in batteries,
- window pane production by casting on liquid tin,
- tin halogenides as stabilizers in perfumes and soap ($SnCl_4$) or as a main component in toothpaste (SnF_2),

11.4 Substitutes

Cassiterite is the most frequent and economically most important Sn mineral and can only be substituted to a limited extent by sulfidic Sn minerals. In all of its metallic applications, it is very difficult to substitute tin, and then only with a deterioration in quality. Depending on the usage, tin can be replaced by other mineral resources or elements; some options are listed below:

- glazes: marble powder, white lead, zinc white, lithopone, titanium dioxide,
- toxic protective paint: cuprous or silicon paint,
- stabilizers in PVC: Ca-Zn compounds.

11.5 Specifications for the raw materials (reference values)

The references give very different minimum contents (cut-off grades) for the mineability of cassiterite deposits:

- deep mining: >1.0 % Sn
- mine tin: >0.5 % Sn or Sn+W
- placer tin: >0.01 % Sn (typical: 0.05 % Sn = 500 g Sn/ton)
- placer mining with floating dredge: 60 g cassiterite/m^3
- placer mining using gravel pumps: 120 g cassiterite/m^3
- large-scale industrial mining: 240 g cassiterite/m^3
- small-scale mining: 300 g cassiterite +columbotantalite/m^3

There are no specifications for commercial concentrates of cassiterite because cassiterite is always smelted directly – depending on the concentration – without further treatment.

Table 11.4: Chemical and mineralogical compositions (% by mass) of different concentrates from Malaysia accruing in the course of cassiterite production and processing.

	Excavator pre-concentrate Berjuntai, Selangor 1)	**Smelting pre-concentrate** average 1)	**Cassiterite-concentrate** 2)	**Amang** Ipoh, Perak 2)
Chemical composition				
SnO_2		95.54	81.37	0.58
$(Zr,Hf)O_2$			0.03	0.51
TiO_2		0.31	3.08	40.57
SiO_2			2.99	18.97
Al_2O_3			1.58	0.90
Fe_2O_3		0.74	8.10	35.93
MnO			0.21	2.30
MgO			0.12	0.05
CaO			0.05	0.02
V_2O_5			0.02	0.06
Nb_2O_5			0.31	0.16
P_2O_5			0.02	0.10
SO_3		0.15	<0.01	0.03
As		200 ppm	85 ppm	26 ppm
Bi		40 ppm	52 ppm	13 ppm
Ce			49 ppm	459 ppm
Cr			110 ppm	242 ppm
Cu		60 ppm	222 ppm	22 ppm
La			<20 ppm	252 ppm
Nd			<50 ppm	1111 ppm
Pb		240 ppm	84 ppm	110 ppm
Ta		<1,000 ppm	778 ppm	143 ppm
Th			<5 ppm	104 ppm
U			440 ppm	39 ppm
W			4694 ppm	118 ppm
Zn			122 ppm	677 ppm
LOI			0.36	-0.96
Mineralogical composition				
Cassiterite	9.7		85.0	
Ilmenite	41.5		9.5	80.7
Rutile	0.5			0.7
Zircon	2.1			12.5
Monazite	2.0			
Staurolite			+	
Garnet			+	
Tourmaline	0.8			+
Hornblende			+	
Quartz	43.4		5.4	6.1

1) Lahner (1982) 2) BGR-analysis

11.6 Size of deposits and resources

These reference values apply to the evaluation of the size of cassiterite deposits according to SUTPHIN et al. (1990).

	All deposits Sn-content
Small	<10,000 tonnes
Medium	10,000 – 100,000 tonnes
Large	100,000 – 500,000 tonnes
Very large	>500,000 tonnes

The estimated global reserves and resources of tin are shown in Figure 11.1.

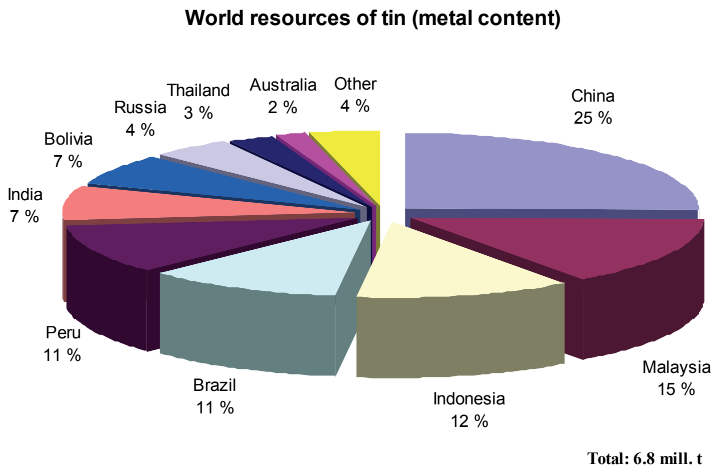

Figure 11.1: Percentage distribution of the known global reserves and resources of tin (metal contents).

11.7 Important producing countries

Figure 11.2 shows the distribution of the global mine production of tin (metal content) from cassiterite and sulfidic Sn-ore in 2007.

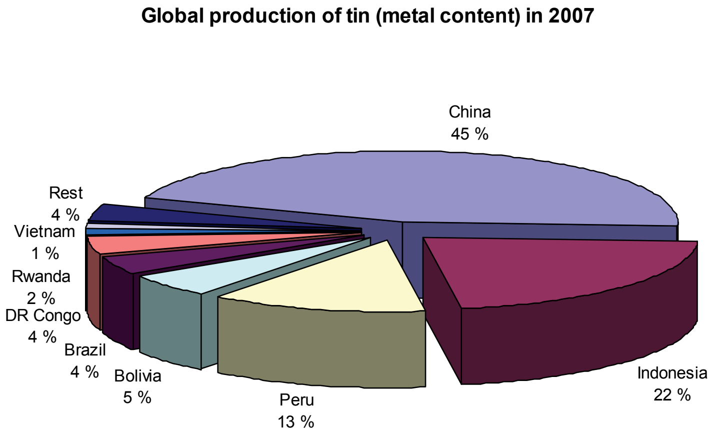

Figure 11.2: Percentage distribution of the global production of tin (metal contents) in 2007.

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12 Columbite-Tantalite

[German: *Columbit*, Spanish*: columbita*, French: *columbite*]
[German: *Tantalit*, Spanish*: tantalita*, French: *tantalite*]

12.1 Mineralogy, petrography, chemistry

Tantalite is the Ta-rich final member, and columbite (niobite) the Nb-rich final member of the solid solution columbite- tantalite. As these final members do not occur in a chemically pure state in nature, mining geologists commonly use the collective terms columbite-tantalite or columbotantalite or the abbreviation "coltan".

Table 12.1: Properties of the minerals tantalite and columbite.

	Tantalite	**Columbite (niobite)**
Formula	(Fe, Mn)$(Ta)_2O_6$	(Fe, Mn)$(Nb)_2O_6$
Chemistry	variable, cf. Tab. 12.3	variable, cf. Tab. 12.3
Bulk density (g/cm^3)	$\leq$8.1	$\geq$5.3
MOHS HARDNESS	6-6 ½	6
Color	black, dark brown, reddish brown	black, dark brown
Magnetic properties	paramagnetic	paramagnetic
Electrostatic properties	conductive	conductive

The most frequent accompanying minerals of columbite-tantalite in pegmatites are beryl, cassiterite and phosphate. Garnet, spodumene, zircon, tourmaline, magnetite, ilmenite, rutile, amblygonite, siderite, topaz, different sulfides as well as U, Th and W minerals are found more rarely. Ta-Nb bearing accompanying minerals are microlite (cf. below), tapiolite (columbotantalite with tetragonal crystal structure) as well as samarskite $(Fe,Y,U)_2(Nb,Ti,Th)_2O_7$. The main inclusions in columbite-tantalite are zircon, cassiterite and tapiolite.

In addition, the only Nb-Ta bearing heavy minerals present in a few placer deposits in mineable concentrations, are:

- struverite $(Ti,Ta,Nb,Fe)_3O_6$ [chemical composition Malaysia: 12-13 % Ta_2O_5, 12-13 % Nb_2O_5, 56-57 % TiO_2, 4-5 % SnO_2 according to KRAUß et al. 1982b], which is enriched similar to
- Ta-Nb rutile [chemical composition: 40 – 77 % TiO_2, 9-17 % Nb_2O_5, 5-26 % Ta_2O_5, 5-13 % FeO, 2-7 % SnO_2, 0.5-1.0 % WO_3, 0.2-2.0 % MnO_2, 0.0-0.2 % ZrO_2 according to HASSAN (1994)], found only in the tin belt of South-East Asia, and in particular in Malaysia in the "amang" (cf. below)
- tapiolite $(Fe,Mn)(Ta,Nb)_2O_6$
- microlite $(Ca,Na)_2(Ta,Nb)_2O_6(OH,O,F)$,
- uranmicrolite (djalmaite) $(U,Ca,Ce)_2(Ta,Nb)_2O_6(OH,F)$, which was mined for a few years in Brazil (cf. Table 12.6),
- pyrochlor $(Ca,Na)_2(Nb,Ta)_2O_6(O,OH,F)$, rare in placers because not very resistant,
- yttrotantalite $(Y,Fe,U,Ce,Zr)(Ta,Nb,Ti,Sn)_2O_6$
- thoreaulite $Sn(Ta,Nb)_2O_7$, both only near Sn-pegmatites

12.2 Formation of deposits and occurrences

Niobium minerals crystallize out in the early phase of magmatic differentiation. Thus, they occur as accessories in nearly all magmatic rocks. They attain increased concentrations in syenites and nepheline syenites. In carbonatites, niobium is frequently enriched in the form of the mineral pyrochlor and is then usually mineable. The largest carbonatite-pyrochlor deposit in the world is in Araxà/Brazil with resources/reserves of approx. 460 million tonnes Nb_2O_5 (corresponding to approx. 500 years at current global demand) and contents of 2.5-3.0 % Nb_2O_5. The largest global columbite-deposit is also in Brazil (Pitinga mine) with deposits of 201 million tonnes of ore and an average content of 0.223 % Nb_2O_5. The Fe-Nb-Ta product has contents of approx. 45 % Nb_2O_5 and 4.3 % Ta_2O_5.

Even though **tantalum** is geochemically very similar to niobium, its genesis is very different. The low tantalum content in magmas only rarely permits the formation of Ta-minerals during the early phase of magmatic differentiation. Tantalum is thus only enriched in pegmatites and there only as tantalite. Alkaline pegmatites, which developed from nepheline syenites, in which tantalum was also fixed in minerals during the intrusion, constitute the exception. Tantalum minerals are only enriched in mineable amounts in granite pegmatites (and the associated placers) (cf. Table 12.2). The largest tantalite mines in the world include Greenbushes and Wodgina/Western Australia (FREEMAN & DONALDSON 2004), Tanco Mine /Manitoba/Canada, Kenticha Mine/Ethiopia, Yichun Mine/China as well as Pitinga and Mibra Mines/Brazil.

Table 12.2: Percentage distribution of the global reserves of niobium and tantalum, and average Nb/Ta-ratios in rocks according to DE KUN (1962).

	Reserves		Nb/Ta ratio	
	niobium	**tantalum**	occurrence	rocks
Carbonatites	98.5	-	75	75
Placers	1.2	61	8	high
Pegmatites	0.1	39	1	1
Granites	0.2	-	7	16

Columbite-tantalite is also a gangue valuable mineral in cassiterite placers being mined in Nigeria and the DR Congo (extraction since 1932, ANOYMOUS 1981), China (Provinces of Guangdong and Hunan), Western Australia (KRAUß et al. 1982b), Malaysia, Thailand and other countries of the tin belt of South-Eastern Asia (cf. Chapter 11).

In many African countries, there is artisanal mining (cassiterite-wolframite) of tantalite-columbite placers, for instance in Burundi, Ivory Coast, Gabon, Liberia, Niger, Nigeria, Sierra Leone, Rwanda, DR Congo, Tanzania and Uganda.

12.3 Applications

Columbite-tantalite, as well as all other Nb-Ta heavy minerals named in Chapter 12.1, are used for the extraction of the metals niobium and tantalum. Areas of application of **niobium** are:

- metal alloy ores for making pipes, car bodies, and ships, for tool steel and railroad tracks,
- Nb-oxide (high index of refraction, high dielectric constant and transmitted light optimization) for camera lenses, computer screen coatings and ceramic capacitors (substitute for tantalum),
- Nb-carbide for tool and cutting steels as well as welding filler material,
- Nb-powder for conductors in electronic circuits,

- metal in the chemical systems industry, defense engineering, jewelry industry and minting industry
- alloy additive with Ti and Sn for superconducting magnetic coils,
- alloy additive with Zr for sodium discharge lamps and chemical plant engineering,
- high purity Fe-Nb and Ni-Nb for the manufacture of super alloys in turbine manufacture and furnace construction.

Tantalum is used as:
- powder for very small capacitors with high capacity in micro-electronics, e.g. for hearing aids, pacemakers, airbags, ignition control and engine control units, GPS, ABS, laptops, cellphones, video cameras, playstations etc.,
- metal alloy ores and accessory for refractory and high-strength alloys, mainly with W,
- Ta-carbide for tool and cutting steels,
- Ta-oxide (high index of refraction, good abrasion resistance) for camera lenses and ink jet printers as well as with Y and P in x-ray films for reducing the duration of exposure and image quality optimization,
- metal in the chemical systems industry, in gas turbine engineering, in vacuum furnace construction and increasingly for medical implants.

12.4 Substitutes

Columbite-tantalite can be substituted by a large number of other Nb-Ta minerals. In particular, niobium has been produced from pyrochlor for a long time, whereas tantalite continues to be the most frequent and economically important Ta-mineral by far. Important secondary raw materials for the production of tantalum and niobium are the remaining melts of cassiterite smelting. Typically they contain 2-9 % Ta_2O_5, 2-15 % Nb_2O_5 and also 0.5-2 % Sn.

Niobium and tantalum can be substituted in part by each other, otherwise very difficult, and then only with a deterioration in quality.

12.5 Specifications for the raw materials (reference values)

The mineability thresholds (cut-off grades) listed below apply to tantalite:
- hard rock: >0.008 % Ta_2O_5 (typical : 0.013-0.015 (0.02) % Ta_2O_5)
- placers: >0.003 % Ta_2O_5 (typical 0.015 – 0.02 (0.05) % Ta_2O_5 = 150-200 (500) g Ta_2O_5/tonne)
- placers: >300 g cassiterite +columbite-tantalite /m^3 sediment

Specifications for commercial concentrates of columbite-tantalite (cf. Table 12.3) are as follows:

- $\geq$60 % (Ta_2O_5 + Nb_2O_5) (typical: 15-65 % Ta_2O_5, 5-45 % Nb_2O_5)
- $\leq$6 (8) % SnO_2
- $\leq$6 (8) % TiO_2
- $\leq$8 % MnO
- $\leq$5 % FeO
- $\leq$0.5 % ThO_2 + U_3O_8
- $\leq$1 % W
- $\leq$0.20 (0.30) % P
- $\leq$50 ppm Sb

Table 12.3: Chemical composition (%) of commercial columbite-tantalite concentrates according to Livan (1980) and Hochleitner & white (2002).

	Nigeria	**Uganda**	**DR Congo**	**Rumong District Guyana**	**Malaysia**	**Idaho USA**	**New Mexico USA**
Nb_2O_5	67.7	57.3	42	52.98	60.2	61.5	58.3
Ta_2O_5	6.3	15.4	35	20.21	15.0	6.0	12.0
SnO_2	1.4	0.2	2	0.1	0.5		
TiO_2	1.5	1.2	1.5	1.84	1.8		2.8
ZrO_2	0.4	0.2	1)	0.28	0.3		
SiO_2							2.7
MnO	2.0	7.8	5.5	7.16	5.0		12.9
FeO	19.1	11.6	14	13.55	13.8		5.5

1) 3.5 % total Sn, Ti, W, U, Pb, Ca and Zr.

According to Lahner (1982), the following evaluation scheme depending on Ta-content is used for cassiterite concentrates for tin smelters in Malaysia .

	Cassiterite Concentrate Ta_2O_5-content (%)
Very low	<0.05
Low	0.05-0.2
Medium	0.2-0.4
High	>0.4

The largely tin-free final slags in Malaysia are evaluated as follows according to Krauß et al. (1982b).

	Final tin smelting slag Ta_2O_5-content (%)
low grade	<2.0
medium grade	average 2.75
high grade	average 3.5

12.6 Size of deposits and resources

For Ta-Nb deposits, the reference values listed in Table 12.4 apply according to the National Committee of Minerals Resources of China: Standards for Size Classification of Mineral Deposits.

Table 12.4: Reference values (in tonnes) for the evaluation of the size of Ta-Nb deposits (Zhu Xun 2002).

	Niobium deposits		**Tantalum deposits**	
	hard rock Nb_2O_5 content	placer mineral content	hard rock Ta_2O_5 content	placer mineral content
small	<10,000	<500	<500	<100
medium	10,000 – 100,000	500-2,000	500-1,000	100-500
large	>100,000	>2,000	>1,000	>500

The estimated reserves and resources of tantalum and niobium are listed in Table 12.5.

Table 12.5: Reserves and resources of tantalum and niobium oxide (in kilotonnes) from mining production or percentage proportion of the three most important countries in terms of global reserves, amended according to DEPARTAMENTO NACIONAL DE PRODUÇÃO MINERAL BRASIL (2009).

	Ta_2O_5 [1]		Nb_2O_5	
	kilotonnes	%	kilotonnes	%
Ethiopia	2.4			
Australia	40.3	25.8	21	0.5
Brazil	88.2	56.5	4,132	98.0
Burundi	1.0			
Canada	2.9		62	1.5
DR Congo	1.4			
Malaysia	0.9			
Mozambique	3.9			
Nigeria	7.0	4.5		
Rwanda	1.4			
Thailand	7.0			
World – total	156		4,215	100.0

[1] Other resources of unknown size in China, Uganda, Zimbabwe, Saudi-Arabia, Greenland.

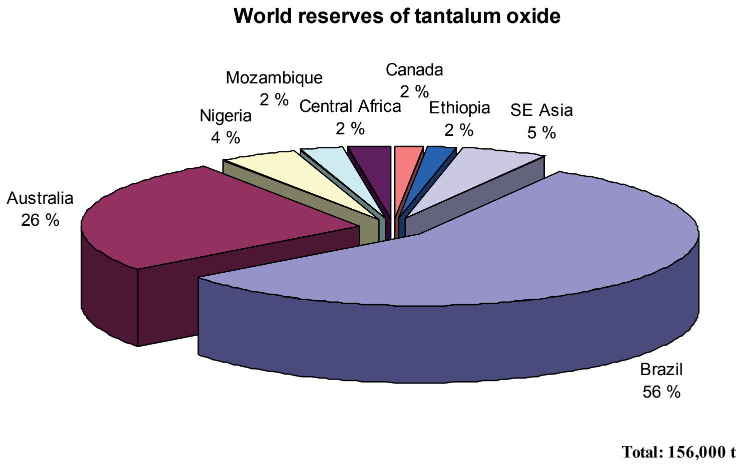

Figure 12.1.: Percentage distribution of the global reserves of tantalum oxide from mining production, amended according to DEPARTAMENTO NACIONAL DE PRODUÇÃO MINERAL BRASIL (2009).

12.7 Important producing countries

Data and information on the global mining production of tantalum ores are shown in Figure 12.2.

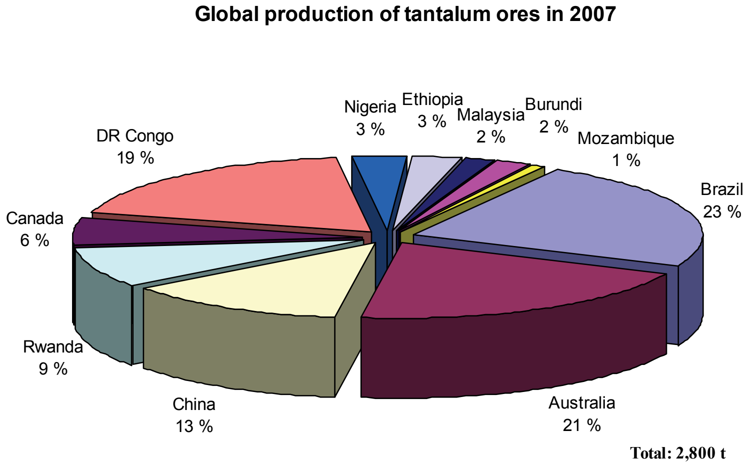

Fig. 12.2: Percentage distribution of the global production of tantalite (from pegmatites: Ethiopia, Australia, Canada, Mozambique, Nigeria), columbite-tantalite (from pegmatites and placers: Brazil, Burundi, China, DR Congo, Rwanda) and struverite (from "amang"; Malaysia) in 2007.

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13 Wolframite and Scheelite

[German: *Wolframit*, Spanish*: wolframita*, French: *wolframite*]
[German: *Scheelit*, Spanish*: scheelita*, French: *scheelite*]

13.1 Mineralogy, petrography, chemistry

Wolframite is the name for mixed wolframites of the mixed crystal series with the Mn-rich final member hubnerite and the Fe-rich final member ferberite (cf. Table 13.1). Selected properties of the minerals wolframite (and/or hubnerite and ferberite) as well as scheelite are listed in Table 13.2.

Table 13.1: Classification of the wolframites due to their chemistry according to NAKAMURA (1964).

	$FeWO_4$	$MnWO_4$	FeO	MnO
	%		%	
Ferberite	100-80	0-20	23.6-18.9	0-4.7
Wolframite	80-20	20-80	18.9-4.8	4.7-18.7
Hubnerite	20-0	80-100	4.8-0	18.7-23.4

Table 13.2: Properties of the minerals wolframite and scheelite.

	Wolframite	**Scheelite**
Formula	$(Fe,Mn)WO_4$ ferberite: $FeWO_4$, hubnerite: $MnWO_4$	$CaWO_4$
Chemistry	variable ferberite: 76.34 % WO_3, 23.66 % FeO hubnerite: 76.57 % WO_3, 23.43 % MnO	80.52 % WO_3, 19.48 % CaO
Bulk density(g/cm^3)	ferberite: 7.51, hubnerite: 7.12	6.10
MOHS hardness	4-4 ½	4 ½- 5
Color	dark grey, brown-black ferberite: black to blackish brown hubnerite: yellowish-brown to brown red, deep red	white, yellowish, brown, grey
Magnetic properties	paramagnetic	nonmagnetic
Electrostatic properties	conductive	not conducting

Wolframites frequently contain minor amounts of Nb, Ta, Sn and Ca (<1.5 %), Sc (<0.4 %), Ti (<0.1 %) as well as traces of In, Mo, Bi, Zr, Hf, Sc and Y. Some of these elements impede the processing of wolfram ores (cf. Chapter 13.5).

Wolframite forms pseudomorphs after scheelite. Wolframite can alter into scheelite. Both minerals weather near to the surface into tungstite (wolfram ochre), $WO_3 \times H_2O$, a tungsten trioxide rich in water.

Due to the isomorphism with molybdenum, there are numerous mixed crystal series of W and Mo minerals, e.g. between scheelite ($CaWO_4$) and powellite ($CaMoO_4$).

The similar crystal structure of columbite-tantalite allows their incorporation in wolframite (up to 20.25 % Nb_2O_5) and vice versa, of wolframite in columbite-tantalite (up to 13 % WO_3).

Scheelite is one of the most fluorescent minerals and is prospected for in the dark using UV-light because of the fluorescent colors (bright blue, and frequently white to yellow due to traces of molybdenum). BIGGA (1965) contains notes on prospecting for scheelite in placers and the behavior of this mineral during transportation.

Other W-bearing heavy minerals according to VIENNADL (1968) and PAVLU (1986), which occur rarely to very rarely in a very few placer deposits:

- yttrotungstite, $(Y,Ce)WO_4(OOH)$, from eluvial cassiterite deposits at Kramat Pulai in the Kinta District in Perak/Malaysia,
- stolzite (lead tungstate), $PbWO_4$, from gold bearing placers at Sumidouro in Minais Gerais, Brazil as well as
- anthoinite, $WAl(OOH)_3$, from eluvial placers with ferberite at Mt. Misombo, Kalima District, DR Congo.

13.2 Formation of deposits and occurrences

The formation of **wolframite** and **hubnerite/ferberite** mainly takes place:

- pegmatitically-pneumatolytically (ferberite, wolframite),
- pneumatolytically-hydrothermally (hubnerite),
- subvolcanically (ferberite) as well as
- submarine-exhalative-sedimentary (ferberite).

Higher contents of Sc, Rare Earths, Nb and Ta indicate genesis of the wolframite in pegmatites and greisens. Low contents indicate genesis in hydrothermal lodes (PAVLU 1986).

Scheelite forms:

- in skarns (contact pneumatolytically), associated with garnet, epidote, diopside, tremolite, vesuvianite, fluorite, chalcopyrite and molybdenite,
- in hydrothermal quartz veins, associated with gold, cassiterite, wolframite, topaz, tourmaline, apatite, beryl, molybdenite and arsenopyrite
- strata-bound, probably submarine-exhalative-sedimentary associated with Sb and Hg mineralisation.

Scheelite is relatively sensitive to physical and chemical exposure. Wolframite is also subject to fast physical weathering because of its pronounced cleavability. Both minerals possess only limited hardness. In spite of their high density, they are rather rare as heavy minerals in placers – if present they are more likely found in colluvial and eluvial placers, but only very rarely in alluvial deposits.

Even though scheelite is mainly prospected for due to its fluorescence (cf. above), heavy mineral analysis for scheelite and wolframite is one of the best prospecting tools for primary hard rock deposits of these two tungsten minerals.

Amongst the few placer deposits of scheelite and wolframite, although completely irrelevant for the global supply of tungsten, are:

- **Australia,** Queensland: 1) at Mt. Carbine: eluvial wolframite-scheelite placers above hydrothermal W-bearing quartz veins, mining with interruptions since the end of the 19th century. 2) at Wolfram Camp near Chillagoe, eluvial wolframite placers with original reserves of 155,000 m^3 sediment with an average content of 2.25 kg wolframite/m^3 corresponding to approx. 350 tonnes of wolframite with an average of 60 % WO_3
- **Bolivia:** ferberite in deposits of formerly large landslides near Tamiñani (reserves/resources of 1.35 million tonnes of sediment with an average of 0.3 % WO_3) and Perfeccionada (reserves/resources of 2.7 million tonnes of sediment with an average of 0.1-0.2 % WO_3), as

well as the terraces cut into these sediments in the Rio Ayopaya canyon at the north flank of the Chicote Grande (0.05-0.24 % WO_3),

- **Burma:** numerous eluvial, more rarely alluvial and littoral wolframite-bearing cassiterite placers on the coast of Tenasserim; extraction of alluvial placers in the Meinda mine east of Tavoy as well as near Khamaunghla; production of marine Sn-W placers in the Heinze River Basin north of Tavoy since the 1930s, large reserves/resources in the Gulf of Martaban; the wolframite contents in the placers over the whole tinstone belt of Southeast Asia decrease from north to south,
- **China:** numerous wolframite and scheelite placers with high percentages of cassiterite and sphene, for instance near Fengtian and Yangmeisi in Jiangxi Province or in the Hanjianggou District in Guangxi Province,
- **DR Congo:** production of wolframite and cassiterite (columbite-tantalite) placers in the Provinces of Shaba, Kivu (Maniema, Etaetu, Ngawe, Tetari, Kabunga, Tshiganda) since 1913/14 (ANONYMOUS 1981).
- **India:** Rajasthan, Degana/Nagaur District: colluvial wolframite placers with original reserves of 3.357 million tonnes of sediment with an average content of 0.04 % WO_3,
- **Canada /Alaska:** 1) littoral gold placers near Nome/Alaska with an average of 40.81 % by mass magnetite (and a little hematite and limonite), 20.69 % by mass garnet, small amounts of cassiterite and ilmenite, as well as wolframite (4.99 % by mass) and scheelite (2.13 % by mass), production of a few tonnes of concentrate during World War I; 2) alluvial gold-scheelite placers in Yukon Territory/Canada, e. g. in Dublin Gulch, in the proximity of the large primary deposits Potato Hill and Scheelite Dome, average contents of 0.015 % WO_3 per m^3 sediment; 3) scheelite placers along the Turnagain River in northern British Columbia/Canada,
- **Malaysia:** extraction of wolframite, more rarely scheelite, from the amang of numerous cassiterite placers (cf. Chapter 11) mostly in the Kinta Valley in Perak. The main deposit there is Pulai with a sediment thickness of approx. 8 m only 30 m away from a granite outcrop which is interstratified with numerous fluorite-scheelite pegmatite dykes. The average WO_3-content in the wolframite of Malaysia is 65 % by mass. Lists and geological data on the different wolframite and scheelite producing mines and regions of Malaysia are published by BRADFORD (1961) and RAJAH (1982).
- **Mongolia:** Production of wolframite and cassiterite at Khujkhaan near Tsernhermandel, Khentii Aimag, in eastern Mongolia. The mainly eluvial-fluvial placers have been mined with interruptions since 1949. The marginal C1+C2 reserves are said to be 4.3 million m^3 loose rock containing 375 tonnes of WO_3 in wolframite. The non-marginal C1+C2 reserves are 66 tonnes of WO_3 in wolframite in 2.2 million m^3 loose rock. According to old expedition reports, the East Khujkhaanii field bears 85 g WO_3/m^3 in the loose rock. The wolframite concentrate currently produced by a company contains about 60 % WO_3.
- **Austria:** fluvial scheelite placers near Tux in Tyrol (BIGGA 1965),
- **Thailand:** Similar to Burma and Malaysia, wolframite and scheelite are by-products of cassiterite extraction in the Takua Pa placer tin mines /Province of Phang-nga, as well as Tambons Ratsada and Ko Kaeo/Province of Phuket
- **USA:** 1) California/Stringer District: eluvial gold placers at the top of scheelite-bearing mesothermal quartz veins with an average of 4.14 % WO_3, higher enrichments of scheelite near Atolia with a sediment thickness of 2-40 m, mining with interruptions since 1937; 2) Colorado/Boulder Co.: discovery of alluvial ferberite placers in 1898 resulted a little later in the development of on average 15-45 cm thick ferberite veins with 2-20 % WO_3; 3) Arizona/Little Dragon Mountains: hubnerite and wolframite placers

In a number of African countries, there is artisanal mining of wolframite (cassiterite-tantalite-columbite) placers, for instance in Niger, Nigeria, Burundi, Rwanda, and most of all in the DR Congo (ANONYMOUS 1981).

13.3 Applications

Scheelite and wolframites are exclusively used for the extraction of the metal tungsten. It is characterized by its:

- high thermal resistance (highest melting point of all metals: 3387 (3422) ^{o}C),
- high tensile strength (highest mechanical strength and smallest coefficient of expansion of all metals),
- (with C or O) very high hardness (very soft in highly pure form),
- good conductivity
- high resistance to atmospheres and acids

Tungsten in turn is used for the manufacture of:

- Tungsten carbide, WC and W_2C, which is mainly used for the manufacture of turning and cutting steels, but also in alloys for armor-plated projectiles because of its very high hardness and its high abrasion resistance even at high temperatures,
- tungsten alloys, together with Co, Ni, Mo, Al, Ta, Re, Th and Zr, for special steels,
- different tungsten chemicals for catalysts, pigments, lubricants, lasers, x-ray devices and also for glass with controllable translucence.

In addition, tungsten in metallic form is used in the

- electronics and electrical industry (light bulb filaments, cathodes, anodes, spark plugs, electric contacts in circuits),
- high-temperature engineering (heating elements, thermo elements, electrodes),
- welding,
- aerospace engineering (rocket nozzles),
- for building furnaces for special glass melts.

13.4 Substitutes

There are no mineable tungsten ores other than wolframite and scheelite and their weathered mineral product tungstite (wolfram ochre).

Depending on the application, tungsten carbide, tungsten metal and tungsten chemicals can usually not be replaced by other chemicals. In the most important application, the manufacture of turning and cutting tools, substitution is possible in some cases by other metal carbides, e. g. TiC, CoC.

13.5 Specifications for the raw materials (reference values)

The cut-off grade for tungsten minerals not mined in artisanal mines is 0.3 % WO_3.

Table 13.3 compiles the international specifications for the chemical composition of scheelite and wolframite concentrates. There are no specifications on the grain size distributions of wolframite and scheelite concentrates.

The quality specifications by the US-government for the purchase of scheelite and wolframite concentrates in and after World War II are listed in Tables 13.4 and 13.5.

The tungsten contents of tungsten mineral concentrates from all over the world held in the US strategic stockpiles by the Defense Logistics Agency and quoted internationally in the internet in November 2004 are listed in Table 13.6.

Producers and buyers often agree on customized specifications for wolframite or scheelite concentrates. These are listed in Table 13.7 based on the example of Bolivian producers. Higher Sn and Mo contents in particular are undesirable. Scheelite with >1.0 % Sn is unsaleable according to AHLFELD (1958).

Table 13.3: International specifications for the chemical composition (in %) of scheelite and wolframite concentrates according to ANONYMOUS (1986) as well as LI & WANG (1955).

	Wolframite			Scheelite		
	General	*Grade* I	*Grade* II	General	*Grade* I	*Grade* II
WO_3	65.00-70.00	≥65	60-64.99	60.00-70.00	≥70	65-69.99 [1]
Sn	1.00-1.50	0.20-1.00	≤2.5	≤0.1		
As	0.10-0.25	≤0.20	≤0.4	≤0.10	≤0.3	
Cu	≤0.10	0.08-0.40	≤1.0	≤0.10	-	
Mo	0.04-0.40	≤0.40	≤1.0	0.05-0.40	≤2.0	≤4.0
P	0.05-0.10	0.03-0.08	≤0.25	0.05-0.10	≤0.1	
S	0.10-0.50	0.20-0.75	≤2.00	≤0.5		
Bi	≤1.00	-		0.05-1.00	≤0.2	
Sb	≤0.50			≤0.05		
Mn	0.00			≤1.00		

[1] Lower grade scheelite ores are usually converted into artificial scheelite direct at the mine or later into ammonium paratungstate, an important intermediate product of the synthesis of tungsten (cf. Table 13.8).

Table 13. 4: Specifications for the chemical composition (in %) of wolframite and scheelite concentrates when purchased by the US-government during World War II (LI & WANG 1955).

	Wolframite		Scheelite		Tungsten ores
Country of origin	USA	Bolivia, Cuba Argentina, Mexico	USA	Bolivia, Mexico	China
WO_3	≥65.00 [1]	≥65.0	≥60.00	≥60.0	≥65.00
Sn	≤1.50	≤1.5	≤0.10	≤0.5	≤1.50
As	≤0.25	≤1.0	≤0.10	≤0.5	≤0.20
Cu	≤0.03	≤0.8	≤0.05	≤0.2	≤0.12
Mo	≤0.40	-	≤0.40	-	≤0.40
P	≤0.03	-	≤0.05	-	≤0.05
S	≤0.50	≤1.5	≤0.50	≤1.0	≤1.00
Bi	≤0.50	-	≤0.50	-	≤0.40
Mn	-	-	≤1.00	-	-
Pb	≤0.10	-	≤0.10	-	-
Sb	≤0.50	-	≤0.10	-	≤0.05

[1] Hubnerite: ≥60 % WO_3

Table 13. 5: Specifications for the chemical composition (in %) of domestic tungsten concentrates when purchased by the US-government after 1951 (Li & Wang 1955).

<table>
<tr><th></th><th>Ferberite</th><th>Hubnerite [1)]</th><th>Wolframite</th><th>Scheelite and /or artificial scheelite</th></tr>
<tr><td>WO_3</td><td>(≥55) 60</td><td>(≥55) 60</td><td>(≥60) 65</td><td>(≥55) 60</td></tr>
<tr><td>Sn</td><td>≤0.20</td><td>≤0.25</td><td>≤1.50</td><td>≤0.10</td></tr>
<tr><td>As</td><td>≤0.15</td><td>≤0.10</td><td>≤0.25</td><td>≤0.10</td></tr>
<tr><td>Cu</td><td colspan="2">≤0.10</td><td colspan="2">≤0.05</td></tr>
<tr><td>Mo</td><td colspan="2">≤0.50</td><td colspan="2">≤0.40</td></tr>
<tr><td>P</td><td>≤0.07</td><td colspan="3">≤0.05</td></tr>
<tr><td>S</td><td colspan="4">≤0.50</td></tr>
<tr><td>Bi</td><td colspan="3">≤1.00</td><td>≤0.25</td></tr>
<tr><td>Mn</td><td>≤1.0</td><td colspan="2">-</td><td>≤1.0</td></tr>
<tr><td>Pb</td><td colspan="3">≤0.20</td><td>≤0.10</td></tr>
<tr><td>Sb</td><td colspan="4">≤0.10</td></tr>
<tr><td>Zn</td><td colspan="4">≤0.10</td></tr>
</table>

[1)] hubnerite: ≥60 % WO_3

Table 13.6: Specifications for WO_3 of lots of tungsten mineral concentrates from the stocks of the Defense Logistics Agency of the USA offered in November 2004 via the Internet.

Country of origin	Scheelite	Hubnerite	Ferberite	Wolframite
Australia	65.20-66.92			
Bolivia	71.80-74.71		65.82-75.52	71.06-74.50
Chile	73.54			
China				68.86-69.42
Canada	75.43			
Lesotho				68.46-72.60
Peru		66.71-74.82		
Rep. South Africa				67.32-72.26
Spain	74.67-75.19			66.27-69.34
Thailand				72.07-72.27
USA	62.48-78.04	72.02-74.72		64.42

Table 13.7: Specifications for the chemical composition (in %) of Bolivian wolframite and scheelite concentrates according to Ahlfeld (1958).

	Wolframite			Scheelite	
	Category A	Category B	Category C	Category D	Category E
WO_3	≥65		≥60	≥60	≥60
Sn	≤1.5			≤0.10	
Bi	≤1.0			≤0.25	
Cu	≤0.05	≤0.10	≤0.20	≤0.05	
Mo	≤0.40			≤0.40	
As	≤0.25		≤1.5	≤0.10	≤0.25
Pb	≤0.20	≤0.30		≤0.10	
Sb	≤0.10	≤0.25		≤0.10	
Zn	≤0.10	≤1.0		≤0.10	
Mn	-			≤1.0	
S	≤0.50	≤1.0	≤3.0	≤0.10	≤0.25
P	≤0.05	≤0.10		≤0.05	

Typical chemical compositions of naturally occurring scheelite, as well as artificial scheelite frequently produced from lower grade or higher molybdenum-bearing scheelite-concentrates directly at the mine, and of ammonium paratungstate (APW), an important intermediate product in the synthesis of tungsten, are compared in Table 13.8.

Table 13.8: Comparison of the chemical composition (in %) of natural and artificial scheelite as well as ammonium paratungstate according to Anstett et al. (1985).

	Natural scheelite	**Artificial scheelite**	**Ammonium paratungstate (APW)**
WO_3	73.00	75.00	89
CaO	22.14	22.25	0.001
SiO_2	2.68	0.40	0.03
NH_3			5.4
Al			0.00005
As	0.001	0.001	
Bi	0.01	0.01	
Fe	1.00	0.30	0.002
Mn	0.03	+	
Mo	1.00	0.02	0.0025
Na			0.002
P	0.01	0.03	
S	0.03	0.30	
Zn	0.02	0.01	
others1)	+	+	
LOI			11
Humidity			0.5

1) Cu, Pb, Sb, Sn

Guaranteed and typical chemical compositions of wolframite and scheelite concentrates from different producers (countries) are listed in Tables 13.9 and 13.10.

Table 13.9: Guaranteed and typical chemical compositions (%) of wolframite concentrates according to Anonymous (1980), Yih & Wang (1979) and Bradford (1961).

	Mt. Carbine RB Mining Pty Ltd. **Australia**	Oakleigh Creek Mine Central Tasmanian Tungsten Pty Ltd. **Tasmania, Australia**	Chambillaya Mine International Mining Co. **Bolivia**	Emramada Mine International Mining Co. **Bolivia**	Minas Da Panasqueira Beralt Tin and Wolfram Portugal SARL **Portugal**	Minas de Argozelo Minargol – Complexo Mineiro de Argozelo SARL **Portugal**	Centromin **Peru**	Climax Mine Amax Tungsten **USA**	Minmetals **China**	**Ferberite** Pulai, Perak **Malaysia**	**Ferberite** Somirwa SARL **Rwanda**
Guaranteed											
WO_3	≥70.00	≥70.00			≥74.00		≥65.00				≥68.00
As	≤0.08	≤0.20					≤0.12				
Ca							≤0.36				
Mo							≤0.01				
P	<0.04	≤0.04									
S		≤1.00					≤1.50				
Sn		≤1.00									
Typical											
WO_3	70.65	70.52	69.62	67.95	75.51	73.56	71.00	70.00	65.8	73.26	68.70
As	0.03	0.11	0.06	0.15	+	0.04	0.03	0.01	0.06	n.d.	0.06
Bi		0.02		+	0.01		0.01	0.01	0.05	n.d.	
Ca	2.86		0.14	0.16	0.04	0.59	0.29		1.53	n.d.	0.06
Cu		+	0.02	+	0.01	0.26	0.08	0.01	0.75	n.d.	+
Fe		14.23	18.37	18.62	16.00	10.44	5.00	8.00	10.26	17.60	19.34
Mn		4.82	1.00	1.40	2.23	6.71	12.50	11.00	8.36	0.60	0.81
Mo		+	+	+	+		+	0.05	+		+
P	0.02	0.02	+	+	+	0.07	0.02	0.01	0.01	n.d.	0.05
Pb		+	+	+	+		0.08	0.01	0.07	n.d.	+
Sb					+		0.01	+			
S	0.68	0.38	0.37	0.30	0.03	0.36	1.20	0.10	0.50	n.d.	0.01
Si					0.07	0.39		0.47	1.36	0.30	0.92
Sn		0.84	0.93	0.50	0.03	0.19	0.05	0.25	1.0	n.d.	0.05
Zn		0.01	0.01	0.01	0.03	0.20	0.10	0.02			
LOI			0.10	0.08	0.34	0.51				0.65	

\+ = traces

Table 13.10: Guaranteed and typical chemical compositions (%) of scheelite concentrates according to Anonymous (1980), Yih & Wang (1979) and BRADFORD (1961).

	Mt. Carbine RB Mining Pty Ltd. **Australia**	Salua Mine Société Minière d´Anglade **France**	Korea Tungsten Mining Co. Ltd. **South Korea**	Sang Dong **South Korea**	Boca de Lage Mine Tungstenio do Brasil Minerios e Metails Ltda. **Brazil**	Coto Minero Merladet S.A. **Spain**	**Coarse Scheelite** Minas da Borralha SARL **Portugal**	**Fine Scheelite** Minas da Borralha SARL **Portugal**	Mines Organisation of Thailand **Thailand**	Pulai, Perak **Malaysia**	Mittersill **Austria**
Guaranteed											
WO_3	≥70.00	≥65.00	≥70.00		≥73.00	≥75.00			≥74.00		
As	≤0.08	≤0.10	≤0.01		≤0.05	≤0.05			≤0.10		
Ca			<17.19								
Mo			≤1.70		<1.00	≤0.02			≤0.02		
P	≤0.04		≤0.03		≤0.05	≤0.05			≤0.10		
S		≤0.55	≤0.05		≤0.30	≤0.10					
Sn			≤0.01		≤0.05	≤0.05			≤1.00		
Typical											
WO_3	75.50	75.00	72.00	71.4	74.00	77.80	75.00	68.50	75.75	79.52	31.4
As	0.04	0.10	0.01		+	0.04	0.05	0.05	0.09	+	+
Bi			0.01	0.01		0.01		0.20			n.d.
Ca			15.82	14.51		14.27	17.00	17.00		13.94	9.93
Cu		0.03	+	+		+	0.15	0.15		n.d.	+
Fe	0.58	2.00	1.00	0.24		0.31	1.35	1.35		0.16	1.06
Mn	0.10		0.03			+	0.40	0.40		+	
Mo		0.22	1.00	1.21	0.80	+	0.04	0.04	0.01		0.16
P	0.09	0.03	0.01	0.02	0.03	+	0.10	0.12	0.08	n.d.	1.00
Pb			+	+		0.01				n.d.	0.03
Sb	+		+			+					
S	0.010	0.55	0.03		0.20		0.30	0.30	0.02		0.06
Si			1.25	0.77		0.56	0.40	0.40		0.17	16.3
Sn		0.05	+	0.01	+	+	0.50	0.50	0.76	0.20	+
Zn			0.02			+					
LOI										0.14	

+ = traces

13.6 Size of deposits and resources

The following reference values apply to W-deposits according to the National Mineral Reserves Commission of China: Standards for Size Classification of Mineral Deposits (ZHU XUN 2002).

	WO_3-content
Small	<10,000
Medium	10,000 – 50,000
Large	>50,000

The estimated global reserves and resources of tungsten are listed in Table 13.11 and depicted in Figure 13.1.

Table 13.11: Global reserves and resources of tungsten (metal content in kilotonnes) and percentage of the global reserves/resources, altered according to PLIMER (1983) and ANONYMOUS (2001, 2005).

	Tungsten	
	kilotonnes	%
Kazakhstan	1,530	34.4
China	1,110	25.0
Canada	660	14.9
Russia	400	9.0
USA	140	3.2
North Korea	113	2.6
Australia	62	1.4
Bolivia	60	1.3
South Korea	58	1.3
Turkey	55	1.2
Kyrgyzstan	40	0.9
Uzbekistan	40	0.9
Portugal	25	0.6
Tadzhikistan	23	0.5
Thailand	21	0.5
France	20	0.4
Norway	18	0.4
Austria	18	0.4
other countries	50	1.1
world total	**4,450**	**100.0**

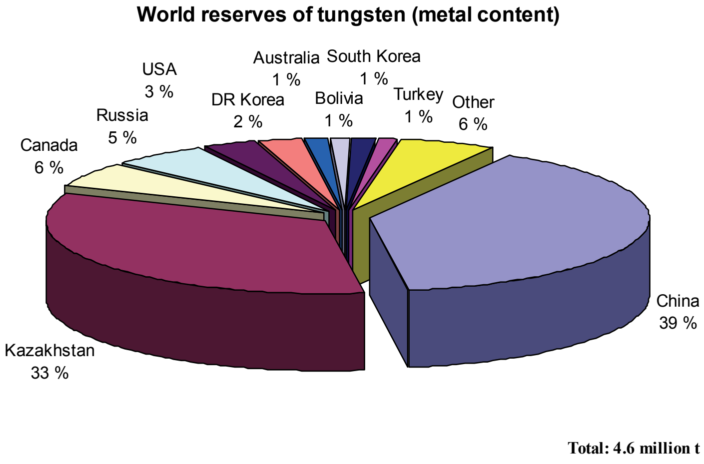

Figure 13.1: Percentage distribution of the global reserves/resources of tungsten (metal content).

13.7 Important producing countries

Mining tungsten minerals started at the end of the 19th century. At that time, production started in Australia, Spain, Portugal, Cornwall and the German Erzgebirge. By 1900, the global production was only approx. 1,000 tonnes of concentrates. It rose slowly, reaching 8,100 tonnes in 1913. During World War I, the German Empire managed to use the special properties of tungsten as a steel hardening agent industrially, thus very quickly turning tungsten into a strategically important metal. In the course of World War I, known deposits in Burma, the USA, Bolivia, Portugal, Spain, Argentina, Australia, Vietnam, Great Britain and the German Erzgebirge were developed and/or their production was stepped up considerably. In 1915, deliveries started from China, since then, the most important producer. Between the world wars, production was low in all countries, but started rising steeply with the start of global armament in 1935. In the main war year 1943, 60,072 tonnes of concentrates with >60 % WO_3 were produced (AHLFELD 1958).

Figure 13.2 shows the distribution of the global mining production of tungsten (metal content) in 2007.

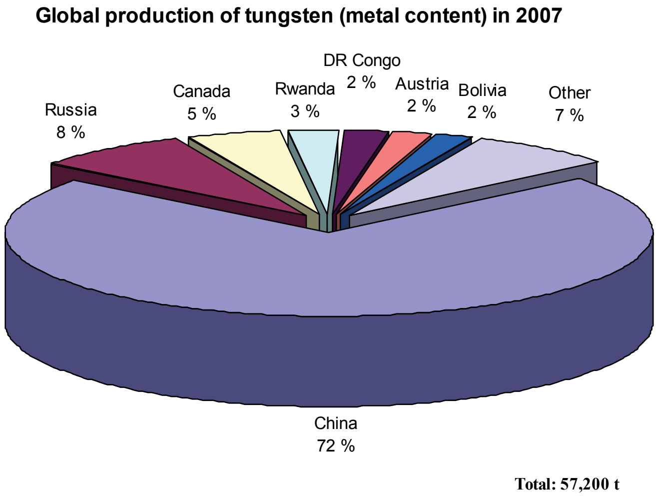

Figure 13.2: Percentage distribution of the global production of tungsten (metal contents) in 2007.

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