BGR Industrieworkshop zur Gewinnung und Verarbeitung von Quarzrohstoffen in Deutschland

Hochreiner Quarz – der feine Unterschied

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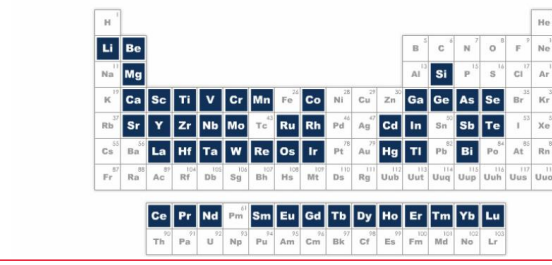

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- **Process Development**
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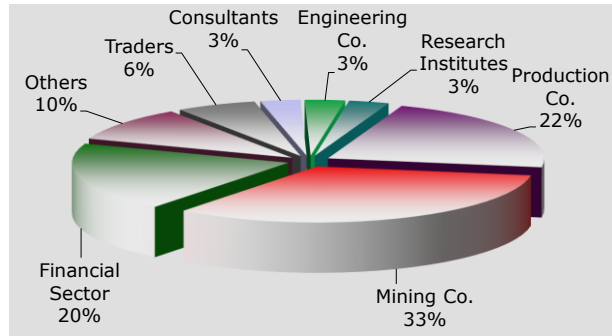
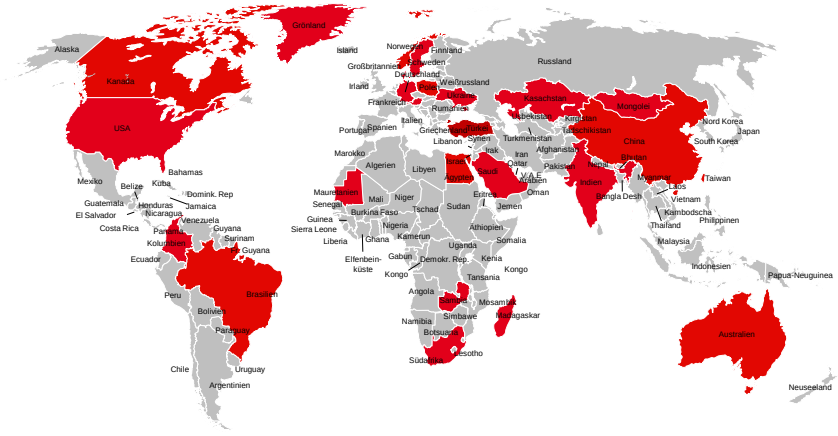
  - Process Design and Technology (Reserves)
  - Mineral Concentration
  - Extraction and Purification
- **Pilot Scale Processing**
  - Sample production and application tests
  - Customer approval
- **Project Valuation and Engineering**

Customer Base



Distribution of recent ANZAPLAN Projects



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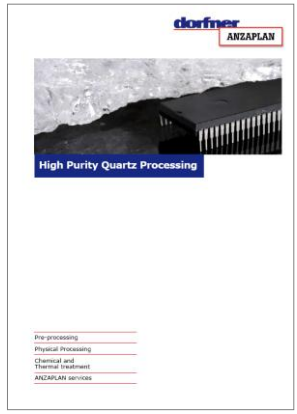
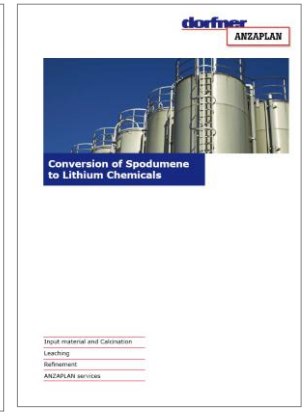




Why getting interested in Quartz?

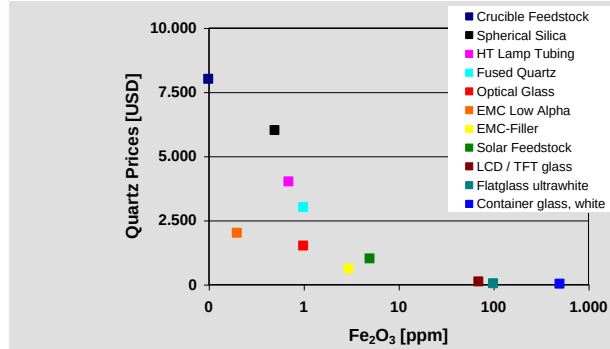
Quartz is used in many applications

Different Quartz Deposits serve Different Applications

Quartz Type	Properties	Preferred Applications
High grade pegmatite and hydrothermal quartz	Chemical purity (>99,9%), pure quartz lumps, white and milky or transparent	High Purity Quartz, optics, lamp tubing, semiconductor (crucibles), UMG-/SoG-silicon, piezo-quartz and microelectronics (EMC filler)
Quartzite, low grade pegmatite and hydrothermal quartz	Chemical purity (>95%), lumpy hard rock	Refractory materials (SiC), MG-silicon, Silicon Alloys (e.g. FeSi); Engineered Stone
Quartzitic Sandstone	Chemical purity (>90%),	Construction industries, dimensioning stones, glass sand, aggregates
Silica (quartz) Sand	Chemical purity (>90%), granulometric properties	Glass sand and foundry industry (molds and cores), filtration, ground silica (filler), ceramics (glazes) and proppants (hydraulic fracking)

… and high purity is of high value

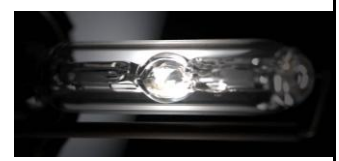
1 ton of quartz can cost as much as one ton of an automobile

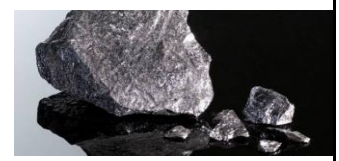


… and high purity quartz is of strategic interest

Main applications in many high growth industries

- High temperature lamp tubing (e.g. Xenon bulbs)
- Telecommunication and Optics
- Semiconductor Applica-tions incl. Crucibles Production
- Microelectronics (EMC Fillers)
- (Solar) Silicon, UMG or SolSilc Processes





… with only limited amount of suppliers and deposits

- US-based Unimin Corp./Sibelco still dominates the global high purity quartz market with its Iota© Brand.
- Since its restart by Hustadkalk AS in 1996 Norwegian Crystallites (NC) became a reliable second source. Nowadays NC joined Imerys to form the Quartz Co.

However, both companies are mining the same deposit located in the US (North Carolina).

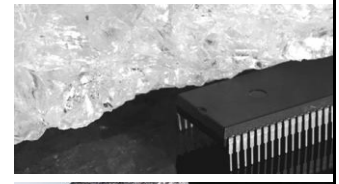
- … with Jiangsu Pacific Quartz (China) claiming a production capacity of 9.000 tpa but limited resources calling for selective mining and small output.

Spruce Pine Pegmatite

… and most stringent specifications

General Specifications strongly related to final application

- **HT Lamp Tubing, Telecommunication and Optics**
  Al less then 20 ppm, metals less than 1 ppm.
  Particle size: 0.1-0.3 mm (sand),
  Total impurities less than 25 ppm.
- **Semiconductor Base Materials / Crucibles**
  Al less then 10 ppm, metals less than 0.1 ppm.
  Particle size: 0.1-0.3 mm (sand),
  Total impurities less than 10 ppm
- **Microelectronics** (EMC Fillers)
  U and Th less then 1 ppb,
  Particle size: < 0.1 mm (powder)
- **Silicon (SoG-/UMG-Silicon)**
  Low Boron and Phosphorous concentration < 1ppm
  Particle Size: 20-80 (120) mm

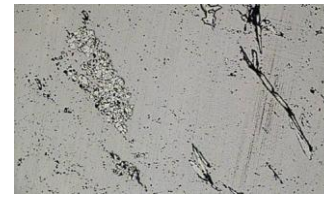


Quartz Processing for High End Markets

Stringent specifications call for detailed raw material analyses

Various impurities are responsible for elevated element concentrations in quartz:

- Structural impurities, e.g. Boron, Titanium and Aluminum
- Mineral impurities, e.g. Phosphate, Iron, Calcium and Aluminum
- Fluid inclusions, e.g. Sodium, Chloride and Potassium

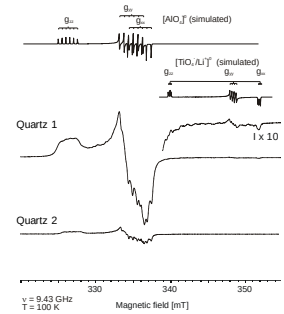


Tremolite and Apatite

Structural Impurities in Quartz

Impact on chemical specification of end product

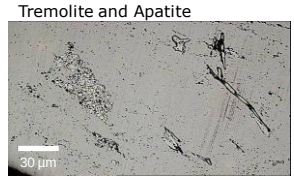
- The electron paramagnetic resonance (EPR or ESR) is a spectroscopic method that detects $[AlO_4]^0$ centres produced by the substitution of Si^{4+} by Al^{3+} in the quartz crystal lattice.
- The technique based upon the interaction between the magnetic moment of the unpaired electrons and microwaves in an external magnetic field.



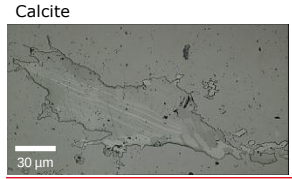
Mineral Inclusions

Impact on chemical specification of end product

Tremolite and Apatite

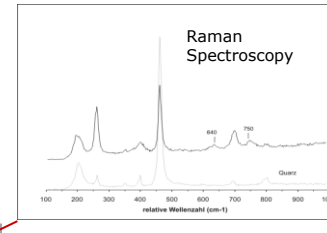


Calcite



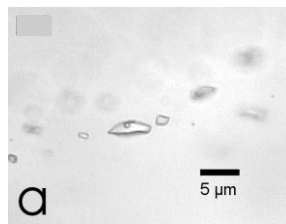
Feldspar

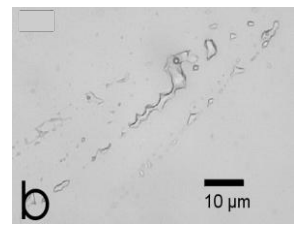
Raman Spectroscopy

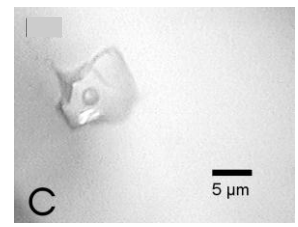


Fluid Inclusions

Impact on melting behaviour in quartz glass







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Quartz Processing for High End Markets

Stringent specifications call for advanced purification processes and tailor made process design

Conversion of raw quartz into refined high purity and high value quartz products needs advanced processing technology considering all mineralogical details to meet final quality requirements.

The main stages of the process may be summarised as:

- Crushing
- Sensor Based Sorting (SBS)
- Comminution and Liberation of Impurities
- Classification
- Physical Processing
- Chemical Processing
- (Vacuum-)Drying
- Thermal Processing

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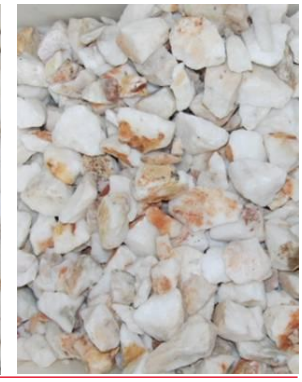
Surface Coatings

Sensor based sorting to separate surface coatings

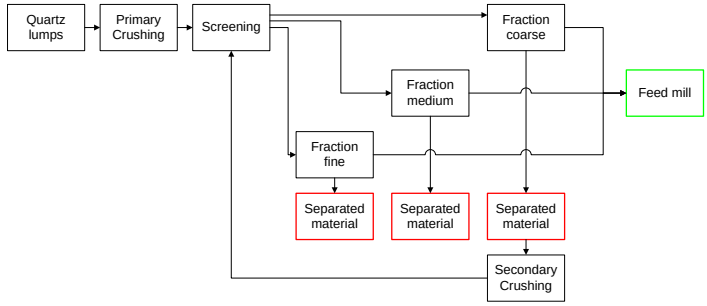
MG-/UMG-Silicon Upgrade

- Separation of quartz lumps with surface contaminations and discolorations by sensor based sorting
- Mass distribution:
  White (good) 76 wt.-%
  Discolored 24 wt.-%



Sensor Based Sorting (SBS)

Process scheme - Sensor based sorting



Use of Quartz in the Silicon Industry

Quartzite and low grade hydrothermal/pegmatitic quartz

Silicon Grade	Fe_2O_3 [wt-%]	Al_2O_3 [wt-%]	CaO [wt-%]	Code
Chemical Grade	0.20	0.20	0.02	2202
Polysilicon Grade	0.30	0.30	0.03	3303
Primary Aluminum Grade	0.40	0.40	0.10	441
Secondary Aluminum Grade	0.50	0.50	0.30	553
Other combinations are also possible: i.e. 3302, 4405, etc				

- Due to furnace restrictions in silicon production only lump quartz 20 mm to 80 (120) mm can be used
- This limits the possibility of purification steps and liberation of impurities

Solar Quartz Upgrade

Chemical results of high grade hydrothermal/pegmatitic quartz

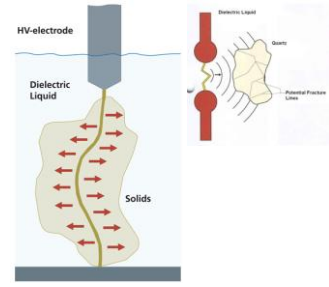
Sample ID	Al [ppm]	Fe [ppm]	Na [ppm]	K [ppm]	Ti [ppm]	Zr [ppm]	Ca [ppm]	Mg [ppm]	P [ppm]	B [ppm]
Sample 1-2										
Crushing and Screening	78	17	26	24	4,2	<0,1	36	6,0	6,5	0,3
Washing and Scrubbing	56	12	23	18	2,7	<0,1	34	4,8	3,5	0,2
Sensor based sorting	28	3	20	14	1,8	<0,1	19	4,4	0,8	0,1

- In SoG-Silicon (solar grade) production lump quartz is being used.
- Besides higher overall purity, Boron and Phosphorous are main critical elements.
- For solar quartz upgrade high grade hydrothermal/pegmatitic quartz deposits are to be considered.
- Al and K bearing minerals (e.g. clays, mica) being separated during washing and scrubbing.
- Additional reduction of Fe and significant improvement of P by sensor based sorting offering best qualities to be used for SoG-Silicon feedstock.

High Purity Quartz Processing

Mineral Liberation - Electrodynamic Fragmentation

- Quartz sample in a dielectric liquid is exposed to high voltage pulses (ns/kV).
- The electrical discharge flows through the material and generates tensile stress by creating internal shockwaves.
- Consequently, composite materials are fragmented along grain boundaries and mineral impurities with a high degree of selectivity.
- Liberated minerals can be selectively separated by post treatment processes



High Purity Quartz Processing

Physical Processing 0,1-0,3 mm

- In order to clean the surface of the quartz particles **attrition** is applied. Thereby fine particles attached to the surface of the quartz e.g. clay minerals or iron oxide coatings are abraded and dispersed in the added liquid.
- In quartz processing **magnetic separation** is used to separate minerals with paramagnetic or even ferromagnetic properties, such as e.g. iron oxides or heavy minerals. Therefore a magnetic force acts on these minerals in the direction of increasing magnetic field strength. Quartz itself has diamagnetic properties. Therefore quartz particles are repelled from magnetic fields. Magnetic Separation can be applied in dry (HGMS) or wet state (WHIMS).
- **High tension separation** is used to separate particles based on their surface charge. The activated feed material is fed between two electrode plates where it is either attracted or repelled by one of the electrodes, depending of the particles surface charge. High tension separation is a dry method.

High Purity Quartz Processing

Chemical Processing 0,1-0,3 mm

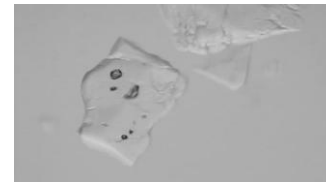
- **Flotation** is a mineral separation process, which separates trace minerals from quartz by taking advantage of differences in their hydrophobicity. Flotation process designs vary in complexity depending primarily on the type of mineral, degree of liberation and the desired purity of the product.
- **Acid Leaching** of quartz is one of the most effective processes to reduce impurities. Such chemical refining is carried out in a medium of strong mineral acids at elevated temperatures. Usually hydrofluoric acid is applied, but a combination of certain acids can be used (HF, HCl, HNO3) to further improve the results of chemical refining.

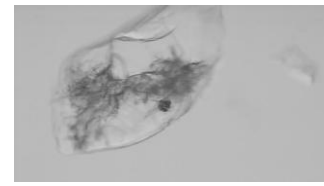
  Trace minerals (e.g. feldspars, micas) which are intergrown with the quartz crystals are dissolved in the course of leaching. Also impurities can be removed which are enriched in micro fissures and along dislocations, owing to an enhanced dissolution rate of quartz in regions where impurities are concentrated.

High Purity Quartz Processing

Thermal Processing 0,1-0,3 mm

- During **hot chlorination process** 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 which are highly restricted in semiconductor applications.
- **Calcination** is a technique to reduce fluid inclusions and improve the melting behavior of high purity quartz. Depending on the type, amount and filling rate of the fluid inclusions, significant improvements in melting behavior can be achieved together with the reduction in alkali concentration which may be present in the fluid inclusions.





High Purity Quartz – Rock to Sand Processing

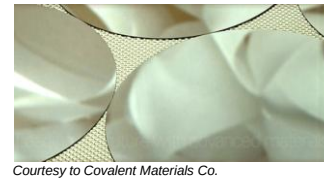
An example

	Al	Fe	Na	K	Li	Ti	Zr	Ca	Mg
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
Original	41,3	12,9	12	15	0,5	1,3	<0,10	3,2	1,3
Preprocessing	23,5	10,3	8,8	8,2	1,2	0,9	0,1	2,9	1,1
Magnetic separation	21,3	**4,9**	6,4	7,6	0,4	**0,5**	<0,10	2,5	0,2
Flotation	**12,3**	3,8	6,9	**3,3**	0,4	0,4	<0,10	**1,4**	0,2
Leaching	10,4	**0,18**	**1,21**	**0,45**	0,25	0,38	<0,01	**0,65**	0,12
Iota Standard	*14,7*	*0,22*	*0,87*	*0,62*	*0,87*	*1,32*	*1,30*	*0,53*	*<0,05*
Hot chlorination	9,2	**0,07**	**0,06**	**0,12**	0,20	0,36	<0,01	0,62	0,11
Iota 6 Data sheet	*8,0*	*0,15*	*0,08*	*0,07*	*0,15*	*1,40*	*<0,01*	*0,60*	*<0,05*

Demand Drivers for High Purity Quartz

Semiconductor

- Demand for high purity quartz products in the semiconductor industries is closely related to new wafer fabs to be built, consuming most of the semiconductor base materials and crucibles.
- SEMI, the global industry association, indicates that total fab spending for equipment needed to ramp fabs, upgrade technology nodes, and expand or change wafer size will be US$ 36.7 billion in 2016.
- Transition from 300 mm to 450 mm wafer manufacturing technology expected to be a major demand driver in coming years.
- In April 2015, Governor Andrew M. Cuomo announced installation of the world's first ever 450 mm immersion scanner at the SUNY Polytechnic Institute's Albany NanoTech Complex.

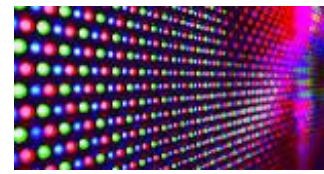


Courtesy to Covalent Materials Co.

Demand Drivers for High Purity Quartz

Microelectronics and Lighting

- Microelectronics packaging market shows double digit growth rates boosting the filler market (semi.org)
- Quartz glass crucibles used in Si crystal growth indispensable in Semiconductor industry
- State of the art: Metal halide lamps (Xenon, halogene) lead the high intensity discharge (HID) product segment
- LED market skyrocketing with CAGR of 27 % between 2014 and 2018 (*source: Navigant*) and Si as alternative substrate taking advantage of low cost semiconductor manufacturing infrastructure



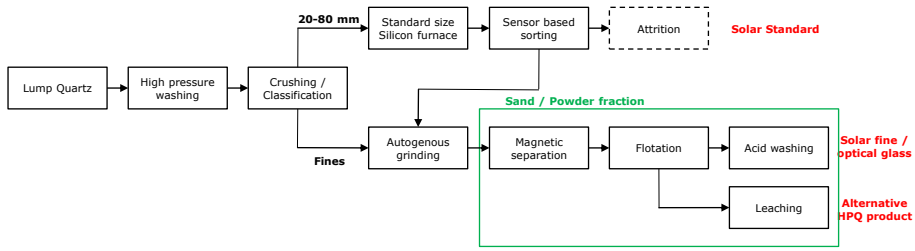
Demand Drivers for High Purity Quartz

Photovoltaics

- 2015, Market research group IHS forecasts a period of strong growth in the global PV module industry due to a new wave of capacity expansions, a relatively stable pricing environment and increasing demand from several established regional markets.
- According to IS global 2016 PV module revenue would hit $41.9 billion, exceeding the previous record set in 2010 by 4%

Using Sand for (SoG-) Silicon under Development

Limited options for purification of lump quartz push sand into the picture



Sand for (SoG-) Silicon under Development

Limited options for purification of lump quartz push sand into the picture

The use of fine grain quartz materials such as high purity quartz sand is generally not seen as viable for the industrial production of Silicon in standard furnaces for various reasons:

- Fines of any type (quartz or carbon) can reduce the porosity of the furnace and prevent the recovery of SiO.
- High levels of quartz fines may interfere with the cavity formation around the electrodes which plays an important role in the process.
- Sand can sinter and interfere with the process dynamics.

Courtesy by JPM Silicon

Sand for (SoG-) Silicon under Development

Limited options for purification of lump quartz push sand into the picture

- JPM Silicon has developed a unique and patented micro-wave heating process for the production of silicon from quartzes studied with impurity levels between 20 and 400 ppm and particle sizes ranging from **0.1 to 3 mm**.
- Evonik is scaling up the innovative Solsilc route which uses **micronized quartz** agglomerated to cm-sized pellets in order to be charged into the electric arc furnace. This offers the advantage to further refine the quartz even below 0,1 ppm in Boron and Phosphorous prior to the furnace process. A pilot plant for production of solar grade silicon has been established in Trondheim 2012.
- Viridis IQ follows three different routes: **quartz fines** are either melted to the glassy stage to form lump pieces, or briquetted with coal or charcoal fines and wood or used in a modified furnace design such that higher pressures are allowed to directly transform the quartz into slag.

Courtesy by JPM Silicon

Summary

Advanced Quartz Qualities

- High purity quartz resources are of limited availability, but of strategic interest to many fast growing high tech industries with robust forecast.
- The detailed specification of advanced quartz qualities very much depend on the final application.
- Due to most stringent specifications there is no standard technology route that applies to process quartz into high purity or advanced qualities.
- Quartz is a main feedstock for silicon, ferrosilicon and photovoltaics production. However, restrictions in content call for high grade quartz resources and advanced processing technologies with sand still in the conceptual stage.

More Details Needed ?

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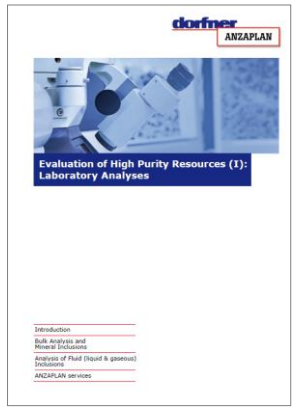

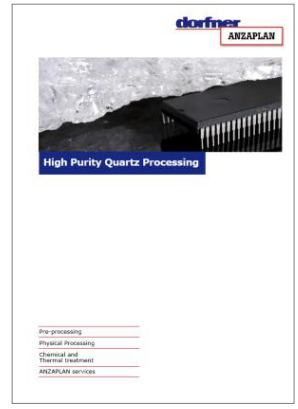


Chapter 2
Assessment of High Purity Quartz Resources

Reiner Haus, Sebastian Prinz and Christoph Priess

Abstract Very high purity quartz for advanced high-tech applications is currently sourced from just a few locations around the world. Such is the expected growth in demand that more sources are required to be found. For successful high purity raw quartz resource identification detailed analysis and appropriate process technology selection is essential. This article reviews general aspects of high purity quartz deposits, exploration requirements, quality evaluation of raw quartz, and provides basic insight into the different specifications and market developments of the high-tech end-user industries reliant on very high purity refined quartz products.

2.1 Introduction

Quartz is one of the most abundant minerals. It occurs in many different settings throughout the geological record (Götze 2009). As the prime source of silica the mineral has wide large volume application in the manufacture of glass, ceramics, refractory materials and other traditional uses (Blankenburg et al. 1994). However, only very few deposits are suitable in volume, quality and amenability to tailored refining methods for speciality high purity applications. As such high purity quartz has become one of today's key strategic minerals with applications in high-tech industries that include semiconductors, high temperature lamp tubing, telecommunications and optics, microelectronics, and solar silicon applications (Blankenburg et al. 1994; Haus 2005, 2010; Moore 2005; Dal Martello et al. 2011a, b).

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Thank you!