

SILICONDIOXIDE - SiO₂ - MINERALS

by

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(eingelangt am 28. 2. 1995, angenommen am 25. 3. 1995)

Abstract

SiO₂ contributes ca. 75 wt% to the earth's crust. Free silica on earth, where water plays a decisive role in rock forming processes, predominantly occurs as quartz. In moon rocks, however, which have been formed under dry conditions, quartz is a rarity, in place of it cristobalite or tridymite occur. - Silica minerals have crystal structures with open SiO₄-tetrahedra frameworks. If they are noncrystalline the structure consists of random tetrahedral networks or of tetrahedra clusters. The only exception from the tetrahedral crystal chemistry is stishovite whose structure represents a nearly closest packing of oxygen with silicon in octahedral coordination. With the exception of the not well equilibrated structures of the tridymites and of coesite, trans-configuration of adjacent tetrahedra governs the structures. - Crystal chemical features are correlated with properties and transformation behaviour. Structural incorporation of impurities via substitution and addition at interstices is discussed in contrast to submicroscopical inclusion of volatile and nonvolatile impurities.

The members of the SiO₂ mineral family are systematically described:

- A) The crystalline minerals stishovite, coesite, quartz with the microcrystalline and water containing species chalcedony and quartzine, moganite, cristobalite, tridymites, cristobalite/tridymite stacking polytypes, opal-C and -CT with the textured varieties lussatite and lussatine and melanophlogite. Paramorphs of quartz after other silica minerals are mentioned.

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- B) The noncrystalline minerals opal-AG with the varieties precious and potch opal, opal-AN (hyalite), lechâtelierite with the species silica fulgurite and impactite.

Introduction

SiO₂ contributes ca. 75 wt% to the earth's crust. It is the major constituent of rock forming minerals in magmatic and metamorphic rocks (s. CONDIE, 1970). Even a great part of minerals in sediments and soils is silicatic (s. SIEVER, 1970). - Free silica on earth predominantly occurs as quartz, which makes up 12-14 wt% of the crust. It should be noted, however, that enormous masses of not or scarcely solidified opal-AG and opal-CT occur at the ocean floors. Differently from rock forming processes on earth - where water plays a decisive role - silicatic bodies, which have been crystallized under hot and dry conditions as e.g. slag, glasses or moon rocks bear quartz only as rarity and only if Na⁺, Ca²⁺ or preferably Li⁺ and Mg²⁺ were present during crystallization. In these cases quartz can crystallize and persist well above its so called temperature of stability (1140 K at ambient pressure) up to 1300-1400 K (SCHULMAN et al., 1949; RIECK & STEVELS, 1951; FLÖRKE, 1955a). Normally, however, cristobalite and tridymite represent the free silica in these bodies.

Principles of SiO₂ crystal chemistry

With the exception of stishovite all known silica minerals have structures with ordered frameworks if they are crystalline, random networks if they are non-crystalline glasslike (-AN), or gel like clusters (-AG) of SiO₄-tetrahedra, sharing all 4 oxygen ligands with their's own kind. The structures have spacy interstices in the crystalline and voids in the noncrystalline minerals. In the latter case even a certain number of nonbridging oxygen (Trennstellen) occurs. The volume demand of oxygen in the elementary cell of the crystalline minerals is ca. 30 - 45 %. Stishovite, however, represents a nearly closest packing of oxygen with 68 % demand.

Four sp³-hybrid orbitals of silicon in the coordination tetrahedron overlap with the two 2p orbitals of oxygen, forming strong sigma-bonds (s. PAULING, 1980). Minor additional pi-bond contributions come from overlap of silicon 3d with the oxygen orbitals and explains the shortening of Si-O bond length with increasing Si-O-Si bond angle (HILL & GIBBS, 1979). The bond character is ca. 1:1 ionic to covalent. The difference of electronegativities of silicon and oxygen is ca. 1.7. This favours Si-O-Si bond angles of about 145° (O'KEEFE & HYDE, 1978). The mean Si-O bond distance is 0.161 - 0.162 nm (Fig. 1). This short distance indicates high bond strength (quartz 452 kJ/mole). In combination with the 3-dimensional tetrahedral linking it causes high elasticity (LEVIEN et al., 1980; compressibility see D'AMOUR et al., 1979) and high melting temperature (cristobalite at ambient pressure 2000 K). It explains the high activation temperature for reconstructive transformations in absence of chemical activation (quartz to cristobalite at ambient pressure ca.

1400 K) and the stranding of these transformations - the monotropic character - if energy is taken away from the system. The hardness of quartz (7 MOHS) and the high transformation- and devitrification-temperature of silica glass (ca. 1400 K) are explained too by these crystal chemical facts. The displacive transformations, however, are reversible and - with one exception at tridymite - cannot be frozen.

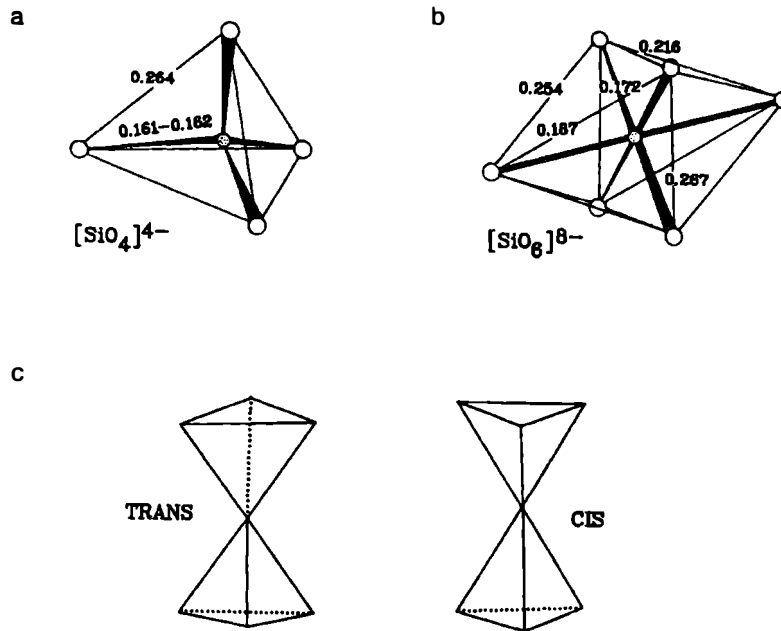


Fig. 1: Silica crystal chemistry; a) tetrahedron, b) octahedron, c) TRANS- and CIS-configuration of adjacent tetrahedra.

The variability of the Si-O-Si bond angle and the revolving of the tetrahedra around their bridging oxygen accounts for the topological and displacive variability of the crystalline frameworks and for the many members of the silica mineral family (Tab. 1). Stacking disorder makes this family still more complex.

In the crystalline structures generally the favourable TRANS configuration of adjacent tetrahedra is realized (Fig. 1). The only known exceptions with mixtures of TRANS and CIS configurations are the tridymites (3/4 TRANS 1/4 CIS) (FLÖRKE & NUKUI, 1981; GRAETSCH & FLÖRKE, 1991) and Coesite. CIS configuration deforms the tetrahedra into slightly stretched trigonal pyramids in tridymite. In coesite it is responsible for an unusually high Debye-Waller factor of the bridging oxygen in the tetrahedra chains which run along the c-direction (GIBBS et al., 1977; GEISINGER et al., 1987).

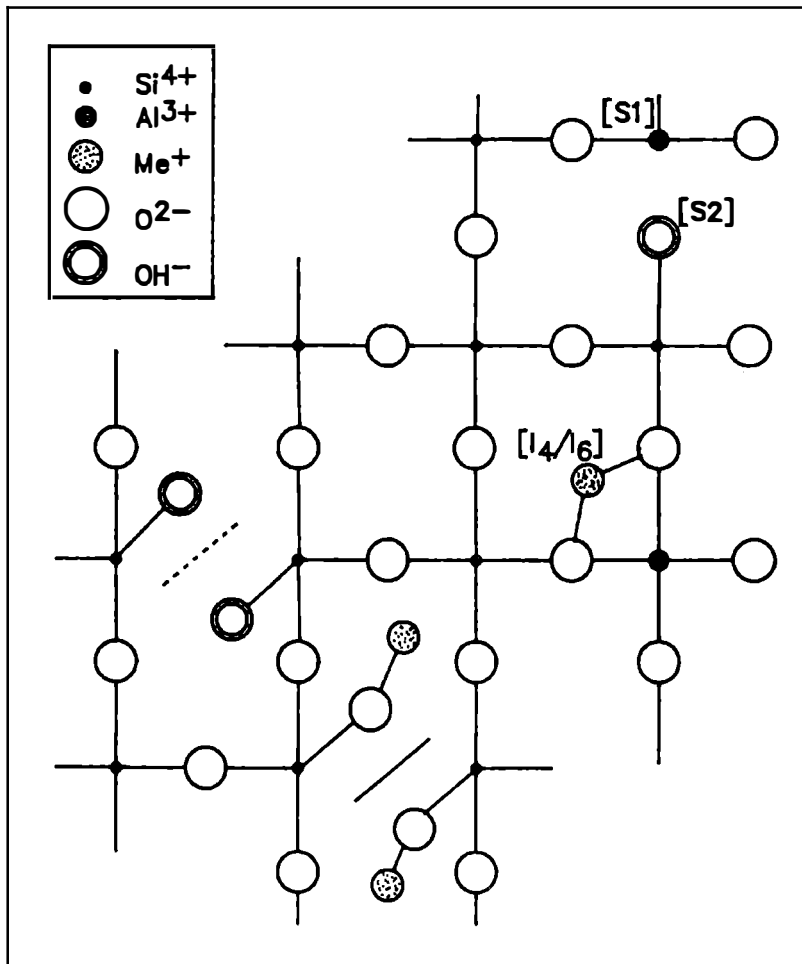


Fig. 2: Schematic 2-dimensional representation of chemical point defects in SiO₂ frameworks; broken line: hydrolytic, solid line: alkaline nonbridging oxygen; S: substitutional, I: interstitial defect (FLÖRKE & MARTIN, 1993).

Impurity traces in silica minerals

The influence of alkali ions and of water (chemical activation) on formation and transformation of silica minerals (e.g. STOECK, 1992) reflects the ability of the structural frameworks to incorporate impurity traces as frame weakening defects. The random network of silica glass is subjected to the same effect, however, it has not the stoichiometric limitations, which are necessitated by the crystalline order. Therefore, the transition from pure silica glass to silicate glasses with increasing concentrations of foreign components is fluid. A tendency of the crystalline silica

minerals for solid solution with their stuffed derivatives (e.g. quartz/eucryptite, cristobalite/carnegieite, tridymite/nepheline) is not observed in nature (cf. PALMER, 1994).

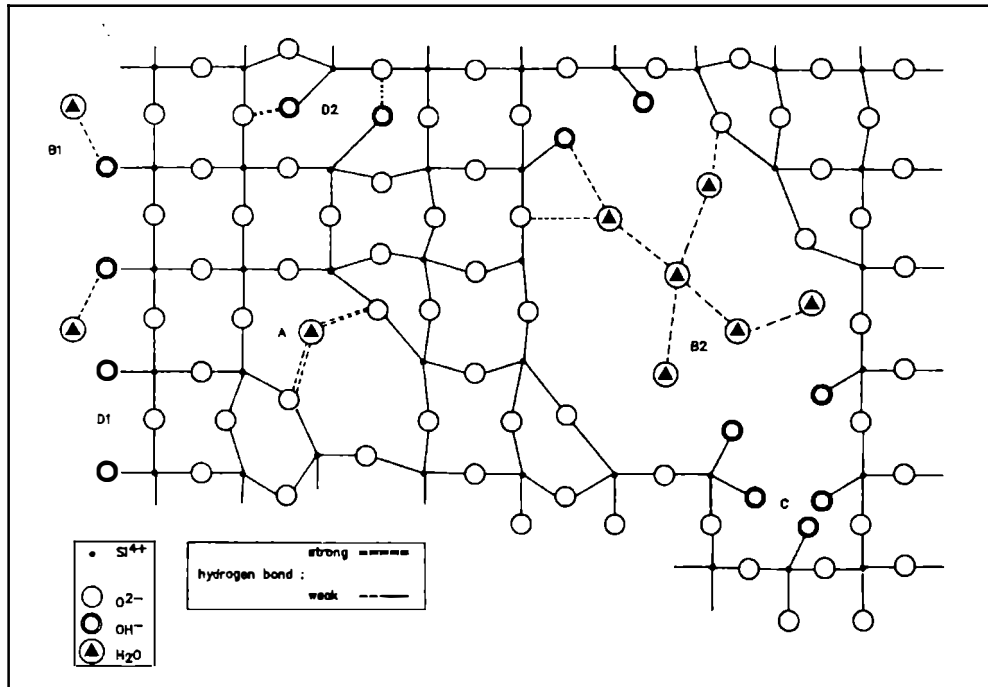


Fig. 3: Scheme of water species binding in and at SiO_2 frameworks; A: strongly bonded, B1: at outer surfaces, B2: molecular water clusters in submicropores, C: substitution of SiO_4 by $(\text{OH})_4$, D1: surface silanol, D2: silanol groups at nonbridging oxygen.

One mechanism of structural incorporation is the substitution of Si^{4+} by Ge^{4+} or Ti^{4+} at small extent. Much more important is the substitution by Al^{3+} or Fe^{3+} (secondarily by B^{3+}) coupled with addition of Li, Na, Mg at interstices.

Less important is the coupled substitution of silicon by Al^{3+} and P^{5+} . Last but not least the formation of hydrolytic or alkaline nonbridging oxygens (Fig. 2) by incorporation of H_2O or M_2O (Li, Na, and in the open framework of cristobalite and tridymite also K, Rb, and in the former even Cs) shall be noted. The high mobility of these defects at comparably low temperatures accounts for activation of the reconstructive transformations as well as for hydrolytic weakening and plastic deformation of quartz under stress at higher confining pressure (cf. NICOLAS & POIRIER, 1976).

All these mechanisms allow the entrance of only traces into the crystalline silica structures. The concentration of nonvolatile impurities in quartz rarely exceeds 600, of protons 800 ppm Si. Higher values point to submicro-inclusions. Water can reach values up to 1000 ppm Si and more if molecules or molecular clusters are included. The models for entrance of water, as revealed by infrared spectroscopy, are shown in Figure 3. The uncertainty of discrimination between structural incorporation and microstructural inclusion goes back to the principal difficulty to differentiate by means of geochemical analysis between these defects of dimensionality 0 and 3 and their fluid transitions. Models for impurity entrance are shown in Figure 4. Growth sector specific inequality is a function of growth velocity, increasing with increasing velocity. Therefore, proton concentrations in the $\langle r \rangle$ sector of quartz (sector beyond the $\{10\bar{1}1\}$ faces) in many natural cases are higher than in $\langle z \rangle$ sectors ($\{01\bar{1}1\}$). The differences may differ in the same crystal from foot to head. The tendency for impurity segregation followed by skeletal growth with impurity inclusion, increases with increasing supersaturation of the mobile mother phase.

After the revolutionary march of the quartz oscillator, the question after the nature of impurity traces more than ever presses for an answer. It is of fundamental importance for choice of beneficiation processes for uses as an industrial mineral (JUNG, 1992).

Cristobalite in well developed microcrystals from 10 years used silica bricks had less than 1 wt.% of nonvolatile impurities. Natural cristobalite in its highly defected microstructure includes higher amounts. Tridymites behave similarly (SCHNEIDER & FLÖRKE, 1982; SEIFERT-KRAUS & SCHNEIDER, 1984; SCHNEIDER, 1986).

SiO₂ mineral family

"Mineral" indicates occurrence in nature, the phase may be crystalline or noncrystalline, and names are only given to minerals. "Keatite", therefore, is a misnomer, for this phase has never been found in nature and "silica-K" would be better. It will not be treated here like other non-mineral silica phases (cf. FLÖRKE & MARTIN, 1993). A detailed treatment of silica minerals is given by FRONDEL (1962). A recent review of silica knowledge is attempted by HEANEY et al. (1994), however, this book suffers from the lack of correspondence between the articles by the different authors. Table 1 lists the hitherto known silica minerals. It includes enantiomorphs and displacive low/high polymorphs. It should be noted, however, that at ambient conditions no high-polymorphs of silica minerals persist. - Agate is a silica rock with different constituent minerals (chalcedonys, opals and others). Other silica rocks are quartzite, quartz arenite, diatomite, porcellanite, radiolarite, geyserite and chert (cf. FLÖRKE & MARTIN, 1993; Tab. 1.4). The petrogenesis of chert has been recently treated by KNAUTH (1994).

Table 1: The silica mineral family

Name	Crystallinity/microstructure	Occurrence on earth
Crystalline minerals:		
Stishovite Coesite	micro macro to micro	impact rocks impact and metamorphic rocks
Quartz left-/right-handed low-/high-polymorphous Chalcedony [*] CH _{LF} Quartzine [*] CH _{LS}	macro to micro micro/fibrous F - " " F +	general hydrothermal to diagenetic milieu
Moganite	micro/lepidospheric	volcanic milieu
Cristobalite left-/right-handed low-/high-polymorphous stacking disordered variations	micro to macro see Fig. 11	hydrothermal milieu, volcanic rocks
Tridymite until now: 5 high-polymorphs 3 low-polymorphs stacking disordered variations	macro to micro see Fig. 11 see Fig. 11	like cristobalite, growth from den- dritic cristobalite nuclei
Crystalline opals ^{**} Opal-C ^{**} Lussatina ^{**} O-C _{LF} Opal-CT ^{**} Lussatite ^{**} O-CT _{LS}	micro predominantly cristobalitic/platy, massy fibrous F - cristobalitic-tridymitic/lepidospheric, massy fibrous F +	hydrothermal to diagenetic milieu, silicic oozes at ocean floors
Melanophlogite ^{***}	micro to macro	rare in hydrothermally active milieu; maybe altered to quartz
Noncrystalline minerals:		
Opal-A [§] Opal-AG ^{**} Precious opal ^{**} Potch opal ^{**} Opal-AN = Hyalite [§] Lechâtellerie ^{§§} Silica impactite Silica fulgurite	gel-like SiO ₂ ·nH ₂ O clusters closest packing of isometric micro-spheres irregular accumulation of anisometric spheres 3-dimensional random tetrahedra network/ botryoidal crusts or spheres with character- istic stress birefringence 3-dimensional random tetrahedra network, free of water	hydrothermal to diagenetic milieu, silicic oozes at ocean floors deposited from hydrothermal silicic fluid on cool rock substrates or into water meteorite impact lightning flash into silica rocks or quartz sand

Footnotes to table 1:

- F : optical character of fibre axes
- * : contains H₂O, predominantly as SiOH
- ** : contains H₂O as SiOH and as molecular water
- *** : contains guest molecules CH₄, N₂, CO₂
- § : hydrothermal silica glass
- §§ : pyrogenic silica glass, not sharply to distinguish from silicate rock glasses
- micro : the individual crystallites cannot be resolved with the naked eye

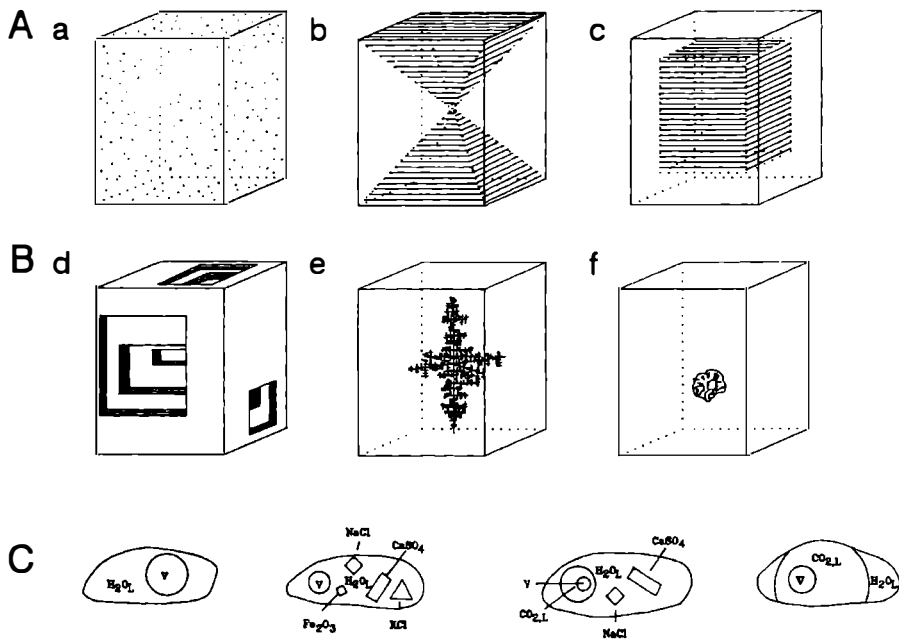


Fig. 4: Principles of impurity distribution in crystals.

A: Structural incorporation, a) at random, b) growth sector specific, c) zonal, oscillatory at stationary, sporadic at nonstationary growth.

B: Microstructural inclusion, caused by d) skeletal growth, e) dendritic growth, f) accumulation and overgrowth, e.g. in fissures.

C: Types of fluid inclusions (after NASH & THEODORE, 1971), L: liquid, V: vapour, polygons: crystals.

It is interesting that the silica mineral family encloses very few minerals which form macrocrystals (Tab. 1), however, very much microcrystalline and noncrystalline members. Figure 5 shows a scheme of the fluid transitions of these states of crystallinity and noncrystallinity.

A: The crystalline silica minerals

Stishovite in the earth's crust is found in impact rocks (CHAO et al., 1962). A review of high pressure behaviour of silica is given by HEMLEY et al. (1994). Stishovite crystallizes in the rutile type (PREISINGER, 1962; SCLAR et al., 1962; SPACKMAN et al., 1987). Under extreme p -, T -conditions Si forms six sp^3d^2 -hybrid orbitals and is octahedrally coordinated with oxygen. The octahedra share two opposite edges and two corners, forming a very close oxygen packing. If not quenched on pressure release, it transforms beyond ca. 1800 K into coesite. At ambient pressure it is metastable and transforms by heating at ca. 800 K into

noncrystalline silica. Contrary to the other silica minerals it is almost insoluble in diluted HF, whereas its solubility in water is comparable with silica glass (BOHM & STÖBER, 1966).

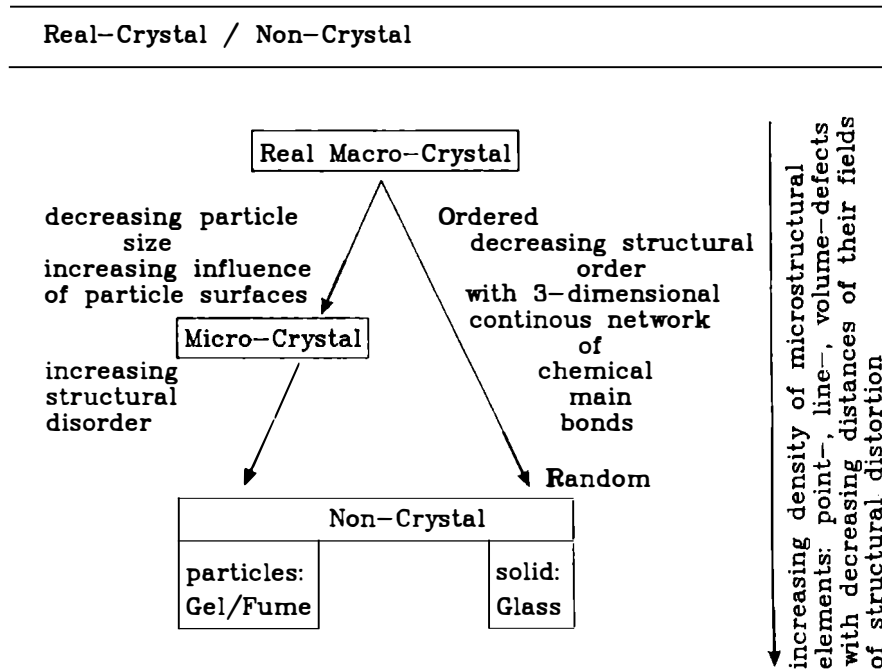


Fig. 5: Scheme of transition from the macro-crystalline into the noncrystalline state.

Coesite occurs in meteoritic impact and in high pressure metamorphic rocks. It crystallizes in its own structure type. Four-membered rings of tetrahedra in UD configuration are interlinked by Si_2O_7 groups in CIS configuration to chains which run along the c-axis. In b-direction these chains are linked by Si_2O_7 groups in TRANS configuration. The apparent Si-O-Si angle in the CIS groups is 180° which is a very improbable value (GIBBS et al., 1981). The Debye-Waller factor of the bridging oxygen is unusually high indicating an average structure of domains with much better equilibrated tetrahedra configurations (GIBBS et al., 1977; LEVIEN & PREWITT, 1981). In diluted HF it is much less soluble than quartz. The solubility in water is similar to quartz (BOHM & STÖBER, 1966).

Quartz is the stable silica mineral under ambient conditions (Fig. 6). A comprehensive treatise of the mineralogy of quartz from alpine shear fissures by POTY (1969), which has not become widespread may be cited here, standing in for the

innumerable papers on quartz mineralogy, many of which are cited by FRONDEL (1962) and JUNG (1992). The most important feature of its structure are helices with a repeat distance of 3 tetrahedra along the c-axis. The winding is left-handed with respect to usually crystallographic setting in space group $P3_22$ and right-handed in $P3_12$. Structural L-quartz turns the vibration plane of polarized light in the definition of BIOT clockwise and R-quartz counterclockwise. The discrimination of L- and R- with morphological arguments in the contrary sense still today causes serious confusion in literature (DONNAY & LE PAGE, 1978). Six structural helices envelop channels with fourfold (I_4) and sixfold (I_6) oxygen coordinated interstitial sites. Polarity along the a-axes accounts for piezoelectricity and makes quartz a voltage-pressure transducer and frequency controller. Tiny tuning forks of quartz oscillate in each electronic watch, and in devices with analog-digital conversion quartz elements work as time keepers.

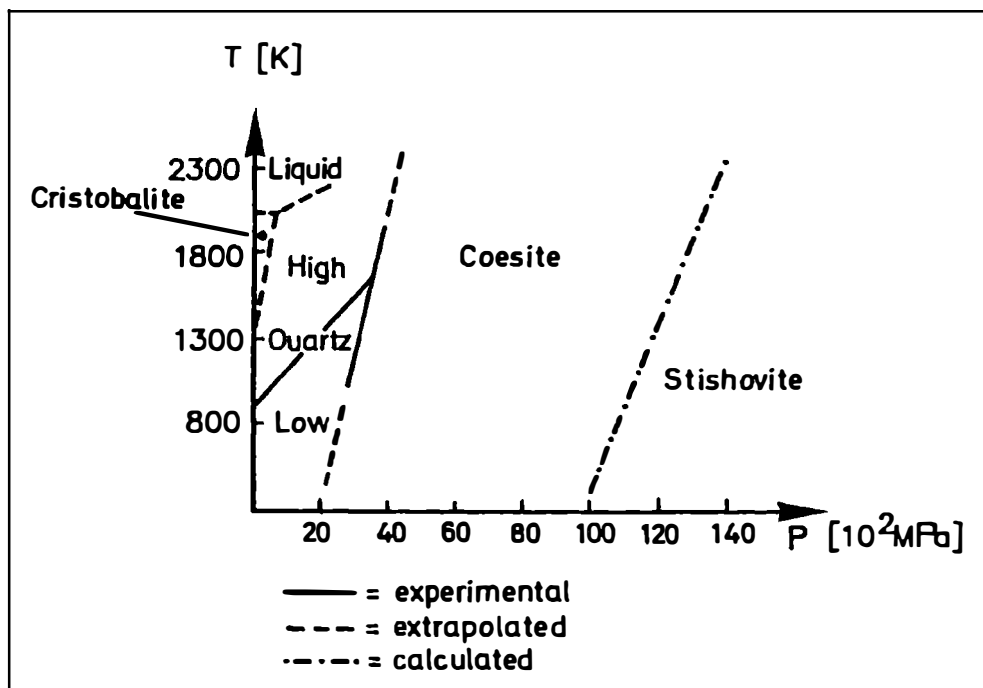


Fig. 6: p-T diagram of SiO₂ minerals; the borderline of tridymite to quartz and cristobalite runs close to the temperature axis from ca. 1200 - 1800 K.

The low/high transformation is rapid, reversible and not freezable. At ambient pressure it takes place at 846 K. The pressure dependence is $+26^\circ \text{kbar}^{-1}$ (COHEN & KLEMENT, 1967). The transformation has premonitory character with increasing rotatory disorder of tetrahedra in dauphiné-twin positions with increasing temperature (ARNOLD, 1962; GRIMM & DORNER, 1975; DOLINO et al., 1983).

Table 2: Quartz gems

Name	colour; appearance; origin of colour ¹ ; remarks
Monocrystalline macroquartz, possibly twinned	
Rock crystal	colourless; transparent
Amethyst	violet different in different growth sectors or coloured in patches; transparent, translucent to milky opaque; Fe(S) + Fe(I) radiation activated colour centres; poly-synthetically microtwinning
Smoky quartz	faint to dark smoky brown to black ("Morion"), frequently zonal or specky colour distribution; transparent, translucent, opaque; (misnomer "smoky topaz") (Al + e)(S) radiation activated colour centres
Citrine	yellow to yellowish brown with smoky cast; transparent; Fe(I) colour centres. Burnt amethyst yellow to yellow brown with reddish tints; transparent to translucent; Fe ₂ O ₃ precipitates; microtwinning like amethyst (misnomer "topaz")
Rose quartz	pale pink to deep rose red, purplish or lavender cast; transparent, translucent, milky; Ti(I) colour centres
Rosa quartz	light rosa; transparent, translucent; (Al + P)(S) colour centres
Blue quartz	in reflected light milky- to lavender-blue, in transmitted light complementary yellowish to brown; translucent, opaque; Rayleigh-scattering at submicroscopical rutile needles
Rutile quartz	colourless or smoky with radiating bundles or gratings (sagenite) of yellow to red or brown rutile needles; transparent
Star quartz	asterism due to oriented precipitation of submicroscopic rutile needles
Milk quartz	white; opaque; scattering of light at minute flaws, pores and colourless inclusions
Polycrystalline microquartz	
Quartz cats aya	grayish green, reflecting a milky wafe of light; translucent; oriented inclusions of fibrous amphibole
Hawk eye	dark greenish blue, fibrous luster, banded; opaque; quartz impregnation of blue fibrous crocidolite asbestos
Tiger eye	yellow to yellow brown, fibrous luster, banded; opaque; quartz impregnation of oxidized crocidolite asbestos
Aventurine	spangled green chalcedony; translucent; inclusions of scales of chromium-muscovite fuchsite
Agate	banded, in reflected light gray to bluish gray or black, in transmitted light complementary brownish and white opaque; translucent and black or white opaque; translucent bands possess open porosity and are colourable by infiltration, white opaque bands are not colourable
Onyx	agate with alternating black and white bands, used for carving of cameos
Sard	brown to red chalcedony; translucent; naturally coloured by infiltration with humic acid iron solutions and precipitation of iron oxide hydrates
Sardonyx	alternating reddish brown or red, black and white bands
Carnelian	red chalcedony; translucent; dispersed Fe ₂ O ₃ particles
Chrysoprase	bright green chalcedony; translucent; dispersed nickel silicate hydrate. Plasma dark to dull green chalcedony; opaque to translucent;
Prase	dispersed ferrous silicates (chlorites, amphiboles)
Heliotrope (Bloodstone)	dark green to grayish green plasma with red spots of carnelian or jasper
Moss agata	various coloured dendritic inclusions in translucent chalcedony
Iris or rainbow agate	specks of monochromatic colours in sard matrix changing by tilting the piece; Bragg-diffraction of light at periodic microstructural features
Jasper	varied red, yellow, brown and green chert; opaque; iron coloured impurities.

¹) (S):substitutional, (I):interstitial.

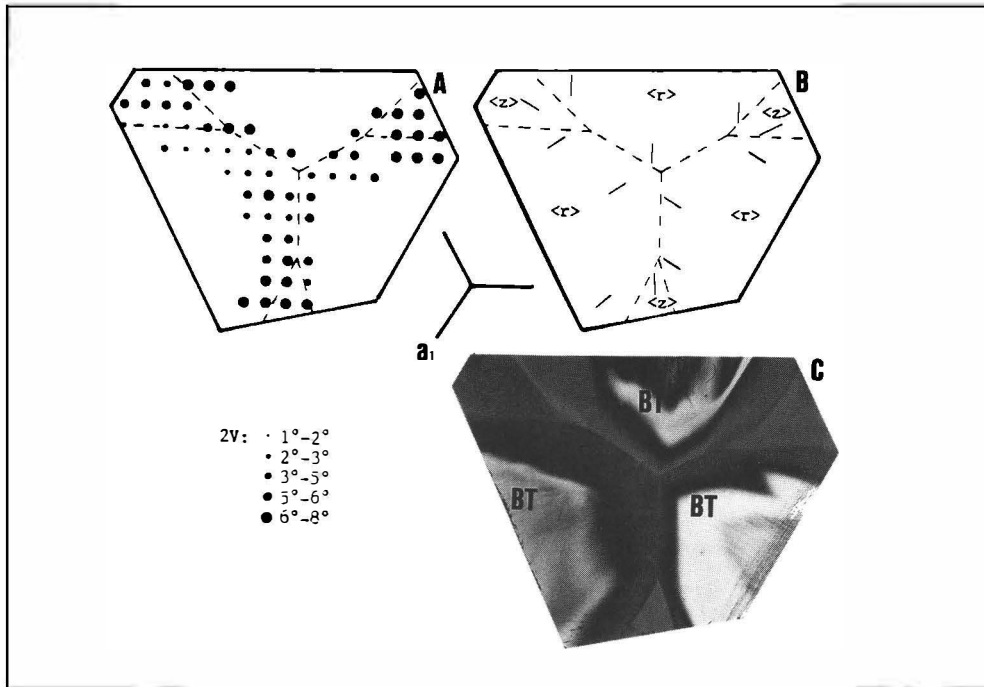


Fig. 7: Map of anomalous biaxial character due to inequivalent Si site occupation by substitutional Fe in amethyst (Bladveld, Namibia) cut parallel (0001); A: axial angles $2V$ (dots), B: traces of optical planes (lines) in different growth sectors, C: plate in the PLM, polars partly crossed, BT: sectors with polysynthetic submicroscopic brazil-twinning, left out for measurement; longest edge of object 3 cm (GIESE, 1983).

Twinning is a frequent feature, predominantly after the dauphiné-law (L-/L- or R-/R- after $[00.1]$ or the brazil-law (L-/R- after $\{11\bar{2}0\}$ or of mixtures of both. Its influence on growth and properties of amethyst was analyzed by RÖLLER (1991). Quartz has a distinct cleavage after $\{10\bar{1}1\}$ (cf. FRONDEL, 1962) which is rather spectacular in hydrothermal or pegmatitic veins (FLÖRKE et al., 1981). Quartz is the only crystalline silica phase which is artificially grown - manmade after JUNG (1992) - in large crystals with a worldwide production of ca. 2 kt/anno.

The gem varieties of monocrystalline quartz are listed in Table 2. The colour varieties amethyst, citrine, rosa, rose and smoky quartz owe their beauty intrinsic trace element defects, which by activation with ionizing radiation produce colour centres (cf. LEHMANN & BAMBAUER, 1973). Radioactivity is the natural source for this radiation. The amethyst centres are produced by Fe, substituting Si, coupled with charge compensating addition of Fe at I_4 -interstices (20 - 100 ppm Si as a rule). Similar Al-concentrations with compensating Li and Na at I_4 -interstices lead to smoky quartz centres.

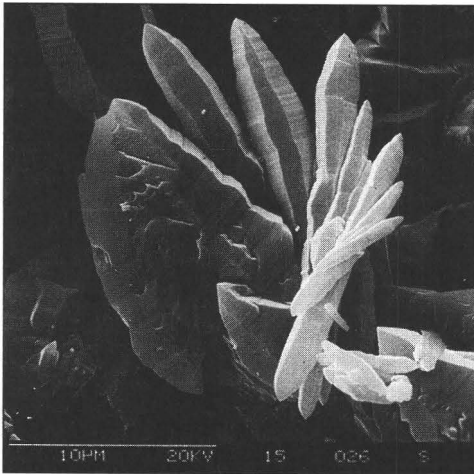


Fig. 8: Twisted aggregate of quartz crystals with tessin habit; hydrothermally grown in 0.01n aqueous NaOH solution at 670 K, 35 MPa by B. MARTIN (Bochum); long edge 30 mm.

Both types of centres are paramagnetic defects, measurable with electron-spin-resonance spectroscopy ESR (SCHNADT & SCHNEIDER, 1970; WEIL, 1984; SIEBERS, 1986; PANKRATH, 1988). Quartz without Fe or less than ca. 50 ppm Si cannot be coloured by radiation and represents true rock crystal. The depth and shade of colouration in smoky quartz increases with the ratio Li/Al ppm Si. With values above 0.15 the smoky colour becomes visible and changes with increasing values from light to dark brown (JUNG, 1992). Growth kinetics produce unequal distribution of colour centres within the crystal. The concentration is higher in $\langle r \rangle$ than in $\langle z \rangle$ sectors (in smoky quartz up to ca. the factor 2). Additional unequal distributions of Al or Fe at the 3 structural equivalent Si sites occur in these sectors. Both inequalities increase with increasing velocity of growth (BARRY et al., 1965; SIEBERS, 1986; PANKRATH, 1988). Whereas the growth sector inequalities cannot be equalized by tempering, it requires long distance diffusion, the site inequalities can be offset by tempering, for this requires only next nearest neighbour hopping. The activation energy for Al is at ambient pressure ca. 210 - 290 kJ/mole and at 200 MPa confining pressure ca. 230 - 440, depending on Li or Na dominance (PANKRATH, 1988; PANKRATH & FLÖRKE, 1994). The site inequality causes anomal biaxial character (BARRY et al., 1965) with values $2V$ of e.g. $2 - 10^\circ$ for amethyst. In the case of biaxial character, produced by elastic deformation, the optical planes are rather irregularly oriented, whereas in the case discussed here they are oriented (Fig. 7).

The zoned, speckled and cloudy distribution of colour shade in amethyst and smoky quartz - on condition of equal, colour centre activating, radiation dose - is directly correlated with the concentration of Fe or Al defects (SIEBERS, 1986; PANKRATH, 1988; JUNG, 1992). The reasons for the differences in colour intensity may be systematized as follows:

- 1) Temporal decrease in supersaturation of the mother solution results in decrease of defectiveness from foot to head and from inside to outside of the crystal, accompanied by decrease of reflection of white light at inner surfaces and increase of equality of impurity segregation and colour centre distribution. Cleavage products after $\{10\bar{1}1\}$ e.g. heal into misshapen crystals with a predominant pair of opposite $\{10\bar{1}1\}$ faces.
- 2) Change of geometry of growth space, cleaving, breaking and deformation of the growing crystal changes the flow dynamics of the mother solution and the anisotropy of transport of matter, accompanied by change of distortion of crystal habit with differences between individuals of different mutual orientation in the growth space.
- 3) Fluctuations in supply, composition and physico-chemical state of the mother solution due to geodynamic events is associated with zonal distributions of irregular zone breadth.
- 4) Rhythmic segregation during stationary growth causes zonal distribution with microscopic pseudoperiodically spaced zones.
- 5) Face specific non-equilibrium incorporation of impurities causes different colours and hue in different growth sectors, e.g. citrine colours in the $\langle c \rangle$ sector in a broken and healing amethyst.
- 6) Dauphiné-twinning causes macro to submicro intergrowth of sectors or slices with different colour centre concentrations. Brazil-twinning is of no primary influence.

The specification and distribution of water is treated for quartz from metamorphic rocks and from other environments by MEINECKE (1993). Fluid inclusions in quartz (Fig. 4c) are mainly composed of H_2O , CO_2 , N_2 , CH_4 and NaCl (POTY, 1967; MULLIS, 1987).

Chalcedony CH_{LF} and Quartzine CH_{LS} , the microcrystalline fibrous quartz varieties, consist of submicroscopical L- and R-lamellae after the $10\bar{1}1$ lattice slice (GRAETSCH et al., 1987; GRAETSCH, 1994). The very abundant chalcedony CH_{LF} microscopically consists of fibres with length fast optical character. It is the constituent mineral of flint, chert and agate. In flint and chert the fibres are microspherulitic and randomly oriented. In agate the white opaque horizontal layers consist preferably of granular microquartz, whereas the translucent layers consist of radiating spherulites of chalcedony CH_{LF} , which have developed by digestion of the formerly opal-C. This had been deposited from a liquid mother phase following the earth's gravity. The microstructure of these layers may contain some residual opal, it cannot be infiltrated by aqueous solutions. Wall lining layers, which during their deposition from the mother fluid did not follow the gravity, have a microstructure of encountering paraboloidal fibre bundles of CH_{LF} , which started from spherulitic nuclei at the outer boundary surface of the layer. Under the microscope at crossed polarizers the paraboloids show wrinkle banding (Runzelbänderung; BERNAUER, 1927) due to systematic rotation of the c-axes of the individual microcrystallites around the fibre direction (a-axes). This phenomenon, for which the reason is not yet known, is not correlated with the twisted growth (Quindel) of quartz macrocrystals, where the individual crystals are of the same handedness (Fig. 8). The microstructure of the wall lining layers can be infiltrated by solutions.

Visually they appear translucently blue-gray in the reflected and brownish in the transmitted light. High hardness and toughness, together with high purity, makes these layers a valuable industrial material. Trials for syntheses have failed yet.

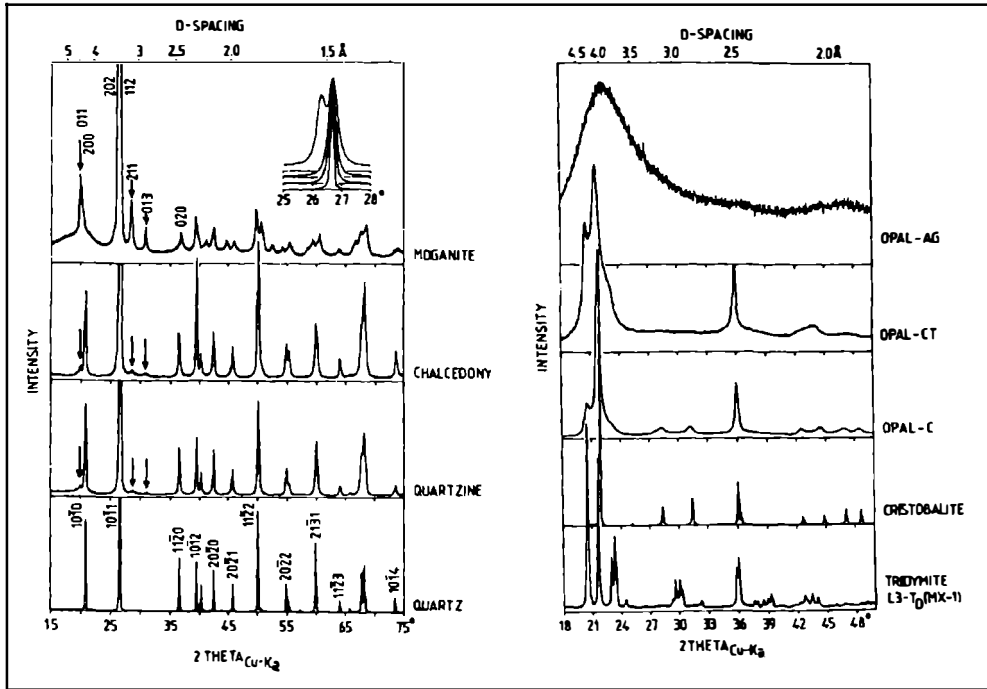


Fig. 9: X-ray powder diffractograms of at left: quartz, chalcedony, quartzine, moganite; arrows indicate additional weak reflections due to pseudoperiodic stacking of L- and R-lattice slices of quartz structure; at right: opal-AG, opal-CT, opal-C, cristobalite C_O , tridymite $L3-T_O$; intensity scaled to equal heights of the first reflection.

Quartzine CH_{LS} with length slow optical character of fibres occurs in agate layers between wall lining CH_{LF} layers in fibre bundles with a characteristic plait pattern on microscopical inspection (MARTIN, 1991).

A description of these microcrystalline quartz species, which are characterized by small, however, decisive water contents, is given by MARTIN (1991), FLÖRKE et al. (1991), GRAETSCH (1994). A broad variety of microstructural features, light scattering and colouring inclusions produces the gem varieties of microcrystalline quartz (Tab. 2).

Moganite with lepidospheric aggregates of length slow optical character forms dense translucently gray or friable white masses. Only the latter consist entirely of moganite whereas the former masses contain admixtures of chalcedony. It occurs in ignimbrites at SW Gran Canaria (FLÖRKE et al., 1984). The crystal structure represents a new type in the group of systematically twinned Ito-structures. One L- and R- $10\bar{1}1$ lattice slice each of the quartz structure are intergrown in the unit cell. Thereby they are characteristically distorted, forming a tetrahedral Si-lattice site in the twin plane which does not exist in the quartz structure (MIEHE & GRAETSCH, 1992; GRAETSCH et al., 1994a, b). Moganite has been postulated to occur widespread (HEANNEY & POST, 1992), however, this goes back to a confusion with the similar stacking faults of quartz (GRAETSCH, 1994) as e.g. in the Brewster bands of amethyst crystals, causing diffuse rods in the reciprocal lattice parallel $r^*_{10\bar{1}1}$ and $r^*_{01\bar{1}1}$ (RÖLLER, 1991). In chalcedony and quartzine these faults have high density and produce by their interaction a pseudoperiodic repeat. The X-ray patterns therefore show weak additional reflections which were first described by GRAETSCH (1985) (Fig. 9). The small amounts of water in moganite, like in chalcedony are mainly bound as silanole group water (Fig. 3).

Cristobalite occurs on earth in the ground mass and in vesicles of volcanic rocks, in dendritic aggregates as devitrification in obsidians, in pyrogenically altered quartz rocks and in the crusts of fulgurites. X-raying reveals that natural cristobalites are stacking disordered. It is the low pressure high temperature modification of SiO_2 (Fig. 6). The structure can be derived from the zincblende type with Si occupying the Zn and Si positions and oxygen between them. The SiO_4 -tetrahedra are all in TRANS configuration with each other (Fig. 1). Sheets of rings of 6 Tetrahedra (6T) in up-and-down (UD) position ($6T_{UD}$ -rings) are stacked in parallel orientation in a 3-sheet sequence ABC. The framework has large interstitial cages wherein trace elements with rather large ionic radii (e.g. Cs^+) can be incorporated. The displacive low-high transformation is rapid, reversible and - though in ordered cristobalite it has a hysteresis of ca. 20 K - cannot be frozen (Fig. 11; FLÖRKE 1957). The missing of suitable macrocrystals prevents precise determination of properties and the discussion of consequences from the enantiomorphy.

Tridymites occur in similar environments, and in most cases they have developed from dendritic cristobalite nuclei, following the nucleation-growth scheme given by FLÖRKE & NUKUI (1988). From hydrothermal transport tridymite crystallizes preferably in tabular crystals. However, even ideally hexagonal looking crystals with smooth surfaces and sharp edges are highly defected in their interior (NUKUI & FLÖRKE, 1987). Analogous to the derivation of the cristobalite structure, the principle of tridymite structure may be derived from the wurtzite type. Sheets of $6T_{UD}$ -rings are stacked in a 2-sheet sequence AC'. The apostrophe indicates that the C-sheet is in antiparallel position to sheet A (cf. FLÖRKE, 1967). The framework has open channels wherein preferably Na and K traces can be incorporated. The Si_2O_7 groups, which are linking the sheets, are in CIS configuration. The structure, therefore, with respect to bonding requirements is much less balanced than the cristobalite structure and requires at the formation the presence of charge screening protons or alcali ions. Tridymites undergo complex displacive transforma-

tions as a consequence of their delicate stability (Fig. 11). Phase relationships and X-ray powder patterns of tridymites are treated by GRAETSCH & FLÖRKE (1991).

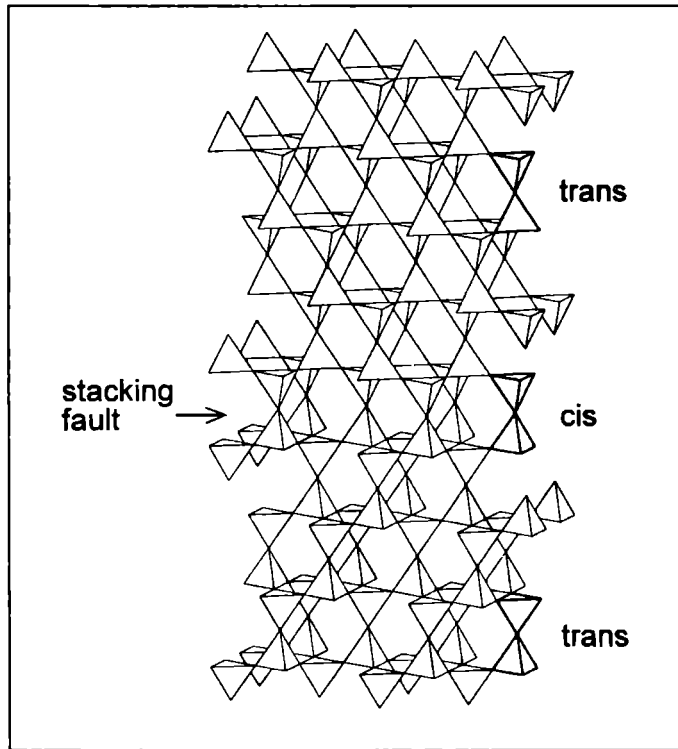


Fig. 10: Tridymite (CIS-) stacking fault in cristobalite (TRANS-) sequences, schematic (GRAETSCH, 1994).

Cristobalite-Tridymite stacking polytypism is provoked by the close structural relationships (analogous to cubic-hexagonal closest packing polytypism JAGODZINSKI, 1954, 1964). During growth or transformation stacking faults of the tetrahedral sheets form in cristobalite and tridymite (Fig. 10) (FLÖRKE, 1955a; SCHNEIDER & FLÖRKE, 1986). 3-sheet and 2-sheet sequences intergrow at random and in varying thicknesses (FLÖRKE et al., 1990).

Stacking disorder changes all properties and especially the low-high transformation behaviour (Fig. 11). Therefore, one has to discriminate thoroughly between ordered and disordered cristobalite and tridymite (C_O , C_D and T_O , T_D). Terms like "tridymite S" or "meteoritic tridymite" and "tridymite M" or "terrestrial tridymite" are misleading and redundant synonyms for T_O and T_D respectively.

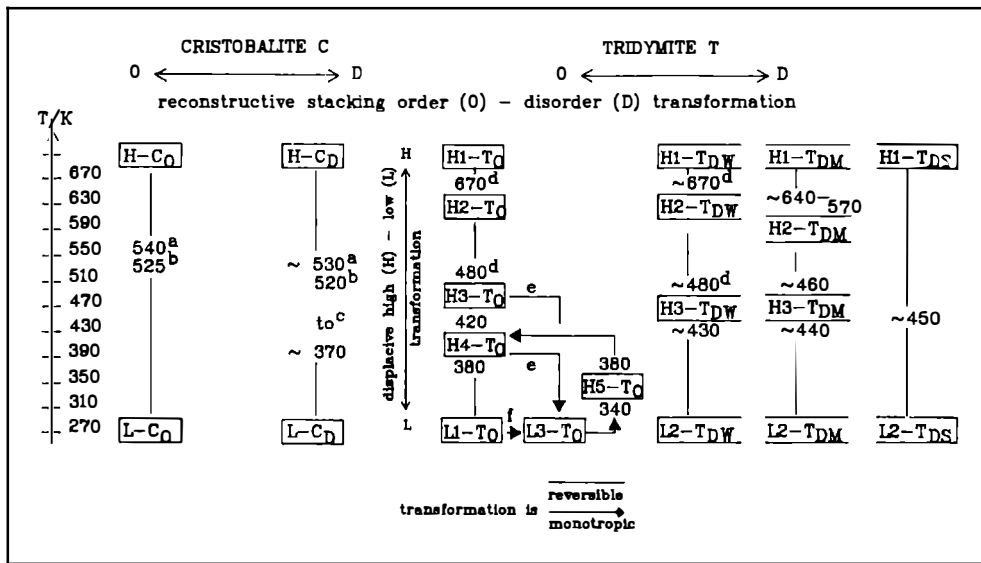


Fig. 11: Displacive polymorphism and stacking polytypism of cristobalite and tridymite; a) on heating, b) on cooling, c) decreasing with increasing stacking disorder, d) gradual, e) on quenching to 77 K, f) under stress; stacking disorder: w = weak, m = medium, s = strong.

Crystalline opal¹, opal-C and opal-CT, produce X-ray patterns with rather diffuse interferences (Fig. 9) (FLÖRKE, 1955b; JONES & SEGNET, 1971; FLÖRKE et al., 1990, 1991; GRAETSCH, 1994). They differ with respect to the degree of cristobalite/tridymite stacking disorder. Opal-C contains ca. 20 - 30 % tridymitic sequences. No extended domains of prevailing cristobalitic or tridymitic sequences exist (GRAETSCH, 1994). The pattern is rather similar to strongly disordered synthetic cristobalite C_{Ds} . In opal-CT a ca. 1:1 mixing of 3- and 2-sheet sequences produces X-ray patterns which are distinctly different from the opal-C pattern (Fig. 9).

Opal-CT crystallizes in submicroscopic platelets forming lepidospheric dense aggregates without preferred orientation. The birefringence is very weak or almost not recognizable. In postvolcanic environments, however, opal-CT which had been deposited from a fluid mother phase, frequently forms botryoidal crusts of radiating spherulites which develop into an encounter microstructure of parallel fibrous bundles and length slow optical character. In this cases the birefringence is distinct. For this microstructural variety the name lussatite (opal-CT_{LS}) should be used (FLÖRKE et al., 1975, 1976, 1991).

¹ All so-called "common" opals fall into this category.

Opal-CT is a main component of silicic oozes at the ocean floors. Opal-C crystallizes in submicroscopic platelets which are aggregated into piles. It is preferably found in horizontal layers of agate. The birefringence is weak and undulatory. If microscopically visible fibres are developed, their optical character is length fast. This is the case when the piles are in rather good mutual orientation. The name **lussatine** (opal-C_{LF}) should be used for this variety (GRAETSCH, 1994).

Both, lussatine and lussatite, show anisotropic small angle X-ray scattering (Fig. 12) (GRAETSCH et al., 1994b). Due to the varying microstructure, the crystalline opals contain varying amounts of non-structural water. The predominant part of it is molecular H₂O(mol), trapped in the pores of the microstructure (LANGER & FLÖRKE, 1974, GRAETSCH, 1994).

Melanophlogite is a very rare silica mineral with a porous tetrahedra framework-structure (porosile) and CH₄, N₂ or CO₂ as guest molecules (templates) in the structural cages (GIES et al., 1982; GIES, 1993). They can be driven out by heating, whereby the hydrocarbons are partly decomposed and leave black residues behind (therefrom the name). It forms in milieu of hydrothermal activity at very low pressure in different geological settings (cf. GRASSELINI-TROYSI & ORLANDI, 1972).

Paramorphs of quartz are reconstructive transformation pseudomorphs after coesite (SCHREYER, 1991), cristobalite, tridymite and melanophlogite (cf. FLÖRKE, 1959). The spherulitic chalcedony of horizontal agate layers is microcrystalline paramorphic after opal-C or -CT wherein it has been nucleated at random (FLÖRKE et al., 1991). The digestion of opal by quartz must not be complete in any case. In cherts, deformed remnants or well preserved paramorphs of this kind can be frequently found.

B: The noncrystalline silica minerals

Opal-AG with its microstructural varieties **precious** and **potch opal** has a gel-like microstructure, consisting of submicroscopical SiO₂.nH₂O spheres with diameters of about half of the wavelenghtes of visible light. The interstices of the sphere packings are enriched with water (LANGER & FLÖRKE 1974). Its X-ray pattern is shown in Figure 9. In precious opal the spheres are homometric and closest packed. Cubic packing with many hexagonal faults is the rule. In potch opal the spheres are heterometric and therefore irregularly packed. The ordered sphere packings act as diffraction lattice for visible light, producing the brilliant display of monochromatic colours for which opal is famous (SANDERS, 1968). Volume parts with coherent packing in themselves but with different mutual orientations produce the arrangement of specks of colour. The irregular packing in potch opal reflects and scatters light. In remission, therefore, they occur bluish-gray and in transmission yellowish-brown. Traces of transition element impurities, especially of iron, may modify the colour by absorption.

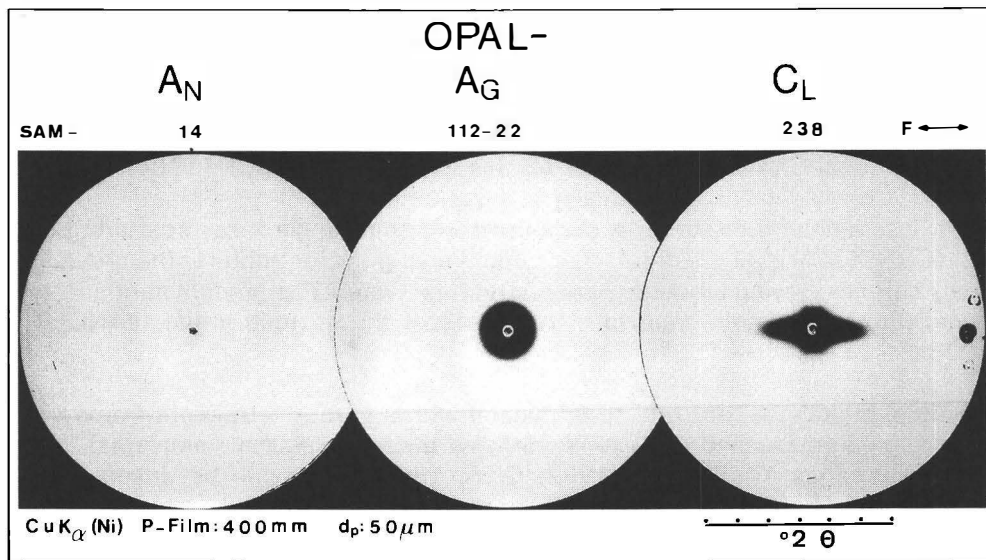


Fig. 12: Small-angle X-ray scattering of opal- C_{LF} (lussatine) at right (F = direction of fibre orientation), of potch opal-AG middle and opal-AN (hyalite) at left; $Cu K\alpha$ (Ni-filtered).

In precious opals light scattering at the boundaries and interstices of the spheres produces the milky veiling of colour display. If reflection and scattering of light are suppressed by non-wavelength-specific absorption, the opals - precious or potch - are called "black". Colloidal iron sulphides are assumed to produce this opaque absorption (cf. LEECHMAN, 1969).¹

Opal-AG forms by flocculation when colloidal hydrous silica suspensions percolate through water-permeable clays or alteration products of volcanic rocks which filter off the silica spheres from the water (JONES & SEGNET, 1969). Due to its parti-

¹ I am very grateful to Dr. Vera M. F. HAMMER, Wien, who made me aware of the language problems in the description of opal appearance. The term "iridescent" means the display of a colour spectrum which changes relatively to the position of the observers eyes. "Iridescence" additionally comprises the selective scattering of light, and that the shine or shimmer of surfaces is associated with a play of colours. "Opalescent" means iridescence associated with blue-whitish (milky) scattering of light. In all these terms, a variety of light-physiological sensations is - not very precisely - tied with physical findings. The German language knows the term "irisieren", meaning to shimmer (in German "schillern") in the colour display of the rainbow. "Opaleszenz", "opaleszent" and "opaleszieren" means to "possess or produce a shimmer like opal by scattering of light".

culate microstructure opal-AG produces isotropic small angle X-ray scattering (Fig. 12) (GRAETSCH, 1994). This is a criterion for discrimination from opal-AN.

Opal-AN (Hyalite) is a water containing silica glass with a continuous 3-dimensional network of tetrahedra. - With small deviations in the half-maximum breadth of the diffuse band at about 4 Å, the X-ray pattern of opal-AN is almost identical with that of opal AG (AN: 8.5° 2 θ Cu-K α , AG: 9°). Water is bound predominantly as silanol group water H₂O (SiOH) at nonbridging oxygen in the network. Opal-AN does not produce small angle X-ray scattering (Fig. 12).

It forms botryoidal crusts in vesicles or at fissures and clefts of volcanic rocks or little spheres in crater lakes if a fluid aqueous silica solution is quenched (FLÖRKE et al., 1974, 1985). Due to the formation process hyalites are of very high purity with respect to nonvolatile traces.

Lechâtelierite comprises the varieties **silica-fulgurite**, formed by lightning strike on quartz sands or silica rocks, and **silica-impactite** originating from silica melts produced by meteorite impact. The lack of distinct stoichiometry makes the boundary between lechâtelierites and silicate glasses fluid. It may be arbitrarily drawn at ca. 3 mol% of nonsilica components. Under this premise lechâtelierites are very rare minerals.

Acknowledgement

Ekkehart Tillmanns gave the impetus for this paper, and it had never been written without his delicate pressure.

References

- d'AMOUR, H., DENNER, W., SCHULZ, H. (1979): Structure determination of alpha-quartz up to 68 x 10⁸ Pa. - Acta Cryst., **B35**, 550 - 555..
- ARNOLD, H. (1962): Die Struktur des Hochquarzes. - Z. Krist., **117**, 467 - 469.
- BARRY, T., McNAMARA, P., MOORE, W. (1965): Paramagnetic resonance and optical properties of amethyst. - J. Chem. Phys. **42**, 2599 - 2606.
- BERNAUER, F. (1927): Über Zickzackbänderung (Runzelbänderung) und verwandte Polarisationserscheinungen an Kristallen und Kristallaggregaten. - N. J. Mineral. Geol. Paläontol., Beilage B., **55**, 92 - 143.
- BOHN, E., STÖBER, W. (1966): Coesit und Stishovit als isolierte natürliche Mineralien. - N. Jb. Mineral. Monatsh., **1966**, 86 - 96.
- CALVERT, S.E. (1983): Sedimentary geochemistry of silicon. - In: ASTON, S.R. (Ed.): Silicon geochemistry and biogeochemistry. - Academic press, London.
- CHAO, E.C.T., SHOEMAKER, E.M., MADSEN, B.M. (1960): First natural occurrence of coesite. - Science, **132**, 220 - 222.
- CHAO, E.C.T., FAHEY, J.J., LITTLER, J., MILTON, D.J. (1962): Stishovite, SiO₂, a very high pressure new mineral from Meteor Crater, Arizona. - J. Geophys. Res., **67**, 419 - 421.

- COHEN, L.H., KLEMENT, W. jr. (1967): High-low quartz inversion: determination to 35 kilobars. - *J. Geophys. Res.*, **72**, 4245 - 4251.
- CONDIE, K.C. (1970): Section 14. - In: WEDEPOHL, K.H. (Ed.): *Handbook of Geochemistry Vol. II-2*, Springer, Berlin.
- DOLINO, G., BACHHEIMER, J.-P., GERVAIS, F., WRIGHT, A.F. (1983): La transformation alpha-beta du quartz: le point sur quelques problèmes actuels: Transition ordre désordre ou displacive, compartement thermodynamique. - *Bull. Minéral.*, **106**, 267 - 285.
- DONNAY, J.D.H., LE PAGE, Y. (1978): The vicissitudes of the low-quartz crystal setting or the pitfalls of enantiomorphism. - *Acta Cryst.*, **A34**, 584 - 594.
- FLÖRKE, O.W. (1955a): Strukturanomalien bei Tridymit und Cristobalit. - *Berichte Dtsch. Keram. Ges.*, **32**, 369 - 381.
- FLÖRKE, O.W. (1955b): Zur Frage des "Hoch"-Cristobalit in Opalen, Bentoniten und Gläsern. - *Neues Jahrb. Mineral. Monatsh.*, **1955**, 217 - 223.
- FLÖRKE, O.W. (1957): Über die Röntgen-Mineralanalyse und die thermische Ausdehnung von Cristobalit und Tridymit und über die Zusammensetzung von Silikamassen. - *Berichte Dtsch. Keram. Gesellsch.*, **34**, 343 - 353.
- FLÖRKE, O.W. (1959): Die Regelungserscheinungen bei der paramorphen Umwandlung von SiO₂-Kristallen. - *Z. Krist.*, **112**, 126 - 135.
- FLÖRKE, O.W. (1967): Die Modifikationen von SiO₂. - *Fortschritte Mineral.*, **44**, 181 - 230.
- FLÖRKE, O.W., JONES, J.B., SEGNI, E.R. (1973): The genesis of hyalite. - *N. Jb. Mineral. Monatsh.*, **1973**, 82 - 89.
- FLÖRKE, O.W., JONES, J.B., SEGNI, E.R. (1975): Opal-CT crystals. - *N. Jb. Mineral. Monatsh.*, **1975**, 369 - 377.
- FLÖRKE, O.W., HOLLMANN, R., VOM RAD, U., RÖSCH, H. (1976): Intergrowth and twinning in opal-CT lepispheres. - *Contrib. Mineral. Petrol.*, **58**, 235 - 242.
- FLÖRKE, O.W., MIELKE, H.G., WEICHERT, J., KULKE, H. (1981): Quartz with rhombohedral cleavage from Madagascar. - *Amer. Mineral.*, **66**, 596 - 600.
- FLÖRKE, O.W., FLÖRKE, U., GIESE, U. (1984): Moganite, a new microcrystalline silica mineral. - *N. Jb. Mineral. Abhandl.*, **149**, 325 - 336.
- FLÖRKE, O.W., FLUX, S., SCHRÖDER, B. (1985): Hyalith vom Steinwitzhügel bei Kulmain. - *N. Jb. Mineral. Abhandl.*, **151**, 87 - 97.
- FLÖRKE, O.W., NUKUI, A. (1988): Strukturelle Pathologie von Tridymit. - *N. Jb. Mineral. Abhandl.*, **158**, 175 - 182.
- FLÖRKE, O.W., GRAETSCH, H., JONES, J.B. (1990): Hydrothermal deposition of cristobalite. - *N. Jb. Mineral. Monatshefte*, **1990**, 81 - 85.
- FLÖRKE, O.W., GRAETSCH, H., MARTIN, B., RÖLLER, K., WIRTH, R. (1991): Nomenclature of micro- and non-crystalline silica minerals, based on structure and microstructure. - *N. Jb. Mineral. Abhandl.*, **163**, 19 - 42.
- FLÖRKE, O.W., MARTIN, B. (1993): Silica modifications and products. - *Ullman's Encyclopedia Industrial Chem.*, **A23**, chap. 1, 583 - 599.
- FRONDEL, C. (1962): *The system of mineralogy vol. III Silica minerals*. - 7th ed., Wiley: New York.
- GEISINGER, K.L., SPACKMAN, M.A., GIBBS, G.V. (1987): Exploration of structure, electron density distribution and bonding in coesite with Fourier and

- pseudoatom methods using single-crystal X-ray diffraction. - J. Phys. Chem., 91, 3237 - 3244.
- GIBBS, G.V., PREWITT, C.T., BALDWIN, K.J. (1977): A study of the structural chemistry of coesite. - Z. Krist. 145, 108 - 123.
- GIES, H., GERKE, H., LIEBAU, F. (1982): Chemical composition and synthesis of melanophlogite, a clathrate compound of silica. - N. Jb. Mineral. Monatsh., 1982, 119 - 124.
- GIES, H. (1993): Porosils. - Ullman's Encyclopedia Industr. Chem., A23, chap. 8, 647 - 651.
- GIESE, U. (1983): Einfluß von Realbau, Verunreinigungen und Kristallwachstum auf einige Eigenschaften natürlicher und synthetischer Quarzkristalle. - Thesis for diploma, Univ. Bochum, Germany, 108 p.
- GRAETSCH, H. (1985): Struktur, Gefüge und Eigenschaften von Chalcedon und Opal-C in brasilianischen Achat-Geoden. - Dissertation (thesis) Univ. Bochum, Germany, 143 p.
- GRAETSCH, H. (1994): Structural characteristics of opaline and microcrystalline silica minerals. - In: HEANNEY, P.J., PREWITT, C.T., GIBBS, G.V. (Eds.): Reviews in mineralogy 29: Silica. - Mineral. Soc. Amer. Washington., 209 - 232.
- GRAETSCH, H., FLÖRKE, O.W., MIEHE, G. (1987): Structural defects in microcrystalline silica. - Phys. Chem. Minerals, 14, 249 - 257.
- GRAETSCH, H., FLÖRKE, O.W. (1991): X-ray powder diffraction patterns and phase relationship of tridymite modifications. - Z. Krist., 195, 31 - 48.
- GRAETSCH, H., TOPALOVIC, I., GIES, H. (1994a): NMR spectra of moganite and chalcedony. - Eur. J. Mineral., 6, 459 - 464.
- GRAETSCH, H., GIES, H., TOPALOVIC, I. (1994b): NMR, XRD and IR study on microcrystalline opals. - Phys. Chem. Minerals., 21, 166 - 175.
- GRASSELINI-TROYSI, M., ORLANDI, P. (1972): Sulla melanoflogite del Fortullino (Livorno). - Atti. Soc. Tosc. Sci. Nat. Mem., A79, 245 - 250.
- GRIMM, H., DORNER, B. (1975): On the mechanism of the alpha-beta phase transformation of quartz. - Phys. Chem. Solids, 36, 407 - 413.
- HEANNEY, P.J., PREWITT, C.T., GIBBS, G.V. (Eds.) (1994): Reviews in mineralogy vol., 29: Silica. - Mineral. Soc. Amer.: Washington.
- HEANNEY, P.J., POST, J.E. (1992): The widespread distribution of a novel silica polymorph in microcrystalline quartz varieties. - Science, 255, 441 - 443.
- HEMLEY, R.J., PREWITT, C.T., KINGMA, K.J. (1994): High pressure behaviour of silica. - In: HEANNEY, P.J., PREWITT, C.T., GIBBS, G.V. (Eds.): Reviews in mineralogy 29: Silica- Mineral. Soc. Amer. Washington., 41 - 81.
- HILL, R.J., GIBBS, G.V. (1979): Variation in d(T-O) and \angle TOT in silica and silicate minerals, phosphates and aluminates. - Acta Cryst., B35, 25 - 30.
- IISHI, K. (1978): Lattice dynamical study of the alpha-beta quartz phase transition. - Amer. Mineral. 63, 1190 - 1197.
- JAGODZINSKI, H. (1954): Wachstums- bzw. Umwandlungs-Polytypie bei SiC und ZnS. - N. Jb. Mineral. Monatsh., 1954, 209 - 225.
- JAGODZINSKI, H. (1964): Diffuse disorder scattering by crystals. - In: RAMACHANDRAN, G.N. (Ed.): Advanced methods of crystallography. - Academic Press: London, 181 - 219.

- JONES, J.B., SANDERS, J.V., SEGNI, E.R. (1964): Structure of opal. - *Nature*, **210**, 990 - 991.
- JONES, J.B., SEGNI, E.R. (1969): Water in sphere type opal. - *Mineral. Mag.*, **37**, 357 - 361.
- JONES, J.B., SEGNI, E.R. (1971): The nature of opal I. Nomenclature and constituent phases. - *J. Geol. Soc. Austral.*, **18**, 57 - 68.
- JUNG, L. (1992): High purity natural quartz; part I. - *Quartz Technol. Inc.*, Liberty Corner, N. Jersey.
- O'KEEFE, M., HYDE, B.G. (1978): On Si-O-Si configurations in silicates. - *Acta Cryst.*, **B34**, 27 - 32.
- KNAUTH, L.P. (1994): Petrogenesis of chert. - In: HEANNEY, P.J., PREWITT, C.T., GIBBS, G.V. (Eds.): *Reviews in mineralogy 29: Silica*. - Mineral. Soc. Amer. Washington, 233 - 258.
- LANGER, K., FLÖRKE, O.W. (1974): Near infrared absorption spectra (4.000 - 9.000 cm^{-1}) of opals and the role of "water" in these $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ minerals. - *Fortschr. Mineral.*, **52**, 17 - 51.
- McLAREN, A.C., PHAKEY, P.P. (1966): Electron microscope study of brazil twin boundaries in amethyst. - *Phys. statu solidi*, **13**, 413 - 422.
- McLAREN, A.C., PITKETHLY, D.R. (1982): The twinning microstructure and growth of amethyst quartz. - *Phys. Chem. Minerals*, **8**, 128 - 135.
- LEECHMAN, F. (1961): *The opal book*. - Ure Smith Pty. Ltd.: Sidney.
- LEHMANN, G., BAMBAUER, H.U. (1973): Quartz crystals and their colors. - *Angew. Chem. Internat. Ed.*, **12**, 288 - 291.
- LEVIEN, L., PREWITT, C.T., WEIDNER, D.J. (1980): Structure and elastic properties of quartz at pressure. - *Amer. Mineral.*, **65**, 920 - 930.
- LEVIEN, L., PREWITT, C.T. (1981): High pressure structure and compressibility of coesite. - *Amer. Mineral.*, **66**, 324 - 333.
- MARTIN, B. (1991): Kristallstruktur, Gefüge und Eigenschaften der mikrokristallinen Quarzspezies Chalcedon CH_{LF} und Quarzin CH_{LS} und der synthetischen SiO_2 -Phase Keatit K_{LS} . - Dissertation (thesis) Univ. Bochum, Germany, 114p.
- MEINECKE, J. (1993): Spezifikation und Verteilung von Wasser in gesteinsbildendem Quarz in Beziehung zu Kristallisationsbedingungen, Druck-, Temperatur- und Verformungsgeschichte. - Dissertation (thesis) Univ. Bochum, Germany, 146p.
- MIEHE, G., GRAETSCH, H. (1992): Crystal structure of moganite: a new structure type for silica. - *Europ. J. Mineral.*, **4**, 693 - 706.
- MULLIS, J. (1987): In: FREY, M. (Ed.): *Low temperature metamorphism*. - Chap. 5, Bladie: Glasgow.
- NASH, J.T., THEODORE, T. (1971): Ore fluids in the porphyry copper deposits at Copper Canyon, Nevada. - *Econ. Geol.*, **66**, 385 - 399.
- NICOLAS, A., POIRIER, J.P. (1976): *Crystalline plasticity and solid state flow in metamorphic rocks*. - J. Wiley & Sons, London.
- NUKUI, A., FLÖRKE, O.W. (1987): Three tridymite structural modifications and cristobalite, intergrown in one crystal. - *Amer. Mineral.*, **72**, 167 - 169.
- PANKRATH, R. (1988): Spurenelementeinbau in Tief-Quarz als Funktion der Wachstumsbedingungen und Umprägungen unter trockenen und hydrothermalen Bedingungen. - Dissertation (thesis) Univ. Bochum, Germany, 239p.

- PANKRATH, R., FLÖRKE, O.W. (1994): Kinetics of Al-Si exchange in low and high quartz: Calculation of Al-diffusion coefficients. - *Europ. J. Mineral.*, 6, 435 - 457.
- PALMER, D.C. (1994): Stuffed derivatives of the silica polymorphs. - In: HEANNEY, P.J., PREWITT, C.T., GIBBS, G.V. (Eds.): *Reviews in mineralogy* 29: Silica. - Mineral. Soc. Amer. Washington, 83 - 112.
- PAULING, L. (1980): The nature of silicon-oxygen bonds. - *Amer. Mineral.*, 65, 321 - 323.
- POTY, B. (1969): La croissance des cristaux de quartz dans les filons sur l'exemple du filon de la Gardette (Bourg d'Oisans) et des filons du massif du Mont-Blanc. - Thèse, Univ., Nancy, France, 161 p.
- PREISINGER, A. (1962): Struktur des Stishovits, Höchstdruck-SiO₂. - *Naturwiss.*, 49, 345.
- RIECK, G.D., STEVELS, J.M. (1951): The influence of some metal ions on the devitrification of glasses. - *J. Soc. Glass Technol.*, 35, 284 - 288.
- RÖLLER, K. (1991): Korrelation von Zwillingsbau und Kristallwachstum bei Fe-dotierten natürlichen und synthetischen Quarzkristallen. - Dissertation (thesis) Univ. Bochum, Germany, 121p.
- SANDERS, J.V. (1968): Diffraction of light by opal. - *Acta Cryst.*, A24, 427 - 434.
- SCHNADT, R., SCHNEIDER, J. (1970): The electronic structure of the trapped hole center in smoky quartz. - *Phys. Condens. Mat.*, 11, 19 - 42.
- SCHNEIDER, H., FLÖRKE, O.W. (1982): Microstructure, chemical composition and structural state of tridymite. - *N. Jb. Mineral. Abhandl.*, 145, 280 - 290.
- SCHNEIDER, H. (1986): Chemical composition of tridymite and cristobalite from volcanic and meteoritic rocks. - *N. Jb. Mineral. Mh.*, 1986, 433 - 444.
- SCHNEIDER, H., FLÖRKE, O.W. (1986): High temperature transformation of tridymite single crystals to cristobalite. - *Z. Krist.*, 175, 165 - 176.
- SCHREYER, W. (1991): Hochdruckminerale als Zeugen tiefer Versenkung von Sedimentgesteinen ins Erdinnere. - *Geographie heute*, 92, 38 - 39.
- SCHULMAN, J.H., CLAFFY, E.W., GINTHER, R.J. (1949): Some observations on the crystallization of silicic acid. - *Amer. Mineral.*, 34, 68 - 73.
- SCLAR, C.B., CARRISON, L.C., SCHWARTZ, C.M. (1962a): Optical crystallography of coesite. - *Amer. Mineral.*, 47, 1292 - 1302.
- SCLAR, C.B., YOUNG, A.P., CARRISON, L.C., SCHWARTZ, C.M. (1962b): Synthesis and optical crystallography of stishovite, a very high pressure polymorph of SiO₂. - *J. Geophys. Res.*, 67, 4049 - 4054.
- SEIFERT-KRAUS, U., SCHNEIDER, H. (1984): Cation distribution between cristobalite, tridymite and coexisting glass phase in used silica bricks. - *Ceramics internat.*, 10, 135 - 142.
- SIEBERS, F.B. (1986): Inhomogene Verteilung von Verunreinigungen in gezüchteten und natürlichen Quarzen als Funktion der Wachstumsbedingungen und ihr Einfluß auf kristallphysikalische Eigenschaften. - Dissertation (thesis), Univ. Bochum, Germany, 133p.
- SIEVER, R. (1970): Section 14. - In: WEDEPOHL, K.H. (Ed.): *Handbook of Geochemistry* vol. II-2, Springer: Berlin.
- SPACKMAN, M.A., HILL, R.J., GIBBS, G.V. (1987): Exploration of structure and bonding in stishovite with fourier and pseudoatom refinement methods using

- single crystal and powder X-ray diffraction data. - Phys. Chem. Minerals, 14, 139 - 150.
- STOECK, R. (1992): Strukturelle Mechanismen der rekonstruktiven Phasenumwandlungen von Quarz und Cristobalit, Nephelin ($\text{NaAlSi}_3\text{O}_8$) in Carnegieit und AlPO_4 -Tridymit in AlPO_4 -Cristobalit. - Dissertation (thesis) Univ. Bochum, Germany, 118p.
- WEIL, J. (1984): A review of electron spin spectroscopy and its application to the study of paramagnetic defects in crystalline quartz. - Phys. Chem. Minerals, 10, 149 - 165.