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Abstract: Gemstones of the quartz group display a wide spectrum of colours, both natural and those colours produced by artificial enhancement. Colour modification methods such as heat-treatment and irradiation or a combination of these processes used on macro-crystalline quartz lead to an interesting colour palette for the jewellery trade. Characteristics of these materials are outlined and testing methods for gemmological distinction between naturally coloured and artificially enhanced quartz are described. In the context of the different types of colour centres, the quartz gems are considered in three groups: iron-bearing quartz, quartz containing mainly aluminium and quartz with high water content. In particular, optical absorption spectra are used in the characterization of different colour varieties of quartz. In addition FTIR-spectra in the near-infrared range as well as the observation of pleochroism, presence of Brazil-law twinning and reaction under the Chelsea Colour Filter may be helpful for the determination of particular quartz types.

Keywords: quartz, causes of colour, colour modifications, heattreatment, irradiation, optical absorption spectra, amethyst, citrine, prasiolite, 'blueberry quartz', bleached quartz, bi-coloured quartz, smoky quartz, 'lemon quartz', green quartz, rose quartz



Introduction

Quartz perhaps shows a surprising variety among gemstones in terms of its macrocrystalline specimens, its micro- to cryptocrystalline structures, and particularly its wide range of colours.

General causes for the varieties of colour in quartz generally can be divided into three groups:

- 1. colour centres
- 2. optical effects
- 3. inclusions

In macro-crystalline quartz (Figure 1) colour is most commonly due to colour centres, which are associated with foreign ions in the structural framework of quartz. Of these, the commonest are iron and aluminium and for this reason the colour-centre mechanisms are discussed under the sub-headings iron-bearing and aluminium-bearing quartz. Comprehensive descriptions of the colours of quartz have been published by Lehmann and Bambauer (1973) and Rossman (1994).

This paper concentrates on colour centres rather than optical effects and inclusions and presents an outline of the commercially important colours and colour modifications of macrocrystalline quartz rather than the finergrained varieties. The currently known mechanisms responsible for each colour variety are described in summary form, and further details may be found in the indicated references. Recent work (Henn and Schultz-Güttler) is augmented with



Figure 1: Some colour varieties of quartz: from left to right — amethyst, prasiolite, citrine (yellowbrown) and smoky quartz. Photo by Rainer Schultz-Güttler.

more illustrations and outlines of possible defects and their interactions (see Box A).

Crystal structure and morphology

The structure of quartz (SiO_2) is represented by a trigonal trapezohedral lattice *(Figure 2)*. Each silicon atom is coordinated with four oxygen atoms and constitutes SiO_4 -tetrahedra. These tetrahedra are helically arranged and form a three-dimensional network of helical chains which are aligned in the direction of the *c*-axis. They are linked in such a way that six-sided channels are formed, and within these channels there are vacant interstitial (I) sites which can offer both tetrahedral (I_4) and octahedral (I_6) coordination to possible foreign elements or ions.

Box A: Defects in quartz related to colour varieties

The illustration shows in a schematic way some possible defect centres in natural quartz.

Quartz has a very simple chemical formula SiO₂, and may be considered as a quite perfect substance. But as shown by innumerable investigations (Salh, 2011), quartz can contain large number of defects involving substitutional and interstitial ions, hydroxyl and molecular water, besides such growth defects as spiral growth, small angle boundaries and twinning. The basic structural unit is the AO₄-tetrahedron [AO₄], whereby A is mainly Si, but can be substituted by Al, Fe and (4 H). Where charges need to be balanced, the coupled ions, occupying interstitial positions, are shown nearby the tetrahedron as Li, Na, $\mathrm{Fe}^{\scriptscriptstyle 2+}$ and OH. This scheme leads to the notation [AO₄/M] used in the text and illustrations to explain the modifications of colours by irradiation and heat treatment. Each [AO₄/M] unit may be neutral (^o), positively (+) or negatively (-) charged, depending on the addition or removal of electrons. Shown also is molecular water (H₂O), which may



interact with all defects shown; its location is not at structural sites but in the channels of the quartz structure or along grain boundaries, twin planes and micro-structural growth defects of the crystals. From these considerations it is clear that a multitude of combinations of defects in natural quartz can exist, any one combination being a reflection of its geological history.



Figure 2: Crystal structure of quartz illustrating the Si sites and the interstitial sites of distorted octahedral (I_{e}) and tetrahedral (I_{4}) coordination (after Lehmann and Bambauer, 1973); a1 and a2 are unit cell parameters.

Silicon atoms can be replaced by foreign ions. In the case of tetravalent ions such lattice sites are labelled S. If tetravalent Si is replaced by an ion of lower valency, this would lead to the need for charge balancing by alkali ions (e.g. lithium) or protons, and the lattice sites occupied in such a mechanism are labelled S₁ and S₂ respectively.

The helical arrangement of the SiO₄-tetrahedrons parallel to the *c*-axis is responsible for the development of right-handed and left-handed crystals with mirror-image symmetry. The crystal morphology of quartz (*Figure 3*) is dominated by rhombohedral and prismatic

faces. The common crystal form is a prism with hexagonal-prismatic habit. The main crystal faces are the first order hexagonal prism \mathbf{m} (10 $\overline{1}$ 0), positive and negative rhombohedron \mathbf{r} (10 $\overline{1}$ 1) and \mathbf{z} (01 $\overline{1}$ 1), second order dipyramid right-hand \mathbf{s} ` (11 $\overline{2}$ 1) and left-hand ` \mathbf{s} (2 $\overline{1}$ $\overline{1}$ 1) and trapezohedra right-hand \mathbf{x} ` (51 $\overline{6}$ 1) and lefthand ` \mathbf{x} (6 $\overline{1}$ $\overline{5}$ 1).

Iron-bearing quartz

In the crystal structure of quartz, iron can be present in both substitutional S sites and interstitial I sites. However, the replacement is limited because of differences in valency and ionic radii. Iron



Figure 3: Morphology of a crystal with doubly terminated prismatic form. Perfect examples are rarely found in nature due to frequent twinning and growth defects. Diagram by German Gemmological Association.

contents of 10 to 350 ppm were indicated for amethyst and citrine by Lehmann and Bambauer (1973). The first electron transition band of Fe³⁺ is located at about 210 nm in the UV, so does not absorb in the visible range and consequently no colour is produced. Those Fe³⁺ ions occupy both substitutional S₁ sites and interstitial I₄ sites and are considered as precursors of the colour centres in amethyst (Lehmann, 1967; Lehmann and Bambauer, 1973).

Colour causes and modifications of iron-bearing quartz are shown in *Figure 4*. Characteristics and distinguishing features are summarized in *Table I*.

Table I: Characterist	ics of iror	<i>i-bearing</i>	quartz.
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Туре	UV/VIS/NIR absorption	Pleochroism	Brazil	Infrared	Upper temperature
	spectrum		law	spectrum	limit of colour
			twinning		stability; °C
Amethyst	bands at 545 and 357 nm as	reddish-violet to bluish-	present	n.d.	350-450
	well as 950 nm	violet			
Citrine:	continuous increase towards	none	present	n.d.	400-600
heated amethyst	UV				
Prasiolite:	broad band maximum at	weak in shades of pale	present	weak H ₂ O and	500-600
heated amethyst	720 nm	green		Si-OH bands	
'Blueberry quartz':	band at 545 nm and	violetish-blue to reddish-	present	n.d.	350-400
irradiated and heated	shoulder at 720 nm	orange			
prasiolite					
'Neon quartz': heated	shoulders at 545 and 357 nm	-	present	n.d.	approx. 400
amethyst					
NB: n.d. = not diagnostic					



Figure 4: Colour causes and modifications of iron-bearing quartz. The possible ways of changing colours are indicated as are the causes. Photo by German Gemmological Association.



Figure 5: Rough amethyst crystals of different colour intensities; some show distinct colour zoning (for example, centre bottom) due to changing growth conditions. Size of specimens from 2 to 4 cm. Photo by Rainer-Schultz-Güttler.

Amethyst

The iron-related colour centres which are responsible for the violet colour of amethyst have been described by several authors (e.g. Lehmann, 1967; Lehmann and Bambauer, 1973; Cohen, 1985; Rossman, 1994). Following Lehmann and Bambauer (1973) the formation of the iron centres relevant to the violet colour of amethyst (*Figure 5*) can be characterized by the following formula: $Fe^{3+}(S_{*}) + Fe^{3+}(I_{*}) \leftrightarrow Fe^{4+}(S) + Fe^{2+}(I_{*})$

The mechanism is due to an electron transition caused by gamma irradiation: an electron is impelled or released from a substitutional Fe³⁺ and trapped by an interstitial Fe3+. Consequently, by losing the negative electron, the substitutional Fe3+ is oxidized to an Fe4+ centre, while the interstitial Fe³⁺ is reduced to Fe²⁺. This electron transition process is reversible by heat treatment. The stability limit of the amethyst centre is approximately 350-450°C. Exceeding that temperature the amethyst colour starts to bleach. The structural position of the Fe4+ centre and the exact mechanism of colour formation is still a matter for discussion. Cohen (1985) described irradiation-related Fe4+ centres, but located on interstitial rather than substitutional sites. Dedushenko et al. (2004) confirmed the model of Lehmann and Bambauer (1973) by Mössbauer spectroscopy, but Burkov et al. (2005) and SivaRamaiah et al. (2011) stress the influence of ferrous iron in amethyst.

In quartz generally, the concentration and distribution of trace elements is related to the growth sectors of the crystal. Generally, concentrations are highest at the positive rhombohedron and reduce at the negative rhombohedron and are lowest at the prism sectors. In amethyst, the violet colour is concentrated in the rhombohedral sectors, with the positive one possessing the deepest colour (*Figure 6*), while the prismatic sectors are colourless or white (*Figure 7*).

A diagnostic feature for natural (as opposed to synthetic) amethyst is the presence of Brazil-law twinning. This is due to polysynthetic twinning in the growth sectors of the positive rhombohedron **r** (*Figure 8*). Twinning of



Figure 6: Two amethyst cross sections indicating different colour intensity in different growth sectors. Sectors of the positive rhombohedron **r** possess more intense violet colours compared to sectors of the negative rhombohedron **z**. Size of specimens 2.5 and 2 cm. Photo by German Gemmological Association.

Figure 7: Group of crystals extracted from an amethyst geode from Brazil. The rhombohedral growth sectors show amethyst colour, while the prism sectors are colourless to white. Size of specimen 6.5 cm. Photo by German Gemmological Association.

Figure 8: Unusually large macroscopic Brazil twin in an amethyst from Bahia, Brazil. Most examples of this type of twin are seen under the microscope. 4 cm length. Photo by Rainer Schultz-Güttler.



Figure 9: Unpolarized absorption spectra of different colour varieties of iron-bearing quartz. The spectra are displaced on the absorption scale for clarity.

this type also is visible in treated amethyst varieties, in particular in citrine, prasiolite, 'blueberry quartz' and bleached quartz.

The visible range absorption spectrum (Figure 9) of amethyst is characterized by a broad absorption band in the yellowgreen, which is responsible for the violet colour (Neumann and Schmetzer, 1984). The maximum is located at 545 nm and is only weakly pleochroic (Rossman, 1994), the reddish-violet to bluish-violet change being caused by varying iron entrapment at crystallographically equivalent Si sites (Neumann and Schmetzer, 1984). Cox (1977) described this phenomenon as an anomalous trichroism. Outside the visible range, a second absorption band of Fe4+ is situated in the UV at 357 nm and is clearly pleochroic; a further band lies in the NIR with a maximum at 950 nm.

Citrine

Most citrines on the gemstone market are heat-treated amethysts. At temperatures of about 350 to 450°C amethyst bleaches to colourless or pale yellow and the concentration of the provisional iron centres $Fe^{3+}(S_1)$ and Fe³⁺(I₂) accumulates (Stock and Lehmann, 1977). Coincidently, the formation of iron particles derived from iron originating from these centres starts and the colour develops from yellow to brown. The particles consist of hematite (Fe₂O₂) with an approximate size of 100 nm. Because the distribution of the hematite particles is dispersed, random and relatively homogeneous, the coloration is isotropic and no pleochroism exists. The higher the temperatures are raised during the heat treatment the stronger becomes the brown



Figure 10: Citrine (heat-treated amethyst) of various yellow to brownish-orange colours: pale yellow, yellow, golden citrine, Palmeira citrine, Madeira citrine (from left to right). Weight of the specimens 7.43 to 10.85 ct. Photo by German Germological Association.



Figure 11: Amethyst (centre), heat-treated prasiolite (green) and irradiated and heat-treated 'blueberry quartz' from Montezuma, MG, Brazil. Size of amethyst 5 cm long, blueberry quartz 1.5 to 2.5 cm and prasiolite 0.8 to 1.5 cm. Photo by Rainer Schultz-Güttler.

Figure 12: Faceted prasiolite (heat-treated amethyst) from Montezuma, Brazil (6 ct). This colour is stable to light and heat up to 500–600 °C. Photo by Rainer Schultz-Güttler.

Figure 13: Faceted 'blueberry quartz', i.e. gamma-irradiated and heat-treated prasiolite (4 ct). This colour resembles that of much tanzanite. Photo by Rainer Schultz-Güttler.

to orange hue (*Figure 10*). The optical spectrum (*Figure 9*) shows a continuous increase of absorption towards the UV (Neumann and Schmetzer, 1984).

In the gem trade, golden-yellow material is called golden citrine; more brownish-orange to orange stones are called Madeira citrine; the name Palmeira citrine describes stones from the Palmeira amethyst mine which provides amethyst suitable for heat treatment to citrine of fine quality, so these particular stones have a Brazilian origin.

Prasiolite

Certain amethysts can turn green on heat treatment (*Figures 11* and *12*). The so-called natural prasiolite is very rare and in Nature it has probably formed as a result of heating from nearby volcanic activities (Schultz-Güttler *et al.*, 2008).

The prasiolite offered on the gemstone market nowadays is heat-treated amethyst, much of it probably coming from the Montezuma mine in Minas Gerais, Brazil. The mechanism of the colour modification is a valency change of the amethyst iron centres. As in the heating process used to produce yellow citrine colours the iron centres $Fe^{4+}(S)$ and $Fe^{2+}(I_4)$ are transformed into the provisional centres $Fe^{3+}(S_1)$ and $Fe^{3+}(I_4)$ of the colourless state. Subsequently, a green colour is produced by heat treatment at 400–500°C when the interstitial $Fe^{3+}(I_4)$ changes to Fe^{2+} which is in octahedral coordination (I_6) (see again *Figure 4*). The colour is stable up to temperatures of 500 to 600°C.

Its visible range absorption spectrum *(Figure 9)* is characterized by a broad band with a maximum at 720 nm. Where there is a yellow component in the colour, as in yellow-green to champagne-coloured material, there is a distinct increase of absorption towards the UV (Schultz-Güttler *et al.*, 2008).

'Blueberry quartz'

Gamma irradiation and heat treatment of prasiolite produces violet, violet-blue

to dark blue colours (Schultz-Güttler, 2006; Schultz-Güttler and Kohigashi, 2006). The violet-blue to blue material is called 'blueberry quartz' in the gem trade (*Figures 11* and *13*).

The absorption spectrum (Figure 9) is characterized by a broad band with a maximum at 545 nm which is caused by the amethyst iron centre Fe4+. Contrary to amethyst, which shows large transmission between 600 and 800 nm, in blueberry quartz a further absorption continues with a shoulder at 720 nm and this is due to Fe²⁺ as in prasiolite. It is this feature which absorbs much of the red wavelength and produces the blue colour. It may be noted that the typical amethyst colour basically is a fine compromise of blue and red components producing lilac. Compared with amethyst the absorption minimum is located at a longer wavelength: at 465 nm rather than the 444 nm of amethyst. That phenomenon is caused by a prior increase of the absorption towards the shoulder in the UV at 357 nm.

Bleached quartz

Heat treatment of amethyst at temperatures above 500°C develops a slightly milky turbidity and bleaching of the violet colour, and some stones of this type have been called 'neon quartz' in the gem trade (Figure 14). At higher temperatures of about 600°C the milky turbidity develops much more strongly and the violet to lilac colour completely disappears. What happens is that silanol (-Si-OH) groups bound in the quartz structure react to the heat by releasing the -OH as tiny water droplets which cause the light scattering and milky turbidity. The resulting appearance resembles adularescent gem materials and such stones are used as moonstone imitations.

The absorption spectrum *(Figure 9)* indicates the presence of amethyst iron centres, but in comparison with the amethyst spectrum, the Fe⁴⁺ absorption bands possess lower intensity and are less distinctly developed as shoulders.

Bi-coloured quartz

The best-known bi-coloured quartz is ametrine *(Figure 15)* and, as the name accurately implies, the stones consist of amethyst and citrine colour zones. The prime natural source of these stones is the Anahí mine, Bolivia (Vasconcelas *et al.*, 1994). The violet amethyst colour is found in the sectors of the positive rhombohedron **r** and is caused by Fe⁴⁺ centres. The sectors of the negative rhombohedron **z** are yellow. Aines and Rossman (1986) described that phenomenon as follows: the rhombohedral **z** sectors contain higher water contents; natural ionizing radiation results in radiolysis, i.e. a breakdown of water into H₂ and O₂ (see also Hashimoto *et al.*, 2001); and the presence of hydrogen prevents the formation of Fe⁴⁺ amethyst centres, so there is no violet coloration.

Colour-zoned amethyst from both Bolivia and Brazil (Marabá/Pará or Brejinho das Ametistas/Bahia) can be heat treated to yellow/colourless stones (*Figure 16*) which are sometimes named 'Lunasol' in the trade. In heat treatment at about 475°C the sectors of the positive rhombohedron **r** can change to colourless ($Fe^{4+} \rightarrow Fe^{3+}$) while the sectors of the negative rhombohedron **z** turn yellow (due to precipitation of Fe_2O_3). The process is partially reversible by irradiation, i.e. the sectors of the positive rhombohedron **r** can be returned to violet (Nassau, 1981).

Quartz containing mainly aluminium

Independently or accompanying iron, aluminium is the other main trace element that can replace silicon in the crystal structure on tetrahedral lattice sites (substitution). The radii of aluminium ions are smaller than those of iron at equivalent sites, so substitution of larger quantities is easier and generally the concentration of aluminium is much higher than that of iron (hundreds to thousands of ppm). The difference in charge produced by the substitution of Si4+ with Al3+ in the structure is compensated for by the presence of alkali ions such as sodium, potassium, lithium, or the hydronium ion (H₂O⁺) or a proton. These ions occupy interstitial sites or reside in the channels of the crystal structure. In quartz, as shown above, there are two types of channel parallel to the *c*-axis, one with a trigonal cross-section of smaller diameter and one with a distorted hexagonal cross section of larger diameter; in addition there are channels perpendicular to the rhombohedral faces and inclined to the *c*-axis whose influence on distributions of substitutional ions have not vet been clarified.

Therefore, there is a number of different sites for the compensating ions to occupy to achieve charge balance, with the result that a number of different configurations of colour centres may be present.

The causes of colour and processes of change of colour in aluminium-containing quartz are shown in *Figure 17*, and characteristics and distinguishing features are shown in *Table II*.







Figure 14: Faceted 'neon quartz', i.e. bleached amethyst. The milky appearance is produced by microscopic fluid inclusions, formed due to heat treatment. Weight of the specimen 4.84 ct. Photo by German Gemmological Association.

Figure 15: Ametrine from Bolivia. The violet amethyst colour is concentrated at the growth sector of the positive rhombohedron **r**, while the yellow citrine colour is limited to the sectors of the negative rhombohedron **z**. Size of the specimen 4.6 cm. Photo by German Gemmological Association.

Figure 16: Bi-coloured colourless/yellow quartz obtained by heat treatment of colour-zoned amethyst. Weight of the faceted stone 6.23 ct. Photo by German Gemmological Association.



Figure 17: Colour causes and modifications of aluminium-bearing quartz. The colour-forming complexes are shown and the ways to change colour are indicated. Photos by German Germological Association.

Table II: Characteristics of	of a	luminium-	bearing	quartz.
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Туре	UV/VIS/NIR	Pleochroism	Brazil	Infrared	Upper
	absorption		law	spectrum	temperature
	spectrum		twinning		limit of
					colour
					stability, °C
Citrine	shoulder at 400	light yellow to	absent	n.d.	200-300
	nm	intense yellow			
Smoky	bands at 427,	brown to	absent	weak	200-300
quartz	486 and 670 nm	reddish-brown		Li-band	
Lemon	bands at 400	yellow to	absent	distinct	200-300
quartz	and 650 nm	yellow-green		Li-band	
				(3483 cm ⁻¹)	

NB: n.d. = not diagnostic

Citrine and smoky quartz

The main colours of this aluminium bearing quartz are all shades of lime green, yellow to yellow-orange (citrine in the real sense with natural colour, *Figures 18* and *19*) and all shades in brown to black, where the range grades into the greyer smoky quartz (*Figures 18* and *20*) and the opaque black variety called morion.

Some crystals contain a wide range of shades of yellow, indicating changing conditions of incorporation of trace elements with changing growth conditions and /or changes in the chemistry of mineral-forming fluids. As Rossman (1994) pointed out, the details of the natures of colour centres in this Al dominated quartz are not yet fully understood. Taking into account the above-mentioned variety of valence-balancing ions which can be incorporated in the quartz structure and more recent work - see for example Götze (2009) and Stevens-Kalceff (2009) - this statement is readily understandable.

The absorption spectra of Aldominated colour varieties typically contain five bands (after Nassau and Prescott, 1975 and 1977) and the hue and colour depth are determined by their relative intensities. They have their maxima at 670 nm (A1), 486 nm (A2), 427 nm (A3), 314 nm (B) and 270 nm (C). The relative intensity of each absorption band in a spectrum determines the shade of yellow, orange, brown or almost black in that stone. It is outside the scope of this work to discuss further the possible allocation of individual bands to certain defects derived from the general case [AlO₄/M], whereby M represents a Na, K, Li, or hydronium ion or a missing electron in an orbital, i.e. a hole. However, it is worth stating that the presence of hydroxyl or hydronium ions will reduce the intensities of any yellow and brown colours (Guzzo et al., 1997).

Thus, as was discussed above for iron, radiation is necessary for the creation of colour centres and therefore for colour in quartz with Al as the main impurity. Natural disintegration of radioactive elements in the quartz veins,



Figure 18: An extensive range of natural-coloured citrine and smoky quartz from Santo Sé, Bahia, Brazil. This locality has recently furnished nearly all natural citrine-related quartz in Brazil. Size of specimens from 3 to 6.5 cm in diameter. Photo by Rainer Schultz-Güttler.

Figure 19a and b: Citrines of natural colour from Zambia. Weight of the faceted stones 7.21 and 8.93 ct. Photo by German Gemmological Association.

Fig ure 20: Smoky quartz from Brazil. Weight of the faceted stone 9.72 ct. Photo by German Gemmological Association.

for example, or in surrounding granites or pegmatites can irradiate quartz which, although maybe in small doses, over long geological time can accumulate and produce the colours found in natural material. In the laboratory, however, very high doses of irradiation, mostly gamma-rays, can produce in much shorter times the desired colour(s). It may be worthwhile to stress that irradiation be it natural or applied at the irradiation facility will turn all material nearly black and the described colours are the product of additional heating.

Heat, either through metasomatic or metamorphic processes in a geological setting or by heating under controlled conditions in the laboratory, increases the electron mobility in the quartz, thus counteracting the intensity of the formed colour centres. By careful observation



Figure 21: Absorption spectra of aluminium-bearing quartz. The typical absorption peaks for each variety are indicated.









Figure 22: Pleochroism of natural-coloured citrine from Zambia. This is a strong colour difference seldom seen in citrine samples. Photo by German Gemmological Association.

under controlled heating any one of the commercial colours can be produced.

With appropriate heat treatment, all colours can be reduced and even completely bleached at temperatures of about 210 to 280°C and over periods of 60 to 360 minutes (Barbosa, 2009).

The absorption spectrum of smoky quartz (*Figure 21*) has a wide band with maximum centred about 427 nm and shoulders about 486 and 670 nm. Greenish-yellow, yellow and yelloworange aluminium-containing crystals (citrine in the traditional sense or socalled 'citrine of natural colour') show a continuous increase in their absorption spectra from red to the ultraviolet with a more or less clearly defined shoulder or absorption band at 400 nm (*Figure* *Table III: Differentiation between natural-coloured citrine, citrine obtained by heat treatment of amethyst and lemon quartz.*

	Citrine, natural	Citrine,	Lemon quartz, Heat-treated
	colour	heat treated	smoky quartz
		amethyst	
Pleochroism	pale to intense	none	yellow to yellow-green
	yellow		
Absorption spectrum	shoulder at 400	continuous	peaks centred at 400 and
	nm	increase	650 nm
		towards UV	
FTIR spectrum	n.d.	n.d.	Li-band at 3483 cm ⁻¹
Brazil law twinning	none	present	none

NB: n.d. = not diagnostic

21). In contrast to the citrine created by heat treatment of amethyst, natural citrine possesses distinct pleochroism *(Figure 22)*, but no twin intergrowth according to the Brazil law.

Lemon quartz ('green gold')

Even though this variety is one of the above mentioned citrines, its economic importance justifies particular attention. In the gem trade, this quartz is known as 'lemon quartz' or 'green gold' (*Figure 23*).

The colour is similar to the colour of the best chrysoberyls, a 'chartreuse', a yellow with a distinct touch of green. Only in a few quartz deposits in Brazil or the rest of the world can this attractive quartz be found. Previous studies (Nunes *et al.*, 2009; Trabulsi, 2010; Favacho Silva, 2000) indicate that this colour can only be found in quartz with a high lithium content. The absorption spectrum *(Figure 21)* of such quartz shows a well defined band centred at 400 nm, and one less pronounced at about 650 nm. The degree of intensity of the band at 650 nm relates to strength of the green component in the colour. The source of colour in this case is the molecule $[AlO_4/ Li, H]^0$, which releases an electron by irradiation and forms the colour centre. It should be mentioned that the intensity of the green component is reduced in the presence of a proton or of a hydronium ion.

The distinguishing features of 'lemon quartz', citrine of natural colour and citrine obtained by heat-treatment of amethyst are summarized in *Table III*.



Figure 23: Range of colours of 'lemon quartz' and citrine from Pará, Brazil. They form a colour gradation from near-colourless to dark olive green brown. Sizes from 2 to 6 cm in diameter. Photo by Rainer Schultz-Güttler.

Quartz with high water content

In the last few years a new, green variety of quartz has appeared (Figure 24). In the gem trade, it is sold under the pseudonym 'green amethyst' or 'greened amethyst' or it can be offered as prasiolite. Most of the raw material of this variety comes from the geode-bearing basalts in the south and southwest of Brazil, i.e. from the states of Rio Grande do Sul, Paraná and southwest Minas Gerais. It has been shown that this colour variety is different from the prasiolite obtained from amethyst (Schultz-Güttler et al., 2008), and each variety can be distinguished easily using a Chelsea Colour Filter: the prasiolite derived by heat treatment of amethyst from the Montezuma deposit, will show green and this new green variety will show red (Table IV).

Optical spectroscopy and infrared studies have shown that this and similar quartz has a very high content (up to 5000



Figure 24: Gamma-irradiated green quartz from Rio Grande do Sul, Brazil. Although the irradiation dose is the same, the difference in colour of the crystals from pale green in the lower left to dark green in the upper right is clearly visible. Size of specimens from 1.5 to 4.6 cm. Photo by Rainer Schultz-Güttler.

ppm, Iwasaki and Iwasaki, 1993; Hebert and Rossman, 2008) of molecular water and silanol, or Si-OH groups *(Figure 25)*. Other trace elements such as Fe, Al or Li are very low or are in the range of normal natural quartz as ongoing investigations showed (Guttler *et al.*, 2009). So the trace elements in prasiolite and this new green quartz are quite different and the causes of their colours are based on completely different mechanisms.

Macroscopic examination of the original material shows a certain peculiar

Table IV: Distinguishing features of prasiolite and green quartz with high water content.

aspect of its appearance that can best

be described as an 'greasy lustre'; this is

certainly connected with the high water

higher than 500°C, the crystals show a

being exsolved as fine microscopic

fluid inclusions, similar to the above-

mentioned opalescent quartz (Iwasaki,

1980). Comparing the spectra of quartz

of pegmatitic origin with those of quartz

with the greasy lustre from geodes (Figure

milky, cloudy opalescence, due to water

On heat treatment to temperatures

content of this type of quartz.

	Prasiolite	'Wet quartz' irradiated to result in green quartz
Main absorption peak in visible range spectrum	720 nm	610 nm
FTIR spectrum	weak H ₂ O and Si-OH bands	H ₂ O band at 1900 cm ⁻¹ Si-OH bands at 1400 and 2200–2400 cm ⁻¹
Colour under Chelsea Colour Filter	green	red



Figure 25: NIR-spectra of different types of quartz. Spectra 1 and 2 are from pegmatitic quartz with contents of Li and Al but no water or OH groups (labelled H_2O and M-OH respectively). Spectra 4 and 5 are from 'wet quartz' from geodes in Rio Grande do Sul, Brazil, and their H_2O and OH peaks are clearly visible. The wavy appearance of spectrum 4 is due to internal reflection of the light beam. The presence of silanol groups is made clear by comparison with spectrum 3, an ultrapure General Electric standard glass, GE 124 with < 5ppm OH.



Figure 26: Absorption spectrum of gamma-irradiated green quartz from Rio Grande do Sul, Brazil. This absorption peak has long been specific for non-bonding oxygen hole (NBOH) defects in silica and glass, and more recently in quartz.

25), the intensities of the water and OH absorption bands are clearly higher in the latter. This type of quartz with high water content should therefore be called 'wet quartz' and its spectral characteristics resemble those of chalcedony as shown by Graetsch *et al.*, 1985.

The presence of molecular water and silanol quenches all tendency towards

the formation of colour centres based on Al or Fe. Therefore, geodes commonly contain amethyst crystals of very pale colour even though their contents of Fe are comparable with those in quartz of intense amethyst colour which has come from other sources.

Since only irradiation produces this green colour one has to assume that



Figure 27: Untreated and gamma-irradiated wet quartz crystals. The same dose of irradiation produces different intensities of colour. Size of specimens between 2 and 4 cm. Photo by Rainer Schultz-Güttler.

gamma radiation interacts with water to form oxygen and hydrogen and that the groups Si-OH and Si-O already present as point or line defects along twin planes or growth defects will be split forming respectively hydrogen and oxygen (Hashimoto et al., 2001). This Si-O group is now electronically active to form colour centres that produce a band at 590 to 620 nm in the visible absorption spectrum (Figure 26) and a strong absorption at 220-260 nm in the UV. This centre is called the 'non-bonding oxygen hole centre' (NBOHC) and occurs in various types of silica, both crystalline and amorphous. The two absorption bands effectively form a transmission window at about 490 to 540 nm which produces the green colour (Figure 27).

These NBOHC defects are quite different from the Fe or Al substitutions described above. Rather, they find themselves on dislocations in the crystal structure with no direct bonding to neighbouring SiO_4 tetrahedra, or they exist in regions with highly strained bonds, such as twin lines, growth defects, spiral growth hillocks, step growth defects and so on. As such, they can be linked to a range of growth features in different crystals (Hosaka *et al.*, 1986; Stevens-Kalceff, 2009).

Perfection of growth in quartz depends strongly on growth velocity and suitability of solution chemistry. Quartz grown rapidly shows striations and the amount and thickness of these is a function of the growth rate. Higher growth rate will produce finer striations, whereas quartz grown slowly, fractions of mm a day, will show hardly any growth defects. In examining green quartzes, one can always find fine striations parallel to the rhombohedral faces —which may be produced by Brazil twins or growth defects.

It must then be concluded that this kind of 'wet quartz' grew rapidly. Since the growth of a crystal is a very local event, e.g. in geodes, it is understandable that there can be several generations of quartz in the same geode, each with certain specific growth features. Crystals which grew slowly can show intense



Figure 28: Bi-coloured quartz with an amethystine core and a green outer layer from Rio Grande do Sul, Brazil, probably reflecting different growth rates in different growth solutions. Crystals with green cores and amethystine layers can also be found. Size 8.3 cm. Photo by Rainer Schultz-Güttler.

amethyst colour and have a relatively low water content, while 'wet quartz' with its rapid growth will be colourless, even though it may have high amounts of iron and/or aluminium.

Sometimes the growth rate may vary and this can affect the number of defects in a single crystal. If initial growth is slow and later growth is fast, quartz can be produced which has a core with amethyst colour (*Figure 28*), but which is green in the outer layers.

Studies of the colour stability of this green variety of quartz have shown that temperatures of 150°C are enough to bleach the quartz within one to two hours (Clerici, 2010), and its behaviour and stability under UV radiation and sunlight are currently being examined.

Rose quartz

Most pink quartz is found in massive compact form, only rarely as smaller euhedral crystals, and has a cloudy or translucent rather than transparent appearance *(Figure 29).* A wide band with maximum at about 500 nm in the absorption spectrum *(Figure 30)* is characteristic. Lehmann and Bambauer (1973) ascribed this band to Ti^{3+} on substitutional sites of the crystal structure. The cause of the cloudy appearance is probably a light scattering process from tiny fibrous inclusions: Ignatov *et al.* (1990) and Goreva *et al.* (2001) found



Figure 29: Massive rose quartz. The cloudy appearance is typical and is probably due to an intergrowth of quartz with dumortierite. Weight of the faceted stone 8.76 ct. Photo by German Gemmological Association.

pink-coloured dumortierite in quartz and attributed the absorption band to Fe²⁺-Ti⁴⁺electron charge transfer. The pink single crystals are intrinsically different from massive rose quartz. In their absorption spectrum they have bands at 338 and 524 nm which have been attributed by Rossman (1994) to an Al O⁻-P-associated complex forming a colour centre. The use of gamma irradiation intensifies the colour of these singlecrystal rose quartzes (*Figure 31*).



Figure 30: Visible range absorption spectrum of massive rose quartz, with a broad peak centred at about 500 nm.



Figure 31: Euhedral rose quartz crystal cluster: pale colour and irradiated sample with strong pink colour, which is quite stable to light. This sample is from Galileia, Minas Gerais; size 5 and 7 cm for each cluster. Photo by Rainer Schultz-Güttler.

Conclusions

Quartz, generally thought of as a gemstone with only a few colour varieties, such as amethyst, citrine and smoky quartz, has a more extensive range of colours, some of them induced by treatments. Heat and irradiation in particular have opened the way to increasing the range and availability of gem materials and to increasing their economic importance. So there is no need to search for deposits of these varieties, since so much colourless quartz with appropriate trace impurities can be found not only in Brazil but also in other parts of the world. The search for criteria to distinguish quartz susceptible to treatment is an ongoing task, since complex natural conditions of growth, as shown in this work, can influence and often determine the resulting colour of quartz.

However, the spectra and comparison tables presented here indicate some criteria that can already be used to identify the different kinds of quartz. Using spectroscopy, wet, hydrothermal quartz can be distinguished from quartz with very little water; using pleochroism and twinning, citrine and smoky quartz can be distinguished.

Besides this it is also important to know whether the colour of a gemstone is natural or induced by means of treatments. From the data discussed in this work it is clear that much has still to be done to decipher all the factors determining each type of colour. But what is now established is that it is easy to separate the two types of green quartz, prasiolite and green quartz by means of use of the Chelsea Colour Filter, and to recognize the colour of 'green gold' as a product of irradiation and heat treatment. The temperatures discussed in the text and on the charts also indicate that jewellers should take special care when using heat in repairing any jewellery that contains coloured varieties of quartz.

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