Chemistry, textures and physical properties of quartz – geological interpretation and technical application

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[Received 15 January 2009; Accepted 30 June 2009]

ABSTRACT

Quartz is one of the most abundant minerals in the Earth's crust and the most important silica mineral, occurring in large amounts in igneous, metamorphic and sedimentary rocks. The mineral is widely used as a raw material in several industrial applications. Because of its chemical composition (SiO₂) and its specific properties, quartz can be used both as a bulk product (e.g. quartz sands in the glass or foundry industry) and as a high-tech material (e.g. piezo or optical quartz).

Dependent on the specific conditions of either natural or synthetic formation, quartz can display typomorphic properties. Variations in crystal shape, specific micro-structure, trace element or isotope compositions, characteristic spectroscopic properties, etc. may be controlled by the genesis of the quartz involved. Accordingly, the defect structure of quartz is a fingerprint of its conditions of formation. A knowledge of the interrelation between quartz genesis and the specific properties developed at that time can be used both for the reconstruction of geological processes and for specific technical applications. Selected examples in the present study give an overview of how to analyse and use the specific information inherent in the mineral quartz.

Keywords: quartz, genesis, chemical composition, physical properties, technical application.

Introduction

THE various modifications of silica (SiO_2) play an important role in geological as well as industrial processes. Quartz is one of the most abundant minerals in the Earth's crust and the most important silica mineral, occurring in large amounts in igneous, metamorphic and sedimentary rocks (Table 1). Due to its highly stable nature, quartz is especially enriched in all siliciclastic sediments and rocks. For instance, sandstones have an average content of 65% quartz (Blatt *et al.*, 1980) and quartz grains may comprise \geq 99% in some mature sands (Götze, 1997).

In addition, natural quartz raw materials represent a complex group of industrial rocks and minerals with interesting chemical and

* E-mail: goetze@mineral.tu-freiberg.de DOI: 10.1180/minmag.2009.073.4.645 physical properties. Single crystals of quartz, polycrystalline material and mono-mineralic rocks are currently used in industry. The application of quartz is widespread, including use as a bulk product (e.g. high-purity quartz sands or quartzite) and perfect natural crystals, as well as a Si ore. Because of the increasing requirements concerning the quality of quartz raw materials, synthetic quartz crystals or silica materials are necessary for certain highly advanced applications (Blankenburg *et al.*, 1994).

The chemical and physical properties of quartz are determined by its actual, as opposed to its theoretical, structure. The type and frequency of lattice defects are influenced by the thermodynamic conditions during mineralization. In addition, subsequent processes such as changes in P-Tconditions during hydrothermal or metamorphic processes, as well as natural irradiation or alteration, can change the original structure of quartz. Dependent on these specific conditions of formation, quartz can therefore be characterized

Rock type	Quartz content $(10^{18} t)$	Relative proportion (%)
Magmatic rocks	8.05	93.6
Metamorphic rocks	0.28	3.2
Sedimentary rocks	0.28	3.2
Lithosphere	8.60	100

TABLE 1. Abundance of quartz in the lithosphere (Rösler, 1981).

by a typical crystal shape or certain growth phenomena, a specific structure, a varying chemical composition and/or characteristic physical properties. Accordingly, the real structure is a fingerprint of the genetic conditions. The knowledge of the interrelation between quartz genesis and specific properties can be used both for the reconstruction of geological processes and for specific technical applications.

Although quartz research has a long history, the questions concerning its chemical and physical properties are far from being answered completely. Modern analytical methods, especially those allowing analysis with low detection limits or spatially resolved analyses (e.g. trace elements, O isotopes, paramagnetic defects, cathodoluminescence), have generated much new mineralogical and geochemical data concerning the origin of quartz. Thus, complex investigations by a combination of different methods have the greatest potential for successful interpretation. Certain results illustrate that even the structure and composition of single quartz crystals can be very heterogeneous and yet bring a wealth of genetic information.

The SiO₂ system and the structure of quartz

Silica (SiO₂), in at least 14 modifications, makes up 12.6 wt.% of the Earth's crust as crystalline and amorphous silica (Table 2). In addition, the dense orthorhombic silica polymorph 'seifertite' was first described by Sharp *et al.* (1999) in SNC meteorites (shergottites). In respect of its occurrence in nature and the amount of technical material used, quartz is the most important silica

TABLE 2. The	e SiO ₂ syster	n (modified after	Strunz and Tenny	yson, 1982).
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Ouartz-tridymite-cristobalite group	(atmospheric and low pressure)
Quartz	trigonal
High-quartz	hexagonal
Tridymite	monoclinic
High-tridymite	hexagonal
Cristobalite	tetragonal
High-cristobalite	cubic
Melanophlogite	cubic
Fibrous SiO ₂ (syn.)	orthorhombic
Moganite	monoclinic
Keatite-coesite-stishovite group (hi	gh and ultrahigh pressure)
Keatite (syn.)	tetragonal
Coesite	monoclinic
Stishovite	tetragonal
Seifertite	orthorhombic
Lechatelierite-opal group (amorpho	ous phases)
Lechatelierite	natural silica glass
Opal	water bearing, solid SiO ₂ gel

modification. At 573°C, trigonal α -quartz transforms reversibly into the hexagonal high-temperature quartz. The lattice parameters for low- and high-temperature quartz are those following (Strunz and Tennyson, 1982):

Low quartz: trigonal-trapezohedral. a = 4.91 Å, c = 5.41 Å (Fig. 1), Si–O spacing 1.61 Å, O–O spacing 2.65 Å, Si–Si spacing 3.04 Å, Si–O–Si angle 144°; lattice energy 12967 to 15043 kJ mol⁻¹, Mohs hardness 7, specific gravity 2.65 g cm⁻³;

High quartz: hexagonal-trapezohedral. a = 5.00 Å, c = 5.46 Å (Fig. 1), Si–O spacing 1.60 Å, O–O spacing 2.65 Å, Si–Si spacing 3.03 Å, Si–O–Si angle 153°; lattice energy 13596 kJ mol⁻¹, Mohs hardness 7, specific gravity 2.51 g cm⁻³.

The crystal structure of α -quartz is composed exclusively of $[SiO_4]^{4-}$ tetrahedra with all Os joined together in a three-dimensional network. Thus, the formula is SiO₂ and the atoms are arranged in a trigonal symmetry. The *c* axis is identical with the optical axis; perpendicular to it there is the circular section of optical isotropy. As to its morphology, the so-called right-handed and left-handed quartz crystals are distinguishable by the position of the trapezohedron face x to the positive main rhombohedron r (Fig. 1*c*). In addition, twinning of quartz is common, and the development of certain growth phenomena such as quartz with macro-mosaic and lamellar structure (Friedlaender and Bambauer quartz respectively), faden or sceptre-like growth, skeletal or doubly terminated crystals can be observed in natural quartz. (Rykart, 1989; Blankenburg *et al.*, 1994).

Quartz crystals with the ideal structure are practically non-existent. Therefore, the properties of quartz are determined by its actual structure. The type and frequency of lattice defects are influenced by the thermodynamic conditions during mineralization. In addition, subsequent processes such as changes of *P*-*T* conditions during metamorphism or natural irradiation can change the original structure of quartz. The lattice defects can be classified according to their structure and size as follows: point defects (zero-dimensional, <10-30 Å); dislocations



FIG. 1. Schematic structure of quartz: (*a*) elementary cell of low-quartz; (*b*) structure and typical morphology of lowquartz (left) and high-quartz (right); (*c*) chains of tetrahedra and typical morphology of left-handed (left) and righthanded quartz (right).

(linear defects); subgrain or twin boundaries (twodimensional); and three-dimensional defects due to microinclusions of minerals and fluids.

Point defects in quartz

Point defects in quartz can be related to the incorporation of foreign ions (e.g. Al, Ti, Ge, Fe, H, Ag, Cu, P) in lattice and interstitial positions, to different types of displaced atoms, and/or to defects associated with Si or O vacancies. According to their characteristics, these defect centres are often classified as either intrinsic or extrinsic. Intrinsic point defects involve atoms of the host lattice only (missing atoms = vacancies, atoms at interstitial positions, and excess atoms), whereas extrinsic point defects belong to foreign atoms in lattice and inter-lattice positions. Furthermore, the defects can be divided, according to their electronic structure, into two classes - diamagnetic and paramagnetic. The presence and structure of such defect centres can be analysed by means of electron paramagnetic resonance (EPR) in combination with traceelement analysis and a variety of spectroscopic methods (e.g. luminescence, UV-Vis-IR absorption). Up to the present, >20 different types of point defects in quartz have been detected (e.g. Kostov and Bershov, 1987; Weil 1984, 1993; Stevens-Kalceff et al., 2000). The most common defect types in quartz are shown schematically in Fig. 2.

Table 3 illustrates that the number of ions substituting for Si is small. This is due to the

small ionic radius of Si⁴⁺ and its high valence. The most common trace-element-related paramagnetic centre in quartz is the $[AIO_4]^0$ centre which is caused by substitution of Si⁴⁺ by Al³⁺ with an electron hole at one of the four nearest O^{2-} ions (Griffiths *et al.*, 1954). The precursor state for this centre is the diamagnetic $[AIO_4/M^+]^0$ centre with an adjacent charge compensating cation ($M^+ = H^+$, Li⁺, Na⁺) in an interstitial position. The $[AIO_4/M^+]^0$ centre can be converted by X-rays or γ -irradiation into the optically active $[AIO_4]^0$ centre, resulting in the formation of smoky quartz (O'Brien, 1955; Cohen, 1956).

Other common trace-element centres in quartz are associated with the incorporation of Ti, Ge and Fe (Weil, 1984, 1993). Additionally, a hydrogenic trapped hole-centre with four H atoms at a Si site was reported by Nuttall and Weil (1981). Centres of the type $[TiO_4/Li^+]^0$ are produced by irradiation of the diamagnetic precursor $[TiO_4]^0$ $(Ti^{3+}$, i.e. electron centre at Ti^{4+}). This precursor is formed by substitution of Ti^{4+'} for Si⁴⁺ at the Si position, where charge compensation is achieved by a Li⁺ ion at a channel position nearby (Wright et al., 1963; Rinneberg and Weil, 1972). The Ge centre is of the same type as the Al centre. Substitution of Si⁴⁺ by Ge⁴⁺ causes formation of the diamagnetic precursor [GeO₄]⁰, which transforms into the paramagnetic $[GeO_4]^-$ during γ -irradiation. At room temperature, these centres can bind diffusing M^+ cations, preferentially forming $[GeO_4/Li^+]^0$ and $[GeO_4/H^+]^0$ (Mackey, 1963; Rakov et al., 1985; Weil, 1993). Some Fe³⁺



FIG. 2. Schematic quartz structure showing the most common defect types.

		Foreign ion centres Si ⁴⁺ Interstitial		Vacancies Oxygen Silicon	
		substitution		vacancy	vacancy
Metastable	electron centres (+e ⁻)	$[TiO_4]^-$ $[TiO_4/M^+]^0$ $[GeO_4]^-$ $[GeO_4/M^+]^0$	$M^+ = H^+, Li^+$ $M^+ = H^+, Li^+$	E' centres: [SiO ₃] ³⁻	
	defect electron centres $(-e^{-})$	$ \begin{bmatrix} AlO_4 \end{bmatrix}^0 \\ \begin{bmatrix} FeO_4 \end{bmatrix}^0 $			O^{-} centres: $O^{-}, O_{2}^{3-},$ $O_{2}^{3-} - M^{+}$
Stable (paramagnetic without charge receive)		$[FeO_4/M^+]^0$ $[FeO_4]^- ?$ $(precursor for [FeO_4]^0)$	$M^+ = H^+, Li^+$ Fe ³⁺		

TABLE 3. Most common paramagnetic defects in quartz (modified after Plötze, 1995).

paramagnetic centres may occur in quartz. One of these defects is characterized by the substitution of Fe³⁺ for Si⁴⁺ with charge compensation by alkali ions or protons – so-called *S* centres [FeO₄/ M^+]⁰ (Stegger and Lehmann, 1989; Mineeva *et al.*, 1991).

Other types of defects can be attributed to O and Si vacancies (Table 3). The group of O-deficient centres (ODC) comprises the neutral O vacancy (\equiv Si-Si \equiv) and the E' centres (Nishikawa et al., 1994). The ODC is diamagnetic and can be detected by luminescence spectroscopy. The paramagnetic E'_1 centre is formed by an O^{2-} vacancy resulting in the transformation of an O tetrahedron into a planar arrangement of three O ions (Weeks, 1956). In consequence, the centre comprises an unpaired electron in a dangling sp³ orbital of a single Si atom bound to these three O atoms. The centre can exist in three different stages E_{1}^{0} , E_{1}^{\prime} and $E_{1}^{\prime\prime}$ (Griscom, 1985), corresponding to its thermal stability and to the reactivity with respect to irradiation.

Oxygen⁻ centres represent different types of defect electrons on O in tetrahedra with Si vacancies. The non-bridging oxygen hole centre (NBOHC: \equiv Si-O·) represents the simplest elementary O-related intrinsic defect in quartz. This centre can be described as the O part of a broken bond (Griscom, 1985). Precursors of the NBOHC can be strained regular Si-O bonds as well as peroxy linkages, silanol groups or Sialkali bonds (Stevens-Kalceff *et al.*, 2000).

Oxygen excess centres in quartz include the

peroxy linkage (\equiv Si-O-O-Si \equiv) and the peroxy radical (\equiv Si-O-O) (Friebele *et al.*, 1979; Baker and Robinson, 1983). Furthermore, H excess from the H₂O crystallization medium can result in the formation of OH⁻ centres in quartz (silanol groups). This defect consists of a proton bound on a regular lattice O of the SiO₄ tetrahedron (Weil, 1984). The resulting negative net charge may be compensated by an additional silanol group or a trivalent substitute in Si⁴⁺ position (e.g. Al³⁺).

Up to the present, several attempts have been made to relate specific paramagnetic defects to certain genetic conditions of quartz formation. One of the first attempts was made by Dennen et al. (1970), who proposed a geothermometer based on the incorporation of Al into quartz as a function of temperature of formation. Based on this thermometer, Agel and Petrov (1990) used the concentration of $[AlO_4]^0$ defects to calculate the crystallization temperature of guartz grains from deep-drilling samples. On the other hand, primary defect centres may be thermally healed by geological processes. Bershov et al. (1975) reported a decreasing number of $[AlO_4]^0$ defects in samples of the Eldjzhurtinski granite with increasing depth and temperature. At a depth of 1850 m ($T=112^{\circ}$ C), these types of defect centres disappeared totally (Fig. 3). The authors concluded that [AlO₄]⁰ and [TiO₄]⁻ centres may be used as indicators of temperature during burial.

The frequency of specific defect centres seems also to show a genetic dependence. High

concentrations of $[\text{TiO}_4/\text{H}^+]^0$ centres were detected in metamorphic quartz, whereas $[\text{TiO}_4/\text{Li}^+]^0$ centres are typical for quartz in igneous rocks (Rakov and Milovidova, 1991; Agel, 1992; Plötze, 1995). Quartz from pegmatites is, in general, characterized by small concentrations of pure lattice defects and only shows elevated contents of trace-element-related point defects (Götze *et al.*, 2004). In addition, investigations of paramagnetic centres in agates and related quartz by Götze *et al.* (1999) revealed that the frequency of E' and O₂³⁻ centres varies between agates from acidic and basic volcanic host rocks (Fig. 4).

Furthermore, different centre types may be indicative of certain ore deposits or certain quartzbearing igneous rocks and, thus, of provenance (e.g. Plötze, 1995; Götze and Plötze, 1997; Götze and Zimmerle, 2000; Götze *et al.*, 2004). The concentration of $[AIO_4]^0$ defects in quartz, for instance, correlates with the Au and Ag content in quartz-bearing rocks, making it applicable to prospecting for noble-metal deposits (Matyash *et al.*, 1987). Botis *et al.* (2006) and Pan *et al.* (2006) showed that the distribution of radiation-induced centres in quartz provides information about the timing and source of U mineralization and also traces paleo-pathways of U-bearing fluids.

The presence of defects in the quartz lattice can change its structural, electrical and optical properties strongly. Many factors, such as type



of raw materials, manufacturing processes, irradiation, mechanical stress, temperature, and the presence of impurities, influence the type and number of defects. Furthermore, new defects may be formed and existing defects transformed into other defect types. Therefore, the analysis of point defects is essential for the use of quartz and silica materials in several highly-advanced technical applications. For instance, different kinds of defects lead to electrical instabilities in SiO₂ insulator layers and lower the quality of optical materials due to loss by dispersion and absorption effects. Poor quality in Piezo quartz can arise from absorption effects and from elevated concentrations of OH-centres which may originate from the aqueous crystallization medium. Furthermore, incorporation of Al during crystal growth can limit significantly the application of optical quartz because of possible colouring during natural or artificial radiation (formation

Characterization of point defects in quartz using cathodoluminescence (CL)

of smoky quartz).

The great interest concerning luminescence studies of quartz is based on the fact that information, not available from other analytical methods, can be obtained. The close relationship



FIG. 3. Concentration of $[AIO_4]^0$ and $[TiO_4]^-$ centres in quartz from the Eldjzhurtinski granite *vs.* depth and temperature (modified after Bershov *et al.*, 1975).

FIG. 4. Frequency of paramagnetic defects related to O and Si vacancies (E' and O_2^{3-} centres respectively) in agates and related quartz incrustations from different volcanic rock types (modified after Götze *et al.*, 1999).

between crystal-chemical properties and luminescence characteristics is the basis upon which to visualize the defect structure of quartz and to reveal different growth generations, internal structures or distribution of trace elements within quartz (Fig. 5). On the other hand, CL is an effective method for spatially resolved analysis of point defects in quartz by



FIG. 5. Polarized microscopy (*a*) and CL (*b*) micrograph pair of a quartz phenocryst in a rhyolite from Euba (Saxony, Germany); the CL image reveals internal growth structures invisible with polarizing microscopy; the related CL emission bands of different zones (*c*) illustrate that the visible CL colour depends on the intensity ratios of the two main emission bands at 450 and 650 nm.

spectral measurements. In combination with electron spin resonance spectroscopy and spatially resolved trace-element analysis, the different emission bands can be related to specific lattice defects in the quartz structure (e.g. Stevens-Kalceff *et al.*, 2000; Götze *et al.*, 2001*a*). The defects causing the different CL emissions in quartz often reflect the specific physico-chemical conditions of crystal growth and can, therefore, be used as a signature of genetic conditions of mineral formation.

The typical CL of igneous and metamorphic quartz consists of two emission bands with maxima at 450 and 650 nm (Fig 5c), which are, in general, the most common emission bands in natural quartz (Götze et al., 2001a; Götze, 2009a). The different visible luminescence colours in quartz depend on the relative intensities of these two dominant emission bands. Most igneous quartz grains show luminescence colours in different shades of blue caused by the predominance of the 450 nm emission. This 450 nm emission is due to the recombination of the socalled self-trapped exciton (Stevens-Kalceff and Phillips, 1995), an electron hole pair on an O vacancy and a peroxy linkage. Recent results have shown that the intensity of this emission is especially high in O-deficient SiO₂ samples (Skuja, 1998). In volcanic and metamorphic quartz, the intensity of the 650 nm emission band is often higher than in granitic quartz. resulting in a visible reddish-brown CL. The 650 nm emission is attributed to the recombination of electrons in the non-bridging O band-gap state, with holes in the valence-band edge (Siegel and Marrone, 1981). A number of different precursors of this NBOHC have been proposed, such as H- or Na-impurities, peroxy linkages (O-rich samples), or strained Si-O bonds (Stevens-Kalceff and Phillips, 1995). The development of typical reddish grain rims in volcanic quartz results from the reaction of early crystallized quartz crystals with the melt (Fig. 5b). This process leads to the generation of defects (bond breaking) in the reaction zone and thus to an increased 650 nm emission band. In metamorphic quartz, mechanical deformation may result in bond breaking and thus, in the formation of the NBOHC

The defect structure and luminescence behaviour of pegmatitic quartz differs from those of quartz from other origins (hydrothermal, igneous and metamorphic quartz). Electron paramagnetic resonance measurements revealed an almost

complete lack of intrinsic lattice defects associated with O or Si vacancies (e.g. the E' centre or O_2^{3-} centre), whereas some trace elements (Al, Ti, Ge, Li) may be enriched and form paramagnetic centres (Götze et al., 2004). Accordingly, the luminescence spectra are dominated by a strong 500 nm emission, which can be related to the alkali-compensated trace-element centres in the quartz structure (Ramseyer and Mullis, 1990; Götze et al., 2005). After electron bombardment, the intensity of the blue luminescence emission falls off rapidly within 30 to 60 seconds (Fig. 6). This can be related to ionizationenhanced diffusion of luminescence centres as was shown by Ramseyer and Mullis (1990) by electrodiffusion experiments. Other CL emission bands, which are characteristic features of igneous, metamorphic or hydrothermal quartz (e.g. those at 450 nm, 580 nm and 650 nm) are



FIG. 6. CL image and related CL emission spectra of quartz from pegmatite (Frikstad, Norway); the intensity of the CL emission strongly decreases under electron irradiation (see inset) due to the interaction of the luminescence centres with the electron beam.

almost completely lacking, indicating that the defects responsible for these CL emissions are absent in pegmatitic quartz.

Hydrothermal quartz crystals may show a variety of luminescence colours, sometimes arranged in distinct zoning. Several studies showed that the CL characteristics of hydro-thermal quartz may also depend on the crystal-lization temperature (Ioannou *et al.*, 2003; Rusk *et al.*, 2008; Jourdan, 2008). At high temperatures (>400°C), a homogeneous blue luminescence predominates, whereas at lower temperatures (<300°C), strong zoning is common and yellow CL can be observed.

The transient blue CL emission at 390 nm is a common feature of α -quartz crystallized from aqueous solutions and was observed both in natural and synthetic hydrothermal quartz specimens (Fig. 7). Therefore, both primary hydrothermal mineralization and secondary hydrothermal processes may be revealed by this characteristic CL emission. The 390 nm emission correlates well with the Al content and the concentration of paramagnetic $[AlO_4/M^+]$ centres in quartz (Alonso et al., 1983; Luff and Townsend, 1990; Perny et al., 1992; Gorton et al., 1996). Therefore, the alkali- (or H-) compensated $[AlO_4/M^+]$ centre has been suggested as being responsible for this deep blue emission band. The transient emission is very sensitive to irradiation damage, with a rapid attenuation of the emission intensity under an electron beam, which results from the dissociation and electromigration of the charge-compensating cations out of the interaction volume under the influence of the irradiationinduced electrical field. The typical decrease of the blue CL emission band under the electron beam is often accompanied by an increase of the 650 nm emission caused by the conversion of precursors (e.g. Si-OH silanol groups from the mineralizing fluid) into the non-bridging O centres due to electron irradiation. This is visible by a change in CL colour from an initial blue to brownish (Fig. 7).

The other typical luminescence band in hydrothermal quartz is the yellow emission at 580 nm. Götze *et al.* (1999, 2001*a*) detected the yellow CL emission predominantly in agates of acidic volcanics and hydrothermal quartz (Fig. 7). Since those quartz samples also have a very high content of lattice defects (especially large concentration of O vacancies, i.e. E'_1 centres), these defects may be responsible for the yellow CL emission band at 580 nm. The close



FIG. 7. CL images and related emission spectra of different kinds of hydrothermal quartz: (*a*) quartz crystal with initial CL; (*b*) CL after 60 seconds of electron irradiation showing the change from blue to brownish; (*c*) displays the opposite behaviour of the ~400 nm and 650 nm emission bands; (*d*) sector zoned hydrothermal quartz crystal; (*e*) agate; (*f*) yellow CL caused by an emission band around 580 nm.

relationship between this emission and large concentrations of defect centres lead to the conclusion that this luminescence can be related to processes of fast crystallization. For instance, the common occurrence of the 580 nm emission band in cryptocrystalline quartz can possibly be related to rapid growth from a non-crystalline precursor.



FIG. 8. CL images of natural and artificial radiation damage in quartz: (*a*) yellow-orange luminescent radiation halo around a zircon inclusion in a quartz from granite; (*b*) related spectra of the host quartz and the damaged area with increasing 650 nm emission; (*c*) radiation rim in quartz due to artificial α -particle bombardment (modified from Krickl *et al.*, 2008).

A high state of lattice damage can be attained in radiation-damaged quartz (Habermann *et al.*, 1997; Krickl *et al.*, 2008; Fig. 8). Such lattice damage causes halos around U- and Th-bearing accessory minerals (e.g. zircon), which are not detectable by conventional polarizing microscopy (Owen, 1988; Meunier *et al.*, 1990; Ramseyer *et al.*, 1988; Götze *et al.*, 2001*a*). As well as recent and previous migration tracks of U-bearing fluids, pores also can be identified by their radiation rims in quartz from sandstones and crystalline rocks. These rims are due to α particles, which create lattice damage when penetrating the quartz. The radiation haloes are characterized by a strong increase in the 650 nm CL emission band (Fig. 8). The creation of NBOHC defects is caused by bond breaking due to the α -particles, which was confirmed by the radiation experiments of Komuro *et al.* (2002) and Krickl *et al.* (2008). Botis *et al.* (2005) reported pronounced CL emission bands in the UV at \sim 350 nm and in the red region (620-650 nm) in natural radiation-damaged quartz.

The presented examples show that luminescence methods are useful in the detection and interpretation of point defects in quartz. Specific luminescence emission bands can be related to different defect centres. The relation between specific quartz crystallization or alteration processes and the formation of characteristic defects allows the recognition and reconstruction of different processes of mineral formation and alteration.

Applications of the characteristic luminescence properties of quartz are numerous. One of the first applications was the evaluation of the provenance of detrital quartz grains in sands and sandstones (Sippel, 1968; Zinkernagel, 1978; Richter et al., 2003). Assuming that quartz from different parent rocks shows different CL signatures (colours), sediments with varying provenance can be distinguished. However, Boggs et al. (2002) have shown that the application of CL colours is sometimes problematic because quartz of different genesis might have similar CL colours. To avoid misinterpretations on the basis of initial or final CL colours, Götte and Richter (2006) additionally used the shift of the CL colour during electron irradiation as an indicator of provenance.

Processes of compaction, brittle deformation, quartz cementation, and porosity evolution in the diagenetic history of reservoir sandstones can also be evaluated using CL (e.g. Houseknecht, 1991; Millikan and Laubach, 2000). This information has also been used to characterize and distinguish different kinds of recent and ancient building sandstones (e.g. Michalski *et al.*, 2002; Götze and Siedel, 2004; Götze *et al.*, 2007).

Cathodoluminescence is an outstanding method which can be used to reveal multiple processes of crystallization or secondary overprint, often not possible by other analytical methods. Several studies have shown, for instance, that the permineralization process of wood is often a multiple and complex process (e.g. Götze and Rößler, 2000; Witke *et al.*, 2004; Matysová *et al.*, 2008; Götze *et al.*, 2008). Figure 9*a* shows an example from Chemnitz (Germany) of silicified wood remains displaying silicification events: a primary silicification (yellow CL) and a secondary hydrothermal overprint (transient blue CL). The recognition of these two events was not possible using conventional microscopy. Müller *et al.* (2000, 2002, 2003*a*) used quartz CL in combination with trace elements to reconstruct the geological evolution of granitic systems. Similar investigations were carried out by Van den Kerkhof *et al.* (2004) to reveal details of quartz recovery in a granulite from the Bamble sector, Norway. Furthermore, effects of shock damage in quartz due to impact events have been revealed by CL in terrestrial and extraterrestrial samples (e.g. Sippel, 1971; Ramseyer *et al.*, 1992; Götze, 2009*a*). The quartz crystals show features of micro-brecciation and shifts of the luminescence emission bands under the influence of high pressure.

Cathodoluminescence studies can also help in the recognition and reconstruction of



FIG. 9. Detection of multiple processes and secondary overprint, respectively using CL; (a) silicified wood from Chemnitz (Germany) showing parts of primary silicification (yellow CL) penetrated by secondary hydrothermal fluids (blue CL); (b) quartz grains from the Witwatersrand conglomerate, RSA, showing radiation rims due to migrating U-bearing fluids..

mineralization processes in ore deposits (e.g. Rusk *et al.*, 2006; 2008). Graupner *et al.* (2000, 2001) used the CL signatures of quartz from barren metamorphic host rocks and Au-bearing parts of the giant Au deposit of Muruntau to obtain information about the origin of the mineralizing fluids and the formation process of the deposit. In the exploration of U deposits, the creation of radiation damage in quartz by radioactive fluids can help to reveal U migration pathways. Figure 9*b* presents a CL image with an example from the Au-U deposit of Witwatersrand, RSA.

Dislocations and internal structures in quartz

Dislocations in quartz are the most important line (one-dimensional) defects. The main types are edge and screw dislocations (Fig. 10). They often originate from the condensation of point defects during crystal growth or by mechanical and thermal influence. Therefore, the type and number of dislocations is closely connected to the specific growth conditions. On the other hand, dislocations may result from mechanical triggering and/or rapid cooling after the growth process.

Especially during metamorphic processes, deformation of a crystal can result in the movement of lattice defects. These moving vacancies or dislocations can cause relative displacements of crystal parts (intracrystalline deformation – Passchier and Trouw, 1998). The increasing number of induced dislocations results in an increasing 'internal strain energy' of the crystal. Therefore, ordering and disordering processes compete during deformation. Following deformation, ordering mechanisms prevail to lower the free energy and to shorten the length of dislocations in the crystal lattice this is termed recovery. Processes of recovery result, for example, in the formation of subgrain boundaries (Fig. 11b; Passchier and Trouw, 1998). Cathodoluminescence can be used to display the microtextures of quartz grains due to the dependence of the CL intensity on the number of local defects in the lattice. Figure 11c.d illustrates that the migration and concentration of point defects and dislocations can result in the accumulation of defects along grain and subgrain boundaries. These areas show high CL intensities.

Dependent on the specific conditions of crystallization and deformation, guartz may exhibit a great variety of internal structures, which can be revealed by polarizing microscopy or CL. Crystallization from magma or solution mostly results in homogeneous, non-undulatory quartz. However, growth zoning and sector zoning are sometimes detectable using CL (compare Figs 5 and 7). Increasing pressure and temperature during deformation will initially create quartz with undulose extinction, followed by deformation breaks between domains of undulatory extinction, formation of a polycrystalline aggregate with elongated crystal fabric follows, and finally a mosaic of polyhedral or polygonized quartz develops (Fig. 11). Accordingly, quartz deformation is a continuum, with a systematic series of processes - deformation, recovery,



FIG. 10. Scheme of the most important line (one-dimensional) defects in quartz – edge (left) and screw dislocations (right).

primary recrystallization, and secondary recrystallization (Passchier and Trouw, 1998). Deformation is reflected optically by undulatory extinction, deformation lamellae and bands, elongated crystal units, and sutured crystalcrystal boundaries (Fig. 11). Recovery is recognized optically by segmented extinction (semicomposite extinction) reflecting polygonization of the crystal. Primary recrystallization occurs when strain-free areas surrounded by dislocation tangles form new crystals, and is recognized optically by the presence of small $(50 \ \mu m)$, non-undulatory crystals. Secondary recrystallization develops large, non-undulatory strain-free polyhedral crystals with smooth crystal-crystal boundaries. The knowledge surrounding the development of internal structures in quartz can be used to

reconstruct metamorphic processes or to recognize the origin of detrital quartz grains in sedimentary rocks (e.g. Folk, 1968; Voll, 1968; Basu *et al.*, 1975; Young, 1976; Basu, 1985; Passchier and Trouw, 1998).

In technical applications, line defects are often visualized in two different ways: treatment with etching techniques and X-ray topography (Fig. 12). During etching, the projection points and lines caused by dislocations are attacked first due to their higher potential. The number of etch pits correlates with the number of line defects. Such natural etching features can also be used as diagnostic features for the specific environments of natural quartz grains, especially in sedimentary petrology (e.g. Krinsley and Doornkamp, 1973; Le Ribault, 1977).



FIG. 11. Internal structures of quartz crystals reflecting different stages of metamorphic deformation and recovery:
(a) elongated quartz grains from a gneiss showing undulose extinction and sutured grain boundaries;
(b) redistribution of dislocations in a scheme of recovery with development of undulose extinction, deformation bands and subgain boundaries (modified after Passchier and Trouw, 1998);
(c,d) polarized light and CL images respectively, of quartz from a metamorphic host rock – the grain and subgrain boundaries are clearly visible in CL due to the accumulation of defects and the resulting high CL intensity.



FIG. 12. Hydrothermally etched (0001) plane of a synthetic quartz crystal (left) and X-ray topography of a synthetic quartz crystal (right) showing an almost perfect core (crystal seed) and numerous line defects in the outer part of the crystal (modified after Blankenburg *et al.*, 1994).

The quality of synthetic quartz crystals is often checked by X-ray topography. This is a nondestructive technique and is sensitive to minute distortions and changes in lattice constants; consequently, the method is used to study dislocations in almost perfect quartz crystals (Blankenburg *et al.*, 1994). The example in Fig. 12 shows a synthetic crystal with a nearly defect-free core (seed crystal) and high defect density in the outer part (probably due to inappropriate growth conditions).

Mineral and fluid inclusions in quartz (threedimensional defects)

During quartz growth, three-dimensional defects of mineralizing fluids or paragenetic minerals (or exsolutions) can be included in quartz crystals. The shape and nature of inclusions in quartz were first described by Sorby (1858), and since that time have been used in genetic studies by many authors. Numerous textbooks and publications deal with mineral and fluid inclusions in guartz (e.g. Ermakov, 1950; Roedder, 1984; Sheperd et al., 1985; Leeder et al., 1987; Van den Kerkhof and Hein, 2001). Inclusions provide information about paragenetic minerals, temperature of formation, chemistry of mineralizing fluids, etc. This information can be used for the reconstruction of mineral-forming processes and provides important data about impurities in raw materials. The major point of interest is based on the observation

that quartz develops specific inclusion features depending on crystallization conditions.

Mineral species included in igneous quartz are mainly feldspar, mica, rutile, zircon, Fe oxides, pyrite, cassiterite, wolframite, Nb-Ta minerals, etc. as well as silicic glass inclusions (Roedder, 1984; Leeder *et al.*, 1987). Typical mineral inclusions in rhyolitic quartz are zircon, rutile, magnetite, ilmenite, hypersthene, aegirine, amphibole, biotite, tourmaline, apatite and fluorite (Thomas and Blankenburg, 1986; Mainley, 1996). Remarkable is the presence of OH-, Fand P-bearing minerals as well as volcanic glass, which are interpreted as representing products of an early crystallization (Clocchiatti, 1975; Hanson *et al.*, 1996).

The spectrum of mineral inclusions in metamorphic quartz depends on the conditions of metamorphism. Whereas mineral inclusions of chlorite, muscovite or amphibole are more characteristic of low-grade metamorphic rocks, kyanite, staurolite or garnet occur especially in high-grade metamorphic rocks. In contrast, glassy inclusions are rare in quartz of metamorphic origin (Wünsch, 1987; Heynke, 1990; Gerler, 1990). Inclusions of anhydrite, gypsum, polyhalite, calcite, several salt minerals, organic matter, etc. have been described in sedimentaryauthigenic quartz. The occurrence of these inclusions clearly documents the sedimentary environment of quartz growth (Richter, 1971; Fruth and Blankenburg, 1992; Götze, 2009b).

Mineral inclusions often form paragenetically with quartz, and are fingerprints of the crystallization environment. On the other hand, the type and number of mineral inclusions influences significantly the trace-element composition of quartz. Furthermore, even traces of refractory minerals (e.g. zircon, aluminosilicates) have to be considered if quartz raw materials are to be used in melting processes (e.g. the glass industry).

The type, frequency, and composition of gas and fluid inclusions, as well as fluid-inclusion thermometry, are important parameters used to reveal the genetic history of quartz. Classical studies of gas and fluid inclusions in quartz are numerous (e.g. Ermakov, 1950; Roedder, 1984 and references therein; Sheperd *et al.*, 1985; Leeder *et al.*, 1987; London, 1985; Walderhaug, 1994; Van den Kerkhof and Hein, 2001) so that quartz of different origins may be distinguished using the distribution and physiography of inclusions, temperature of homogenization, and chemical composition of fluid inclusions. Using the distribution characteristics of the inclusions in the host mineral, it is often possible to distinguish between gas-liquid inclusions of primary, pseudosecondary and secondary origin. Primary and pseudo-secondary inclusions both formed during primary mineral growth, however, the latter occur on (mostly short) healed microfractures. In contrast, secondary inclusions clearly formed after quartz formation and occur on trails crosscutting all older microstructures.

A careful thermometric and cryometric analysis of primary gas-fluid inclusions can provide minimum temperatures and minimum pressures of formation of the quartz, whereas microthermometric measurements on secondary inclusions yield information concerning conditions of secondary alteration of the host mineral. Additionally, results of modern analytical methods such as microchemical analysis, capillary electrophoresis, infrared spectroscopy, Raman spectroscopy, isotope measurements, INAA or LA-ICP-MS provide data concerning the chemical composition of fluid inclusions, which can be used to distinguish inclusion characteristics of various formation environments (e.g. Klemm, 1986; Gerler and Schnier, 1989; Götzinger, 1990; Ghazi et al., 1993; Hanson et al., 1996; Hallbauer, 1997; Channer et al., 1999; Flem et al., 2002; Müller et al., 2003b; Götze et al., 2004).

Elevated contents of fluid inclusions in quartz can also influence the chemical composition and quality of quartz raw materials. Additionally, the type and number of fluid inclusions may influence the melting behaviour of quartz. Figure 13 illustrates the thermal behaviour of different quartz types during the production of pure silica



FIG. 13. The dependence of the quartz-cristobalite phase transition at 1400°C on the number of fluid inclusions (FI) in used quartz raw materials (modified after Gemeinert *et al.*, 1992).

glass. The conversion of quartz to cristobalite at 1400°C depends strongly on the number of fluid inclusions in the raw material (Gemeinert *et al.*, 1992). Large numbers of fluid inclusions appear to enhance the conversion of quartz to cristobalite during thermal treatment. This may be due to decrepitation effects and the alkali elements (flux) within the inclusions. In contrast, the quartz type and inclusions therein have almost no influence on the melting behaviour of raw materials for silicate glasses, where the granulometric properties appear to be more important (Götze *et al.*, 1993).

Trace elements

Quartz is one of the purest minerals in the Earth crust. Nevertheless, trace-element contents are important geochemical parameters. Impurities in the form of trace elements can either be incorporated into the crystal structure or bound to microinclusions (fluid or mineral inclusions). Figure 14 illustrates that few elements are present in quartz in concentrations >1 ppm. As already mentioned, this is due to the limited number of ions which can substitute for Si⁴⁺ in the crystal lattice. The structural incorporation in a regular Si⁴⁺ lattice position was proved for Al³⁺, Ga³⁺, Fe³⁺, Ge⁴⁺, Ti⁴⁺ and P⁵⁺ (e.g. Weil, 1984; 1993).

Aluminium is the most frequent trace element in quartz (up to a few 1000 ppm), which is due to its common occurrence in the Earth's crust and the similar ionic radii of Si⁴⁺ and Al³⁺. In the case of Ti⁴⁺ and Fe³⁺, the relatively large ionic radii may result in the preferred incorporation in marginal parts of the crystals (Götze and Plötze, 1997), or exsolution phenomena (e.g. formation of rutile inclusions) at lower temperatures (Götze et al., 2004). Other cations such as H⁺, Li⁺, Na⁺, K⁺, Cu⁺ or Ag⁺ can be incorporated in interstitial positions, sometimes acting as charge-compensating ions. Whereas Li seems to be more frequently incorporated into the quartz structure, Na and K may also be hosted by fluid inclusions (Götze et al., 2004). Several authors have emphasized the role of H^+ in the charge compensation of $Al^{3+}-Si^{4+}$ substitution (e.g. Bambauer, 1961; Miyoshi et al., 2005). The latter authors postulated that the replacement of Si^{4+} by $Al^{3+} + H^+ \pm Li^+$ is the principal mechanism for the structural incorporation of these trace elements into hydrothermal quartz.

For most elements in quartz however, their



FIG. 14. Average abundance and variations of trace elements in quartz (modified after Gerler, 1990 and Blankenburg *et al.*, 1994).

presence in microinclusions is most important (e.g. Rossman et al., 1987; Gerler, 1990; Jung, 1992; Blankenburg et al., 1994; Monecke et al., 2002a; Götze et al., 2004). Gerler (1990), for instance, showed a strong correlation of the elements Cl, Br, Na, Ca, Sr and Mn with the water content of fluid inclusions, and concluded that up to 100% of Cl, Br and I may be concentrated there. Other studies have revealed that fluid inclusions may host a wide range of additional elements (e.g. Czamanske et al., 1963; Sucevskaya et al., 1970; Pickney and Haffty, 1970; Malinko et al., 1976; Baranova et al., 1980; Naumov et al., 1984; Gerler and Schnier, 1989; Channer et al., 1999; Yardley et al., 1993; Klemm, 1994; Kostova et al., 2004). The results of Rossman et al. (1987), Ghazi et al. (1993) and Monecke et al. (2002a) suggest that along with Rb and Sr, the lanthanides are preferentially hosted by the fluid inclusions. On the other hand, the elements Ti, Al, K, Ca, Mg, Ba, Cs, Rb, Fe, Cr, Co, Cu, Mn, Pb, Sc, W, U and the REE can also be related to microscopic mineral inclusions in quartz (e.g. Gerler, 1990; Jung, 1992; Götze et al., 2004).

Despite the variable mechanisms controlling their incorporation into quartz, trace elements are considered important petrogenetic indicators for interpreting the conditions of mineral formation, in order to reveal either the provenance of quartz, or to reconstruct the genesis of ore deposits and the origin of metal-bearing fluids (e.g. Bambauer, 1961; Dennen, 1964, 1966, 1967; Walenczak,

1969; Lyakhovich, 1972; Suttner and Leininger, 1972; Stenina et al., 1984; Hallbauer, 1992; Heynke et al., 1992; Götze and Lewis, 1994; Götze and Plötze, 1997; Monecke et al., 1999, 2000; 2002a; Götze and Zimmerle, 2000; Larsen et al., 2000, 2004; Poutivcev et al., 2001; Müller et al., 2002, 2003a,b, 2008; Götze et al., 2004; Kostova et al., 2004; Götze, 2009b). For genetic interpretations, the contrasting behaviour of different trace elements in quartz has to be considered. Elements such as Al, Ge, Li, REE and the element ratios of Ge/Fe or Th/U appear to be reliable indicators of specific geological settings. For instance, the 10Ge-Ti-Al/50 triangle (Fig. 15) shows some general trends for different quartz types. Concentrations of other elements (e.g. Be, Cs and Rb in Li-pegmatites or Nb and Ta in Nb-Ta pegmatites) do not reflect the specific mineralization and, thus, cannot be used as petrogenetic indicators (Götze et al., 2004). This fact has to be considered if trace elements in quartz are to be used as pathfinder elements for geochemical processes.

According to Schrön *et al.* (1982), quartz from early crystallization stages is characterized by low Ge/Fe ratios (large Fe content), whereas this ratio is high in quartz from later generations. Therefore, characteristic features of quartz from pegmatites are large Ge and small Fe contents compared to quartz samples from other origins (Schrön *et al.*, 1988, Götze *et al.*, 2004). Observed variations of the Ge/Fe ratio (4.5-0.1) can be related to the crystallization sequence. The Ge speciation is also illustrated in the 10Ge-Ti-Al/50 triangle (Fig. 15), where pegmatitic quartz plots within a field far from the trace-element composition of granitic and rhyolitic quartz respectively.

Several studies have shown that the geological evolution and fractionation of granites and pegmatites is recorded in the trace-element composition of quartz (Larsen *et al.*, 2004; Jacomon, 2006; Müller *et al.*, 2008). These last authors found differences in the trace-element composition (Al, Li, Fe, Ge and Ti) between synand late-/post-orogenic pegmatites from Froland, Norway. Whereas the quartz from syn-orogenic pegmatites has a consistent trace-element signature, quartz from late- and post-orogenic pegmatites shows more variations in trace-element composition, i.e. a lowering of Li and Al and an increase of Ti and Ge compared to syn-orogenic pegmatites.

Trends in trace-element composition can also be observed in hydrothermal systems. Different temperatures of hydrothermal quartz formation may result in different concentrations of Ti (large concentration at high *T*) or Al (large concentration at low *T*) (e.g. Götze *et al.*, 2001*b*; Rusk *et al.*, 2006, 2008; Jourdan, 2008). Furthermore, the formation of agate and chalcedony often results in the accumulation of elements such as Al, Ge, B and U from alteration processes of the surrounding volcanics (Götze *et al.*, 1999, 2001*c*). The results of these studies illustrate that there may be a drastic trace-element zoning



FIG. 15. Characteristic trace-element ratios of quartz from different host rocks in the 10Ge-Ti-Al/50-triangle (modified and extended after Schrön *et al.*, 1988).

in hydrothermal quartz due to changing physicochemical conditions, crystallization effects, etc. Accordingly, the use of average trace-element contents for interpretation purposes may be difficult. Jourdan (2008) showed that traceelement variations are often accompanied by variations in isotopic composition.

The REEs also show a tendency to create specific patterns related to the host rocks and the conditions of crystallization. The comparison of REE contents of quartz from different geological environments reveals marked differences in the chondrite-normalized distribution patterns (Fig. 16). The REE distribution pattern of chert reflects a marine signature, which is similar to that of ocean water with a negative Ce anomaly. Quartz from granite is characterized by a crustal signature with a negative Eu anomaly due to fractionation effects. In contrast, guartz from acidic volcanics often lacks the negative Eu anomaly because of the early crystallization of quartz compared to feldspar. Metamorphic quartz is characterized by low REE contents and a crustal signature without fractionation effects.



FIG. 16. Chondrite-normalized *REE* distribution patterns of quartz from different rock types; note the 'tetrad effects' in the *REE* distribution of quartz from pegmatite (modified and extended after Götze, 1998).

The position of pegmatitic quartz in the late stage of magmatic evolution often results in a pronounced negative Eu anomaly and 'tetrad effects' (Fig. 16). Recent results of Monecke et al. (2002b) showed that the convex tetrad effect (i.e. 4 curves of REE groups) in samples from magmatic environments can most likely be explained by formation within the magma-fluid system before emplacement in the subvolcanic environment where phase separation causes a split of this system into fluid and magma subsystems. The negative Eu anomaly is also assumed to be a characteristic feature of late magmatic fluids (especially in evolved granitic systems), although there is no relationship between the intensity of the Eu anomaly and the development of tetrad effects (Monecke et al., 2002b).

Knowledge of the specific trace-element features in quartz can be used for genetic interpretations and the reconstruction of geological processes. As already mentioned, Dennen *et al.* (1970) developed a geothermometer based on the Al concentration in quartz. Although the results of Agel and Petrov (1990) confirmed the thermometer, Plötze (1995) and Götze *et al.* (2001*b*) found no direct correlation between temperature of quartz formation and the concentration of Al or paramagnetic Al centres in quartz. On one hand, there appears to be a saturation concentration of Al into quartz (Plötze, 1995);

larger concentrations of Al may also be present in form of microinclusions. On the other hand, Mullis and Ramseyer (1991) discussed the role of tetrahedrally coordinated Al in the mineralizing fluid/melt for the structural incorporation into quartz. Evidently other factors, such as the number and type of compensating cations, or the pH, have to be taken into account (Mullis and Ramseyer, 1991; Plötze, 1995). More recent studies, (Wark and Watson, 2006), have indicated, that the incorporation of Ti into quartz may be an alternative route to reconstructing the temperature of crystallization.

Specific trace elements may also be used as indicators for ore mineralization. Figure 17 shows the *REE* distribution patterns of a barren metamorphic host rock in comparison to quartz from areas with a hydrothermal overprint and Sn mineralization. The *REE* signature clearly reveals the hydrothermal overprint by mineralizing fluids. Another example illustrates that the concentrations of Rb and Sr in quartz can be used to distinguish barren host rocks from those associated with Sn or Au mineralization (Fig. 17).

Last, but not least, trace elements are also important criteria for the application of quartz raw materials in industry (e.g. Blankenburg *et al.*, 1994; Götze, 1997; Müller *et al.*, 2005). Iron and other elements have very small concentration limits (Table 4). Especially in high-tech applications (e.g. the optical industry) these conditions



FIG. 17. (*a*) *REE* distribution pattern in quartz of metamorphic host rocks compared to those from hydrothermally overprinted quartz in the exocontact to a Li-F granite with Sn mineralization; (*b*) Characteristic trace-element contents in metamorphic quartz of barren host rocks and related Sn- and Au-mineralizations respectively (modified from Monecke *et al.*, 2002*a*).

	Fibre optics	Special optical glass	Crystal glass	Window glass	Bottle glass
SiO ₂	>99.9 wt.%	>99.8 wt.%			
Fe ₂ O ₃	<2.0 ppm	<20 ppm	<150 ppm	<0.1 wt.%	0.5-4 wt.%
TiO ₂	<1.5 ppm	<25 ppm	**		
Al ₂ O ₃	11	<500 ppm			
Cr_2O_3	<0.01 ppm	<0.1 ppm			
CoO	<0.05 ppm	<0.05 ppm			
CuO	<0.05 ppm	<0.1 ppm			
MnO	<0.1 ppm	<1.0 ppm			
NiO	<0.1 ppm	<0.15 ppm			
V_2O_5	<0.5 ppm	<15 ppm			

TABLE 4. Chemical composition of high-purity quartz raw materials for different applications (data from Blankenburg *et al.*, 1994).

can often only be fulfilled by synthetic quartz material.

Industrial use of quartz

Quartz is one of the most frequently occurring minerals in the Earth's crust with a relative abundance of >12%. More than 90% of the total is found in igneous rocks. In contrast, more than 95% of quartz raw materials applied in the industry come from sedimentary rocks. In Germany, for instance, more than 80% of industrially used quartz raw materials are quartz sands for the foundry and glass industry (Blankenburg et al., 1994). This fact clearly shows that a strong dependence between the properties of quartz raw materials and the properties for industrial use exists. Data concerning quartz properties are necessary to evaluate the usability of quartz raw materials, the limitations of processing and also the prognosis and search for new deposits (e.g. Blankenburg et al., 1994; Götze, 1997; Müller et al., 2005).

Natural quartz raw materials represent a complex group of industrial rocks and minerals, which are used as single crystals and polycrystalline material or mono-mineralic rocks in the industry. The applications of quartz are wide-spread, including its use as a bulk product (e.g. quartz sands in the foundry and glass industry or quartzite for refractory materials), and perfect crystals (piezo- and optical quartz), as well as Si ore for the production of Si alloys or semi-conductor Si (Blankenburg *et al.* 1994). In all these applications, the requirements concerning the specific properties of the quartz raw material may differ widely. Therefore, different quartz types are being used in various industrial fields (Table 5).

One of the most important applications of quartz raw materials is their use as foundry sands in casting processes. Casting forms are prepared using quartz sands with different binding agents such as clay and bentonite, water glass and/or organic materials. The quality of the casting forms depends strongly on perfect interaction between the quartz grains and the binding material. Therefore, granulometric properties (grain size, grain shape, surface properties) play the most important role among the properties of the quartz raw material.

High-purity quartz sands are also the main raw materials for the production of silicate glasses. The amount of quartz may be as high as 80 wt.% in several glass products. Chemical purity (prevention of glass colouring) and the grainsize distribution (consistent melting behaviour) are among the most important parameters for the use of quartz in the glass industry (compare Table 4). Sometimes the use of synthetic silica raw materials is preferred in the case of highpurity silica glasses.

During the 1950s, the need for perfectly crystalline and extremely pure quartz crystals (e.g. Al <1 ppm) in modern technologies resulted in the development of hydrothermal quartz synthesis (e.g. Nacken, 1950; Mosebach, 1955). Although quartz frequently occurs in nature, the quality of most natural quartz is too low to satisfy the requirements for optical and piezo quartz.

Quartz type	Properties	Preferred application
Magmatic/postmagmatic Quartz of alaskite ('Iota quartz')	chemical purity	synthetic high-purity silica material
Pegmatitic and Hydrothermal quartz	chemical purity, perfect crystal order	optical and piezo quartz, quartz synthesis ('lascas') solar silicon
Metamorphic		
Quartzite	SiO_2 up to >98%	refractory materials
Metamorphogenic mobilizates	chemical purity	quartz synthesis ('lascas')
Sedimentary		
Quartz sands	chemical purity, granulometric properties	glass and foundry industry, cristobalite, quartz powder
Sedimentary quartzite	chemical purity, cryptocrystalline silica	refractory materials

TABLE 5. Interrelation between genesis and specific properties of different quartz types and their preferred application in the industry.

Outstanding optical and electrical properties such as refractive index, dispersion, optical activity, piezoelectricity or the transparency from 150 to 3000 nm are being used in several high-tech applications. Some 1000 t/y of synthetic hydrothermal quartz crystals (Fig. 18) are currently produced worldwide in autoclaves at 350–400°C and 100–120 MPa. Only quartz with very low



FIG. 18. Synthetic quartz crystal (*a*) grown under hydrothermal conditions $(350-400^{\circ}C, 100-120 \text{ MPa})$ in an autoclave; note the development of crystal faces which is different from that of natural quartz crystals; (*b*) indication of the crystal faces of synthetic quartz.

impurity contents, such as high purity pegmatitic and hydrothermal quartz can be used as raw materials (the so called 'lascas') for crystal growth.

All these examples show that the knowledge of the interrelation between quartz genesis – specific properties – parameters for technical application is necessary for the successful use of quartz raw materials in many industrial applications.

Conclusions

The knowledge surrounding quartz, one of the most frequent minerals of the Earth's crust, has been strongly increased due to the development and application of advanced analytical methods. In recent years, techniques with low detection limits and/or high spatial resolution have provided a wealth of new data concerning the real structure and chemistry of natural and synthetic quartz. Quartz is characterized by specific properties (indicator properties) - ranging from point defects up to macroscopic crystal shape - all of which are dependent on the geological history and specific conditions of formation. Thus, investigations concerning the typomorphic properties of quartz help to reveal the relations between quartz genesis, specific properties and industrial use. These data may help to reconstruct the geological history and to determine the viability of a possible industrial application.

Acknowledgements

The reviews of Th. Götte (Bochum) and an anonymous reviewer, which improved the quality of an earlier version of the manuscript, are gratefully acknowledged.

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