ROUNDTABLE

INDUSTRIAL MINERALS RESEARCH

ROUNDTABLE

China's Industrial Minerals & Markets

New Horizons, New Mindsets

中国的工业矿物和市场 新地平线，新思维模式

Regal International East Asia Hotel, Shanghai, 23-25 September 2013

Murray Lines

Stratum Resources, Sydney ,Australia

Key uses and growth markets for high purity quartz

STRATUM resources

References include:

- ANZAPLAN (Germany)
- Quartz Corporation (Imerys/Norwegian JV)
- Unimin/Sibelco (USA)
- Creswick Quartz (Melbourne)
- Springer Geology – Jens Gotze & Robert Mockel

  (Quartz: Deposits, Mineralogy & Analytics 2012)
- Saudi Geological Survey (Jeddah)

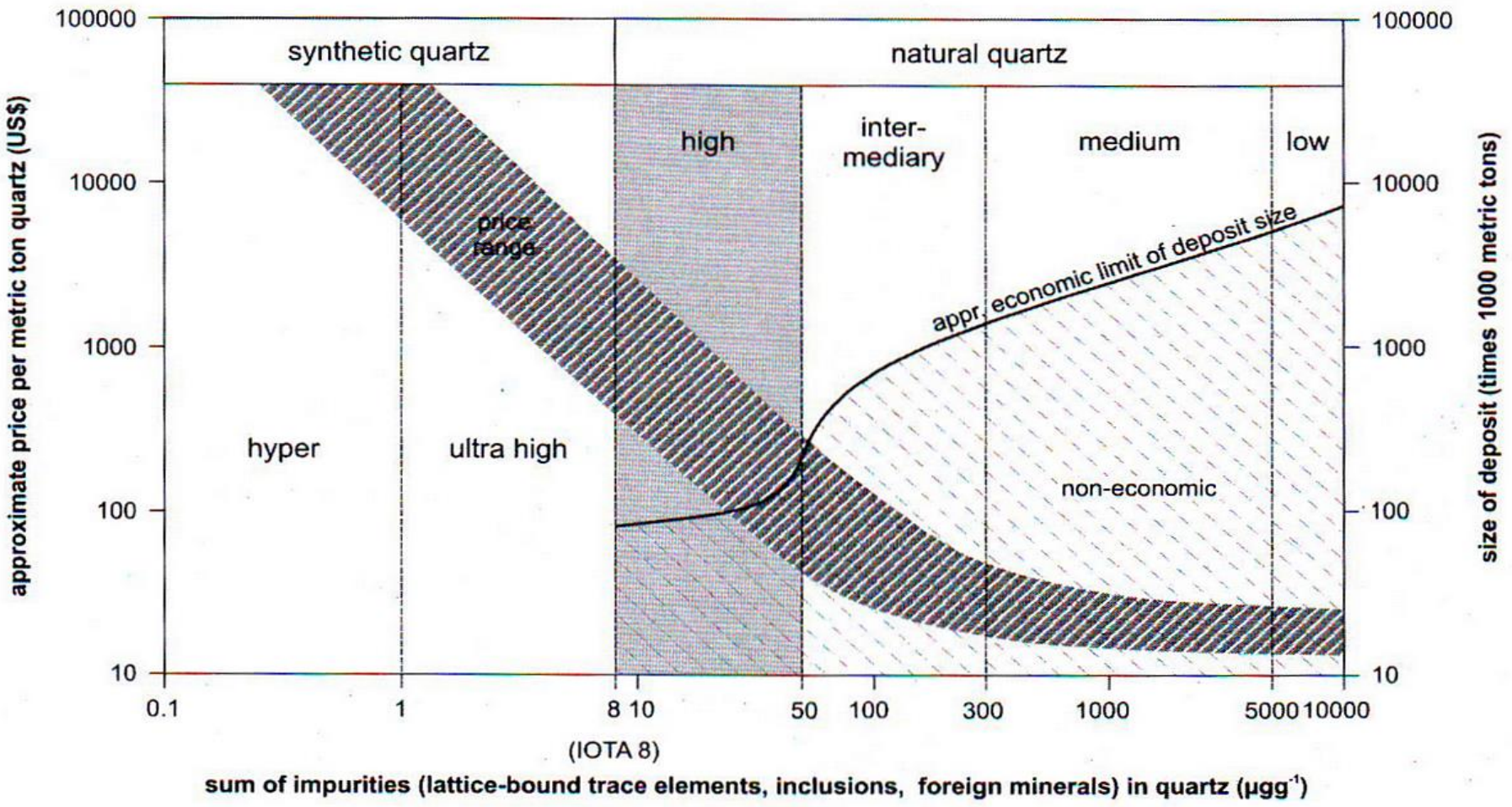
ROUNDTABLE

Agenda:

- Quartz classification
- Summary Chart purity & applications
- Quartz - Phase diagram
- Quartz varieties
- Inclusions - solid, liquid, gaseous
- Example of high purity quartz deposit
- End uses – examples
- Chinese Quartz city …

ROUNDTABLE

Classification of Chemical Quartz Qualities



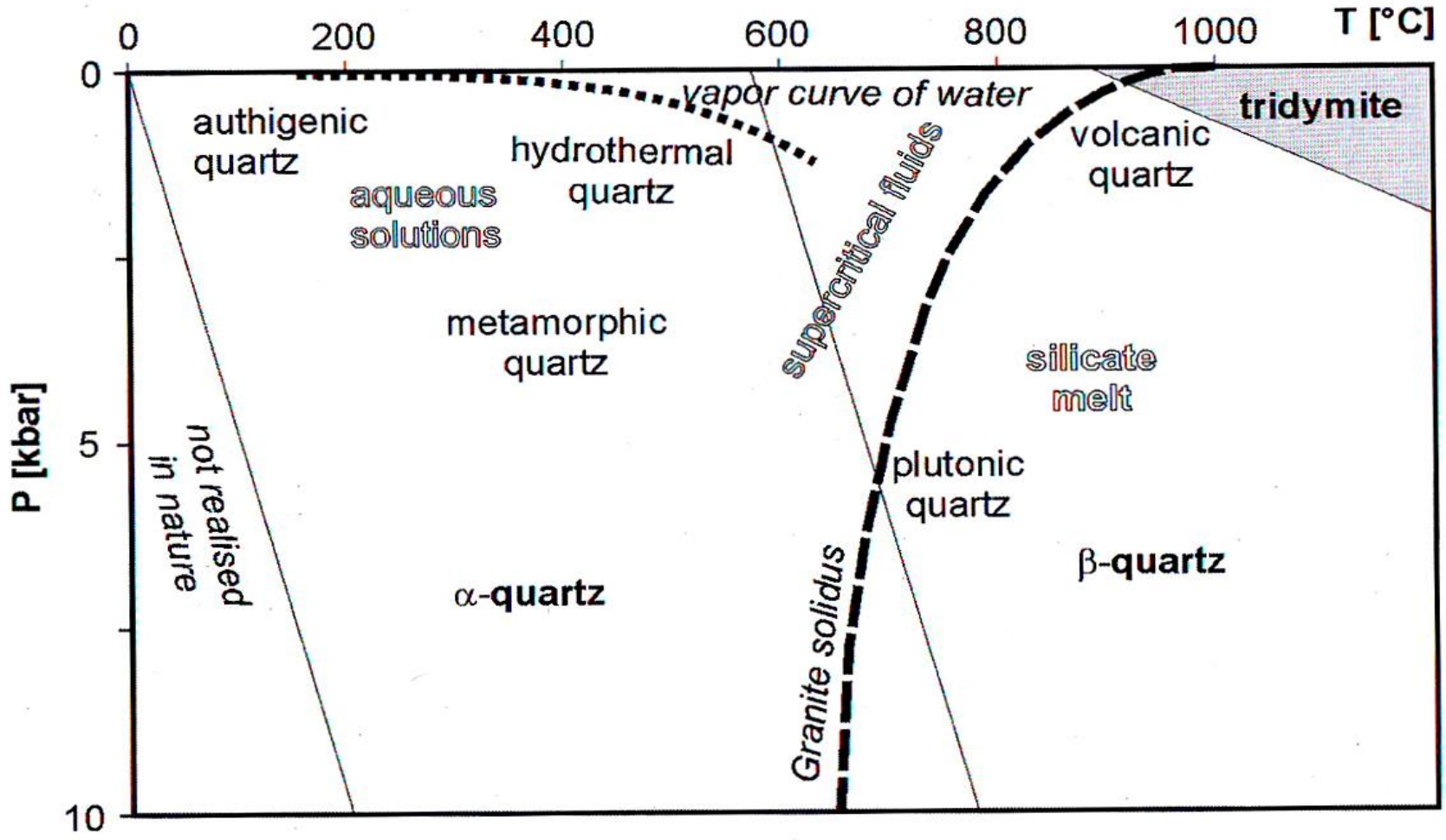
ROUNDTABLE

Summary chart

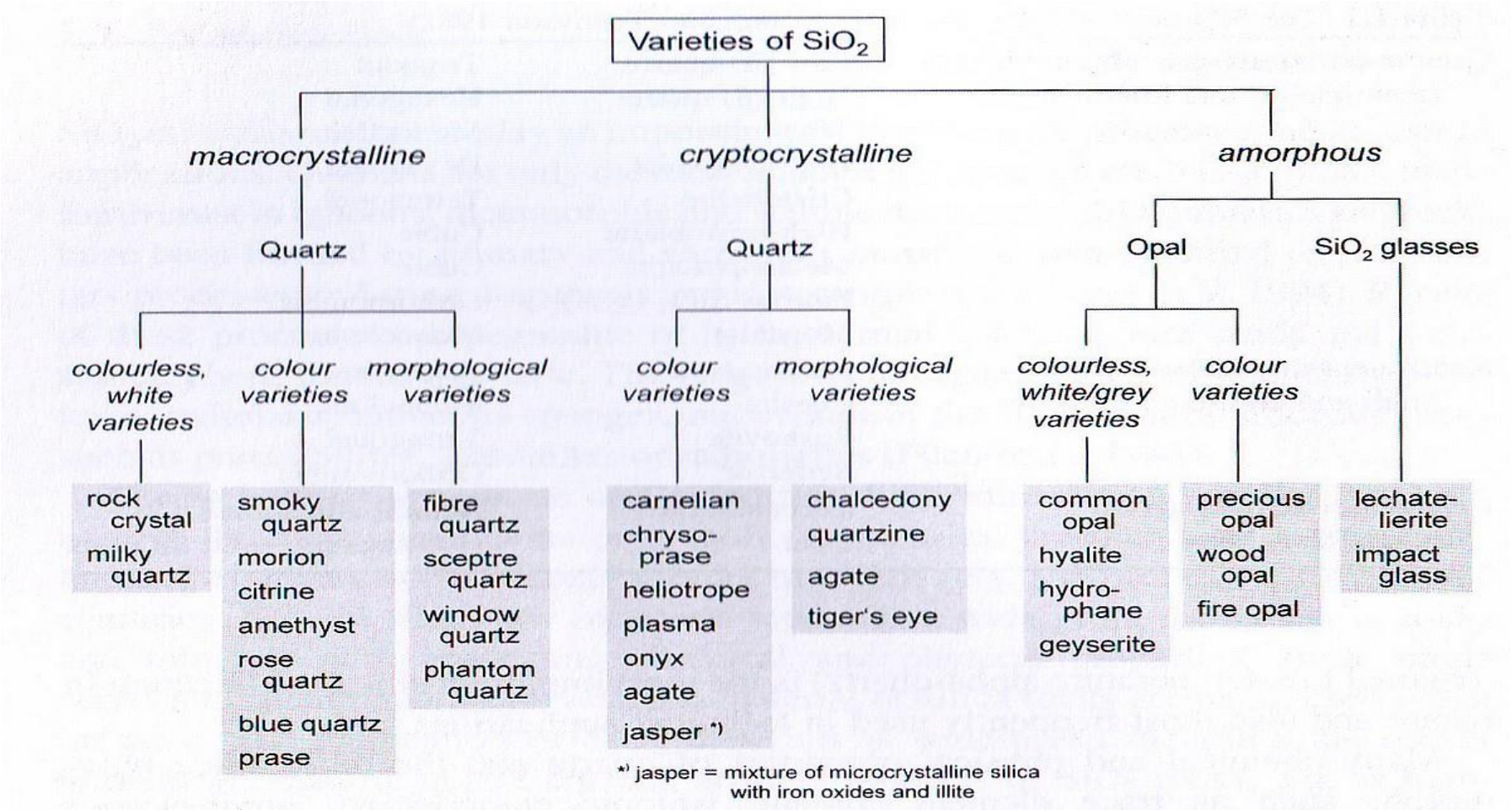
Type or application	Si02 min %	Other elements max %	Other elements max ppm	Estimated Market size	Indicative price /t
Clear glass sand	99.5	0.5	5,000	>70	30
EMC,LCD & Optical	99.8	0.2	2,000	2	160-400
Intermediate HPQ	99.95	0.05	500	0.75	300-600
High grade HPQ	99.99	0.01	100	0.25	500-800
Ultrahigh HPQ	99.997	0.003	30	<0.1	5-8,000
Hyper HGQ	99.999	0.001	10	<0.01	12,000

Phase diagram of Quartz

Indication of different formation environments



Varieties of Silica



Source: Quartz Deposits, Mineralogy & Analytics, Springer Gotze & Mockel

Classification of non- and microcrystalline silica phases

Crystal structure or phase	Variety	Subvariety/ synonymous name	Microstructure	Optical character	Water content (weight-%)
Quartz	Microquartz		Granular	Positive	<0.4
Disordered quartz (often with moganite)	Chalcedony		Fibrous [11$\bar{2}$0]	Length-fast	0.5–2
	Quartzine		Fibrous [0001]	Length-slow	0.5–1
Moganite			Platy (110), lepidospheric	Length-slow	1.5–3
Disordered cristobalite	Opal-C	Lussatine	Platy (111)*	Length-fast	1–3
Cristobalite/ tridymite	Opal-CT	Lussatite	Fibrous [110]*	Length-slow	3–8
		Common structureless opal	Platy, lepidospheric	Nearly isotropic	3–10
Non-crystalline	Opal-AG	Precious opal	Close packing of homometric spheres	Play of colour, anomalous birefringence	4–8
		Potch opal	Close packing of heterometric spheres	Isotropic	4–8
	Opal-AN	Hyalite	Botryoidal crusts and lumps	Strain birefringence	3–7
	Lechatelierite	Fulgurites	Vitrified tubes	Isotropic	<0.3
		Impact glass	Meteoritic silica glass	Isotropic	<0.3

C—cristobalite, T—tridymite, A—amorphous, G—gel-like, N—network (glass)-like
* Indices refer to cubic setting of cristobalite

(Modified after Graetsch 1994)

Source: Quartz Deposits, Mineralogy & Analytics, Springer Gotze & Mockel

Creswick Quartz

- Creswick Quartz, located 90 km NW of Melbourne, has high purity pebble-type quartz found in deep-leads beneath 100 m of basalt

- The high natural purity (99.99% SiO2) means washing with water is sufficient to prepare this material without the need for expensive chemicals

Inclusions – 3 types occur

- Solid, Liquid, Gaseous
- Solid – include zircon, apatite, monazite, feldspar, monazite, feldspar, mica & others
- Fluid inclusions – typically micro > 1 micron
- Water is the most common
  - Primary fluid inclusions
  - Salts may precipitate as daughter crystals
  - Halite the most common but other salts & some silicate minerals also can be present.
  - Gaseous inclusions include Co2, methane, nitrogen

High Purity Quartz at Creswick
Illustrative only

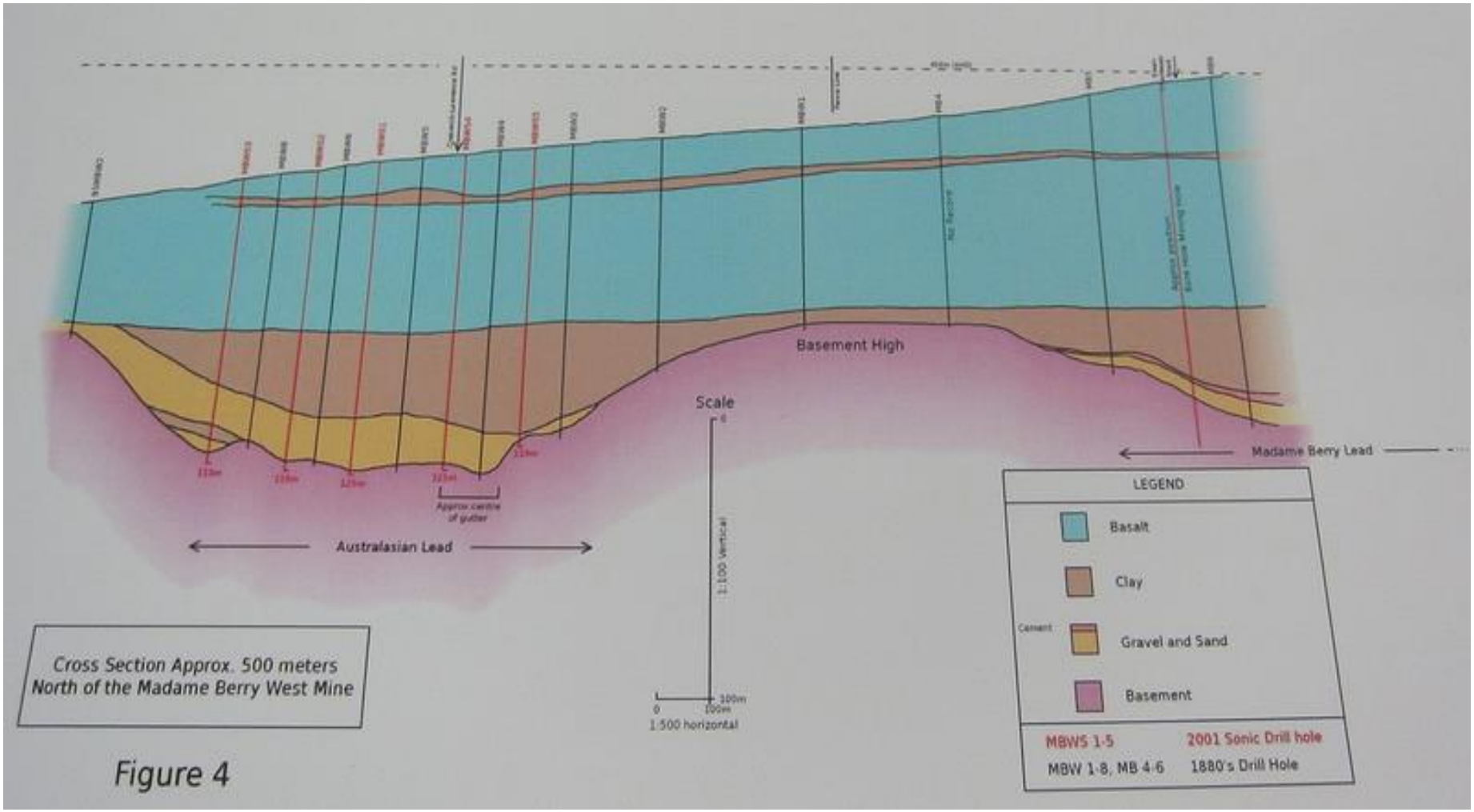


Figure 4

Creswick Quartz

Sample evaluation of Creswick's Quartz

			Co-washed Quartz sample
Picture of Quartz			
ICP Analysis	Al	ppm	10
	Ba	ppm	10
	Ca	ppm	2
	Fe	ppm	2
	Mg	ppm	<1
	Nb	ppm	<1
	Ti	ppm	4
	Na	ppm	5
	K	ppm	2
Foreign Substance by X ray	≧200um	piece/45g	0
	200~100um	piece/45g	0
	≦100um	piece/45g	0
Extraction	Na+	ppm	1.3
	EC	uS/cm	2.5
	pH	-	5.4/5.4
Remarks			The result was fine.

Typical Value of Lump Size Quartz in India & Sri Lanka

			Typical Value in India & Sri Lanka
Extracted Component	Na+	ppm	4.0
	Cl-	ppm	4.0
	EC	uS/cm	2.7
Chemical Component	SiO2	%	98.87
	Al2O3	ppm	276
	Fe2O3	ppm	7
	CaO	ppm	18
	MgO	ppm	3
	Na2O	ppm	15
	K2O	ppm	10

Creswick Quartz

New Producer of hyper-pure quartz

- Creswick Quartz, located 90 km NW of Melbourne, has high purity pebble-type quartz found in deep-leads beneath 100 m of basalt
- The high natural purity (99.99% SiO2) means washing with pure water is sufficient to prepare this material without the need for expensive chemicals

High Purity Quartz

- Quartz is one of the most abundant minerals and occurs in many different geological settings.
- However, only very few deposits are suitable for high purity applications.
- Therefore, high purity quartz has become one of today's key strategic minerals with applications in high-tech industries:
  - semiconductors, high temperature lamp tubing, telecommunication & optics, microelectronics, solar silicon applications.
- Beneficiation of raw quartz into refined high purity products involves several steps which need to be adapted to minimize the specific impurities of the individual raw quartz feed in line with end-use applications.
- As a result, high purity quartz with impurity levels less than 20 ppm may be achieved so creating a valuable raw material which commands up to 5 Euro/kg.

Hot chlorination

- Chemical refining is one of the most efficient operations to reduce mineral impurities in high purity quartz. During acid treatment, medium to strong mineral acids are used at elevated temperatures. Usually hydrofluoric acid is applied, but a combination of several acids can be used (HF, HCl, HNO_3) to improve chemical purification results.
- Allied minerals (e.g. feldspars, micas), difficult to liberate during physical processing, are dissolved in the course of leaching. Additional impurities, enriched in micro fissures and structural dislocations, are removed by the enhanced dissolution of quartz. This kind of purification procedure is regularly applied in lamp tubing as well as semiconductor applications of high purity quartz.

Chemical Leaching

- Hot chlorination is a highly advanced technique for achieving exceptional high purity. During the chlorination process high purity quartz is heated to temperatures up to 1,200°C in a chlorine or hydrogen chloride gas atmosphere. Chlorination causes structural impurities to be forced from the crystal lattice into the gas phase. Chlorination is particularly efficient for the reduction of alkali, alkali earth, and transition metals.

- ANZAPLAN (Germany) has a hot chlorination test facility - a valuable tool to validate & optimize the chlorination process specific to the mineralogical, physical & chemical properties of the raw material.
- Variations in gas composition, reaction temperature & duration determine optimum parameters for the material undergoing hot chlorination.
- A maximum purity of the quartz is achieved in order to fulfill the stringent requirements of the semiconductor industry.

High Purity Quartz Applications

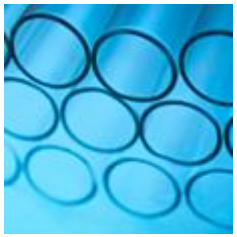
Crucibles – demand depends on solar panel production levels

Optical – modest volume but high values

Halogen lamps- technology moving this way. Auto sector driven

Quartz wool – potential growth 5%pa

High Purity Quartz Applications



Quartz glass - large volumes especially tubes of various sizes

Fillers – several new entrants EMC most important

Silicon metal-huge volumes China dominance

Quartz Glass Crucibles

Quartz glass crucibles are made by arc-melting of high purity quartz sands.

Quartz glass crucibles are used by the semiconductor and solar industries for growing single crystal ingots from silicon metal by using the Czochralski crystal growing process.

In order to produce metallic silicon suitable for production of high-quality semiconductor wafers, polysilicon is placed into a quartz glass crucible heated to a high temperature and a silicon mono-crystalline ingot is drawn out of the melt. Fused quartz glass is the only material that combines the high purity and heat resistance required for this process.

Natural and cleaned high purity quartz raw materials are used in the production of crucibles. The raw materials are optimized for the customer's application, in order to ensure a constantly high level of quality in the crucibles.

The opaque quartz crucibles can also be used in other industrial applications such as glass melting, chemical processing and powder calcinations because of their high purity and excellent chemical resistance.

ROUNDTABLE

Optical lenses

Silica glass has better ultraviolet transmission than any other glass, and so it is used to make lenses and other optical devices for the ultraviolet spectrum. Its low coefficient of thermal expansion also makes it a useful material for precision mirror substrates.
Thanks to the excellent transmission properties in the ultraviolet to the infrared part of the optical spectrum of silica glass, its physical and chemical stability, silica glass is an ideal transmission media for light and as a stable refractive optical material. It is used for lenses, prisms, windows and other optical components where UV transmission is required.
To obtain the best light transmission in the optical device, the content of Fe, Ti, Cr, Ni, Mn, Cu etc. should be as low as possible in the glass. The only way to make glass with the best transmission properties is to use a glass made from synthetic silica or natural high purity quartz.

Optical lenses are needed in any optical systems. Lenses can be used in a variety of applications both in research, industrial, medical and consumer optics, such as in high power laser collimators and for focusing optics for head-up-displays, binoculars, microscopes (eye-piece lenses for microscopes), sports optics (rifle sight), sensors, digital projection, cameras, laser projection, bar code scanning, holography, optical information processing and computing, medical applications etc.

Optical fibres

- An optical fibre is a flexible, transparent fibre made of a pure silica glass.
- An optical fibre functions as a "light pipe", to transmit light between the two ends of the fibre.
- Optical fibres are widely used in fibre-optic communications, which permits transmission over longer distances and at higher bandwidths (data rates) than other forms of communication.
- Fibres are used instead of metal wires because signals travel along them with less loss and are also immune to electromagnetic interference.
- Optical fibre typically includes a transparent core surrounded by a transparent cladding material with a lower index of refraction.
- The core is usually made from synthetic silica while the transparent cladding material can be made from glass of natural high purity quartz. Only the purest available natural high purity quartz can be used for this application.
- Fibres are also used for illumination, and are wrapped in bundles so they can be used to carry images, thus allowing viewing in tight spaces.
- Specially designed fibres are used for a variety of other applications, including light transmission, sensors and fibre lasers.

Halogen lamps

- In lighting, tubes of silica glass are used to envelope the high temperature tungsten filament.
- A halogen lamp is an incandescent lamp with a tungsten filament contained within an inert gas and a small amount of a halogen such as fluorine, chlorine, iodine or bromine.
- The glass in the halogen lamp glass has to have excellent optical transmission properties and ability to withstand extreme temperatures and thermal shock without being deformed or cracking. The tungsten filament is glowing at a temperature of 2,500°C only a few mm away from the glass wall. Only high purity quartz glass has these properties.
- Quartz glass tubes are made in a continuous melting process; the tubes are divided in smaller parts that are shaped to bulbs.

Quartz Wool

High temperature thermal insulation can be made from silica fibres arranged into a texture similar to wool.

Fused Quartz Wool has the same properties as pure quartz glass.

The fibres are non-flammable and incombustible.

The fibres maintain their usable mechanical properties up to temperatures higher than 1,100°C.

Quartz Glass

- Fused quartz, silica glass and quartz glass are synonyms for melted glass made from high purity quartz. It is manufactured by melting naturally occurring quartz crystals of high purity at approximately 2,000 °C, using either an electrically heated furnace (electrically fused) or a gas/oxygen-fuelled furnace (flame fused).
- Fused quartz is normally transparent.
- The optical and thermal properties of fused quartz are superior to those of other types of glass due to its purity. It is used in markets such as semiconductor fabrication & laboratory equipment.
- It has better ultraviolet transmission than other glasses, and so is used to make lenses and other optical devices for the ultraviolet spectrum. Its low coefficient of thermal expansion also makes it a useful material for any application where wide temperature differences are vital.
- The purity needed is a SiO_2 content of >99.995% and the physical properties of this pure quartz are what give it this exceptional material quality that makes it the choice of uses. A number of unique optical, chemical, mechanical, electrical & thermal properties have made quartz glass an indispensable material in the fabrication of high-tech products.

Quartz fillers

High purity crystalline quartz powders for filler applications has the characteristics of a narrow particle size distribution with a D50 (average grain size) between from 5 up to 30 µm.

Needs to have high transparency high purity in addition to an extremely low content of other particles / impurities than quartz.

Examples of applications for high purity fillers:

- Dental use, to make artificial teeth & fillings.
- Raw material for high purity silicone
- Filler in silicone
- Speciality glasses

Spherical silica filler for micro-electronics

Starting material to make spherical silica fillers for EMC (epoxy moulding compound)

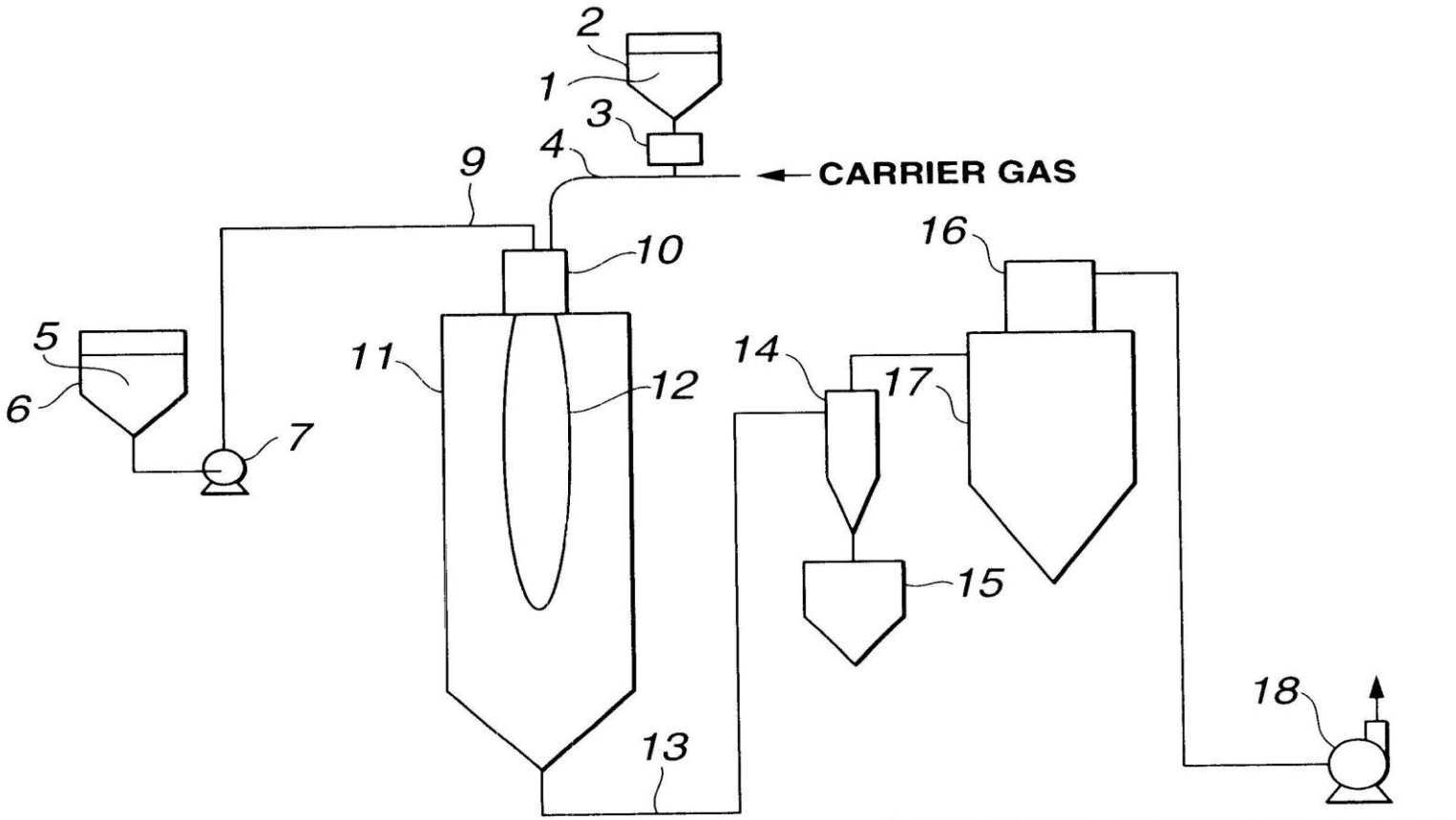
Several companies are make flame fused spherical silica glass particles.

These spherical silica glass particles are used as filler in EMC for the microelectronics industry as a packaging materials for encapsulation of microelectronics devices.

Spherical silica glass fillers are used because it acts as an electrical insulator, that also lower the thermal expansion in the EMC.

ROUNDTABLE

Spherical silica flame furnace



Spherical silica filler for micro-electronics

- The packed silica particles allows exit of excess heat produced by the semiconductor.

- Radioactivity can harm the conducting properties of the semiconductor.

- Therefore the silica filler must have an extremely low content of the radioactive elements Uranium and Thorium (<0,5ppb – or - <0,00000005%)

- To make these low Uranium & Thorium fillers it is necessary with a quartz raw material with a similar low Uranium & Thorium content.

- The Quartz Corporation and a few other companies have access to this very rare quartz raw material.

Silicon metal (1)

- All silicon metal produced has its origin in quartz (SiO_2).
- Quartz is converted (reduced) to silicon (Si) in a high temperature melting process using carbon and large amounts of energy.
- To create the qualities that are good enough for solar silicon, the silicon must be very clean, 99.9999%, and to be used in the semiconductor industry it must be even cleaner, 99.999999999%.
- There are no quartz products that can be purified above 99.999% SiO_2, therefore the silicon metal has to go through successive purification processes even if it is made of the purest quartz available.

Silicon metal (2)

- Silicon metal is normally made through a metallurgical process starting with lump quartz of medium to low purity together with carbon.
- This metallurgical silicon is upgraded though several cleaning processes into higher qualities like solar grade and semiconductor grade
- This upgraded silicon metal becomes the raw material for silicon crystals.
- These silicon crystals are cut into thin slices or wafers.
- These thin wafers are the active part of the solar cells or in the semiconductor in electronics.

Solar Silicon

- Now most solar grade silicon (SoG-Si) production uses the SIEMENS Process.

- It provides highest purity but it is a very high energy consuming process resulting in prices as high as 40-50 US$kg.
- The quality requirements for solar grade silicon are less than high-end microelectronics grade silicon (ME-Si).

- To meet the specifications required by the photovoltaic (PV) industry, alternative production technologies arise on a much lower investment and process cost base by using quartz of sufficient purity & carbon.

- New opportunities developed via direct carbothermic reduction or refinement of metallurgical grade silicon (UMG-Si) need to avoid certain metal impurities as well as phosphorus & boron in the raw material.

- Since carbon mainly derives from synthetic processes the source of most of the impurities is the raw quartz. In order to control the purity of the silicon, the quality and refining processes of the raw quartz are crucial to comply with PV industry standards.

High purity quartz powder

Sample evaluation of Creswick's Quartz

			Co-washed Quartz sample
Picture of Quartz			
ICP Analysis	Al	ppm	10
	Ba	ppm	10
	Ca	ppm	2
	Fe	ppm	2
	Mg	ppm	<1
	Nb	ppm	<1
	Ti	ppm	4
	Na	ppm	5
	K	ppm	2
Foreign Substance by X ray	≧200um	piece/45g	0
	200～100um	piece/45g	0
	≦100um	piece/45g	0
Extraction	Na+	ppm	1.3
	EC	uS/cm	2.5
	pH	–	5.4/5.4
Remarks			The result was fine.

Typical Value of Lump Size Quartz in India & Sri Lanka

		Typical Value in India & Sri Lanka	
Extracted Component	Na+	ppm	4.0
	Cl-	ppm	4.0
	EC	uS/cm	2.7
Chemical Component	SiO2	%	99.87
	Al2O3	ppm	276
	Fe2O3	ppm	7
	CaO	ppm	18
	MgO	ppm	3
	Na2O	ppm	15
	K2O	ppm	19

High-Purity Quartz and Glass Sand.

High-purity quartz from Spruce Pine is used in the crucibles to make polysilicon. Unimin's deposit has been the foremost producer of high-purity quartz ,amounting to ~ 80% of all mined & processed quartz for use in the electronics industries. The balance has mainly come from India, and recently from Norway. Australia is a likely new supplier soon. Japan, China, South Korea & Taiwan are major buyers.

The three principal markets for this high-purity quartz include:

1.Electronics for semiconductors.

2. Solar markets for the production photovoltaic cells.

3. Applications in the lamp tubing market.

Quartz ore processing in China

- Quartz ore is arguably the most important element of quartz sand production.
- While leaching, chlorination, & other purification steps can improve the impurity content of the final product, the natural composition of the quartz decides what the final chemical composition of the product is.
- Quartz ore for Donghai is sourced from a number of locations, including domestically (Donghai, Shanxi, Hubei, etc.), Angola, Madagascar, India, Russia, Zambia, and the Sudan. Others are being offerred from other countries also.

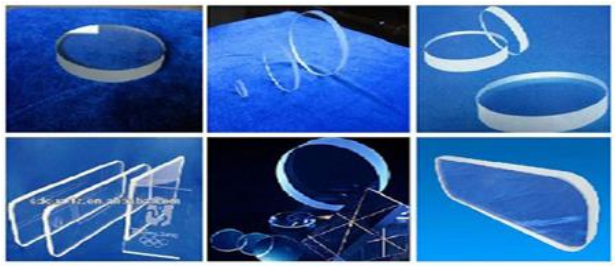
Quartz ore processing in China

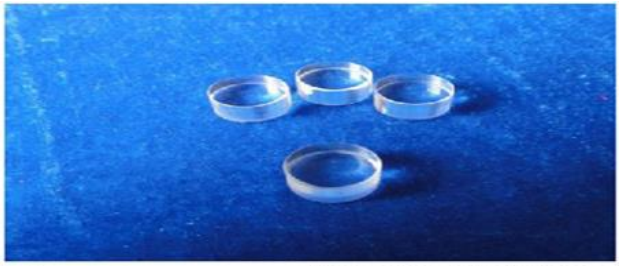
- The prices of the ore from each place varies drastically, although the average price paid for ore is somewhere between $150 and $1,000 per tonne, depending on the quality and quantity of the material.
- This ore is then processed by sand makers into the raw products used to make quartz tubes, rods, and ingots, which are then fabricated into a variety of products used in a number of industries.
- Sand producers are sometimes vertically integrated, producing tubes, rods, and ingots from their own sand also.

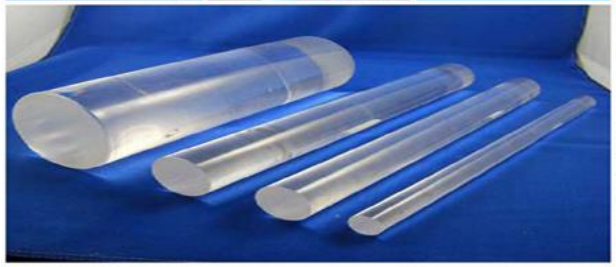
ROUNDTABLE

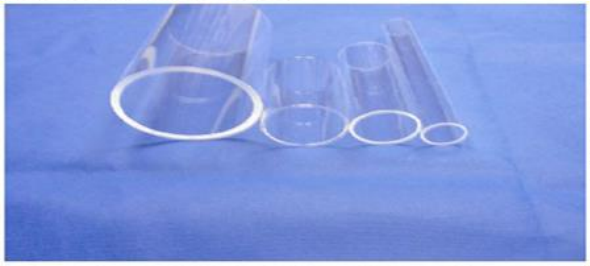
Donghai Shengda

Quartz Products Co









Donghai Shengda

Quartz Products Co.

- Donghai is known in China as Crystal City
- Maybe 90% of all Chinese quartz is processed in this area.

Nesodden Quartz, Norway

ROUNDTABLE

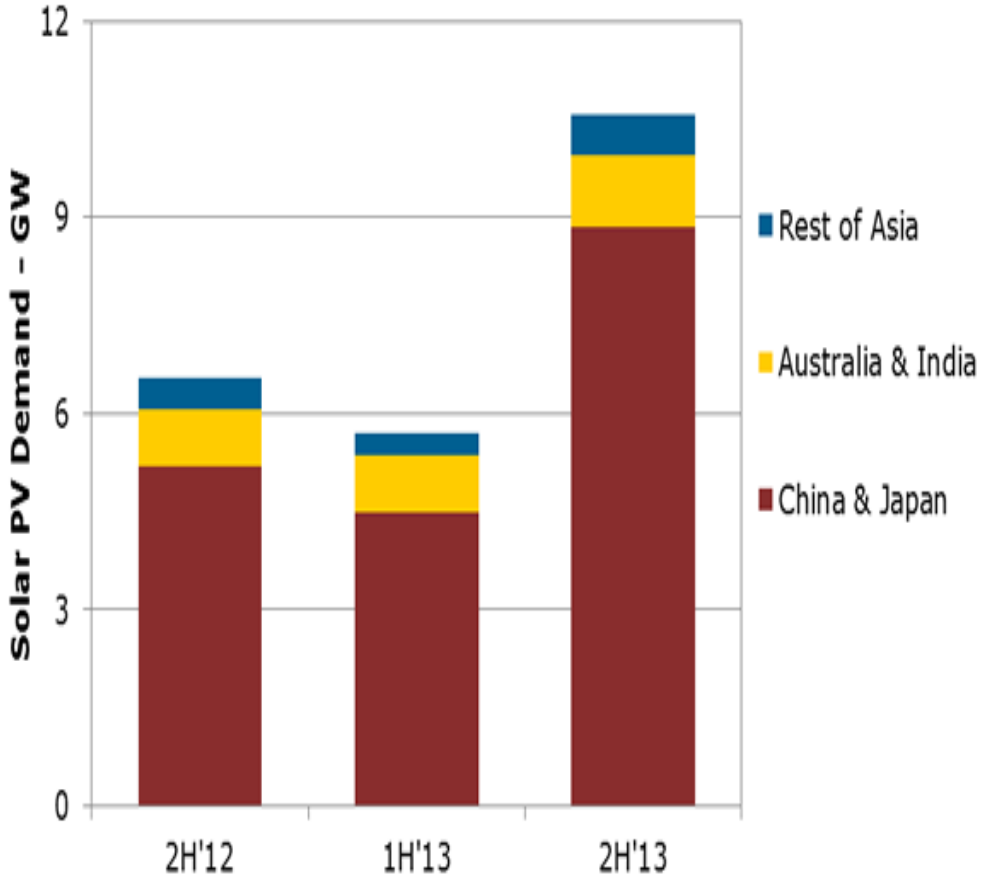
Unimin raw material & product

Fusion Draw Process

Courtesy Corning

- Corning takes the silicon dioxide (SiO_2) and combines it with other chemicals before melting it down into a glass melt. The resulting glass is **aluminosilicate** .The glass also contains sodium (Na) ions, which become important in the next phase of manufacturing.
- Corning pours the molten glass into a V-shaped trough but doesn't stop at filling the trough to the top. The company continues to add molten glass until the glass begins to overflow the sides of the trough. Automated robotic arms draw the sheets of glass from the edge of the trough. Each sheet is just over 0.5 mm thick.
- If you were to use this glass for a screen on your electronic devices, you'd end up with a very clear covering. But it's not damage-resistant like Gorilla Glass -- it's just aluminosilicate glass. Special post – treatment make the gorilla glass harder and scratch resistant.

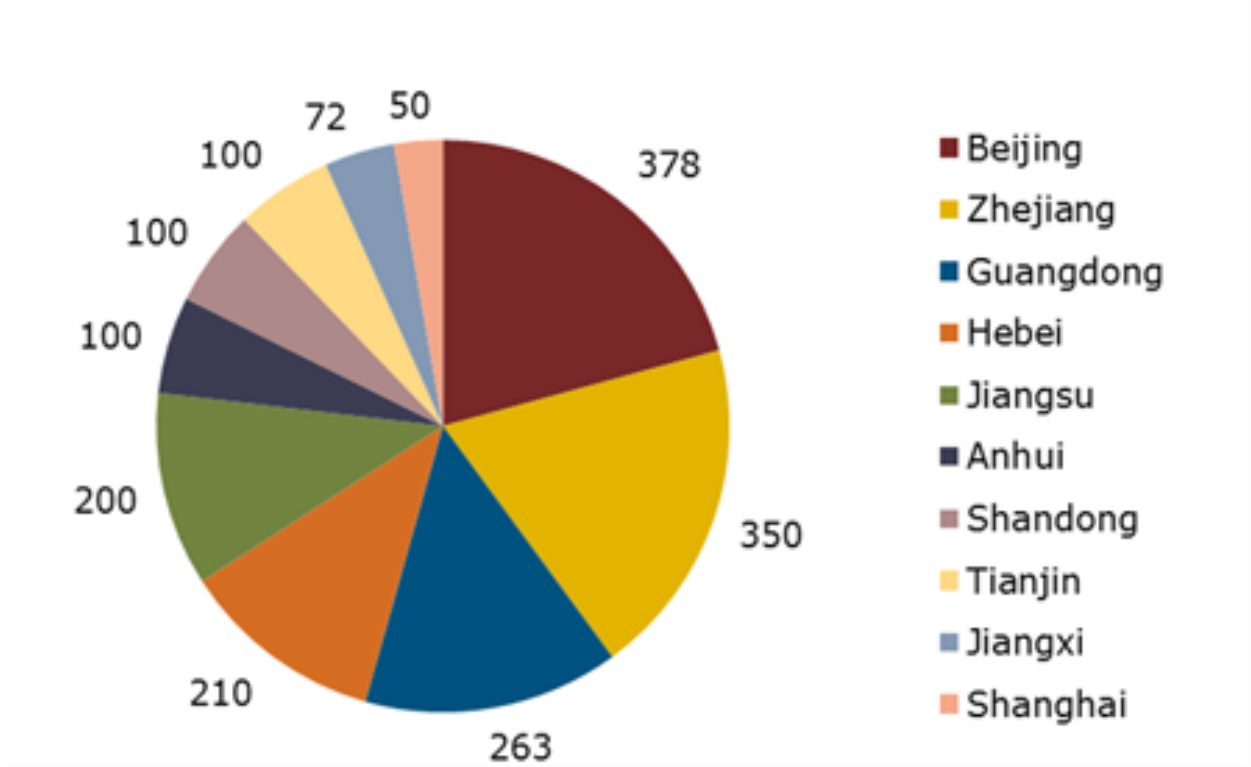
Solar PV Demand - the Asia Pacific Region



- Solar photovoltaic (PV) demand from China and Japan during 2H'13 is forecast to reach 9 GW, representing an increase of 100% compared to 1H'13 and 70% compared to 2H'12.
- Overall, PV demand from the Asia Pacific (APAC) region will exceed 16 GW during 2013, up 90% Y/Y, and will account for over 40% of global PV demand this year, according to findings in the new NPD

Source: Solarbuzz

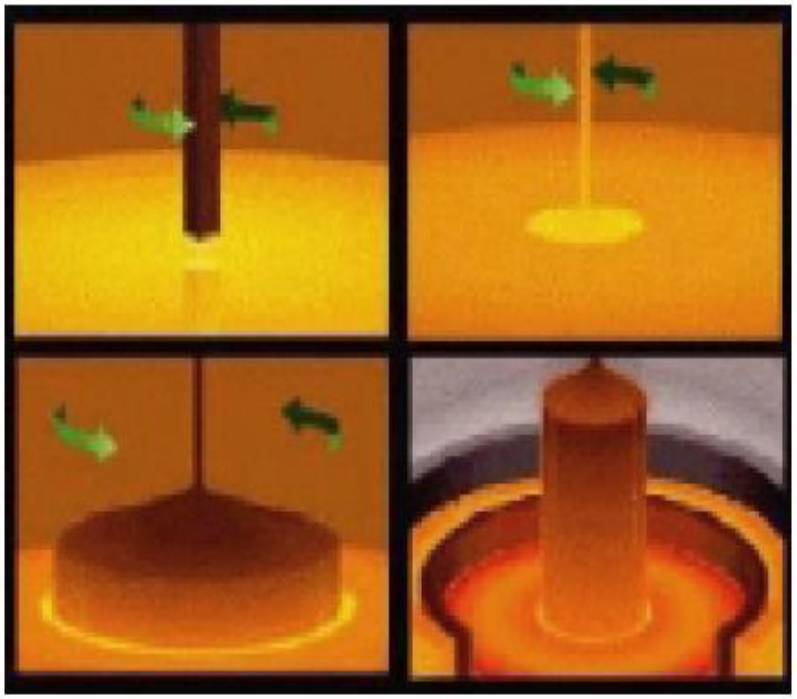
PV Generation Application Demonstration Parks by regions (MW)



Source: NPD Solarbuzz

Making the Silicon Ingot
The Czochralski (CZ) method

- A pure silicon seed crystal is placed into the molten sand bath. This crystal will be pulled out slowly as it is rotated. method. The result is a pure silicon cylinder that is the ingot.



Silicon Thermal Properties

Thermal Conductivity (solid) 1.412 W/cm-K
Thermal Conductivity (liquid) 4.3 W/cm-K
Specific Heat 0.70 J/g-K
Thermal Diffusivity .9 cm**2/s
Melting Point 1683 K
Boiling Point 2628 K
Critical Temperature 5159 K
Density (solid) 2.33 g/cm**3
Density (liquid) 2.53 g/cm**3
Vapor pressure
  at 1050C 1e-7 Torr
  at 1250C 1e-5 Torr
Molar heat capacity 20.00 J/mol-K

Japan – some comments

- Volumes of imported silica sand are stabilising as more electronic JV's are formed in South Korea, Taiwan, China, Singapore, Thailand, Malaysia etc. Containers are thinner & use more recycled glass.
- Overall values per tonne are rising, indicating larger % of added value grades for TFT etc
- Volumes for standard float & container glass as well as foundry use are flat as capacity moves to China, India etc.

South Korea – some comments

- **Second only to Japan in size - Silica sand imports**
- **Joint ventures popular in South Korea**
- **Major Glassmakers include:**
  - Samsung Precision Glass (Corning JV for glass)
  - LG Chemical (Asahi Glass JV for glass)
  - Hanglass
  - KCC

Taiwan – some comments

- Severe lack of silica sand reserves apart from construction materials due to volcanic geology of whole island
- Strong in float and container glass for many years
- Many Taiwanese have shifted/expanded glass & ceramic capacity to China. Around 33% of companies in China are owned/managed by Taiwanese.
- Growth in high value LCD screens being a leader in technology

ROUNDTABLE

Thank you…

www.stratum.com.au

STRATUM resources