Cathodoluminescence colours of α-quartz

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Abstract

A new cathodoluminescence-microscope has been developed with a considerably improved detection limit. Time-dependent luminescence intensity changes observed during electron bombardment enabled the recognition of short-lived, long-lived, and brown luminescence colour types in α-quartz.

Short-lived bottle-green or blue luminescence colours with zones of non-luminescing bands are very common in authigenic quartz overgrowths, fracture fillings or idiomorphic vein crystals. Dark brown, short-lived yellow or pink colours are often found in quartz replacing sulphate minerals. Quartz from tectonically active regions commonly exhibits a brown luminescence colour. A red luminescence colour is typical for quartz crystallized close to a volcanic dyke or sill.

The causes of these different and previously poorly understood luminescence colours were investigated using heat treatment, electron bombardment and electrodiffusion. Both natural and induced brown luminescence colours reflect the presence of lattice defects (nonbonding Si–O) due to twinning, mechanical deformation, particle bombardment or extremely rapid growth. The bottle-green and blue linearly polarized luminescence colour, characterized by a plane of polarization parallel to the c-axis, both depend on the presence of interstitial cations. The yellow and red luminescence colours in α-quartz both exhibit a plane of polarization perpendicular to the c-axis and appear to be related to the presence of trace elements in an oxidizing solution and to ferric iron respectively.

KEYWORDS: cathodoluminescence, α-quartz.

Introduction

CATHODOLUMINESCENCE colours of α-quartz were first detected in vein quartz and smoky quartz by Goldstein (1907) during experiments on the nature of cathode rays in evacuated discharge tubes. Sippel (1965) and Smith and Stenstrom (1965) used this property as a petrological tool for the distinction of detrital quartz grains of igneous or metamorphic origin from their overgrowth cement.

The luminescence intensity of blue, violet and red cathodoluminescence colours displayed by igneous and metamorphic quartz remains stable or changes only slightly during electron bombardment. These may be termed 'long-lived' cathodoluminescence colours. Zinkernagel (1978) developed an improved cathodoluminescence microscope which enabled him to discover short-lived blue, bottle-green and violet luminescence colours in hydrothermal quartz. Another category of α-quartz cathodoluminescence colours ranges from reddish to bluish brown and is characterized by a measurable increase in luminescence intensity during excitation by electrons. This luminescence behaviour occurs in α-quartz of igneous, metamorphic, hydrothermal or diagenetic origin.

The purpose of this paper is, with the help of a high-sensitivity cathodoluminescence microscope (Ramseyer et al., in prep.): (1) to show the wide range of luminescence colours in α-quartz precipitated from an aqueous solution; (2) to show the time-dependent intensity decrease of the short-lived type; and (3) to discuss the origin and significance of the luminescence colours found in α-quartz crystallized from aqueous solutions. The cathodoluminescence of α-quartz originally crystallized from a melt is not considered further.

Methods

The luminescence behaviour of quartz was examined using a special cathodoluminescence microscope developed for the investigation of low

luminescence intensities (Ramseyer *et al.*, in prep.). Polished thin sections were bombarded with electrons using an energy of 30 keV and a beam current density of 0.4 μA/mm^2. Colour slides of the luminescence features were taken with Ektachrome 400 (27 DIN) colour transparency film and developed at 800 ASA (30 DIN). The exposure times varied from 100 to 150 seconds depending on the objectives used (2.5 × or 6.3 ×). The luminescence colours are described according to their appearance under visual observations. The spectral response of the luminescence was recorded at a speed of 5 nm/sec using a SPEX Minimate monochromator equipped with a Hamamatsu R446 photomultiplier. The monochromator was linked to the cathodoluminescence microscope via a flexible optic fibre bundle. The setting of the entrance and exit slits of the spectrometer determined an effective spectral resolution of 10 nm. The spectra obtained were corrected between 350 and 730 nm for the spectral response of the instrument which had previously been determined by means of a calibrated tungsten lamp. An appropriate exponential decay function was fitted to the observed time-dependent decay of the short-lived luminescence colour using the Marquardt (1963) algorithm.
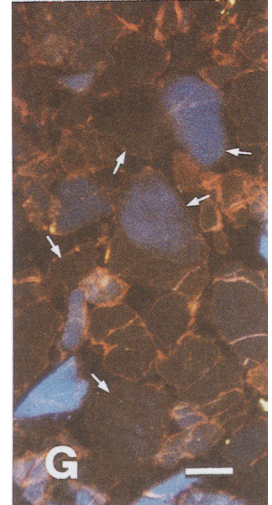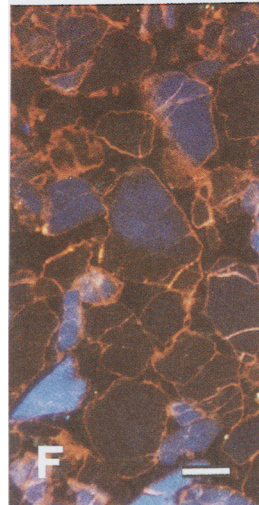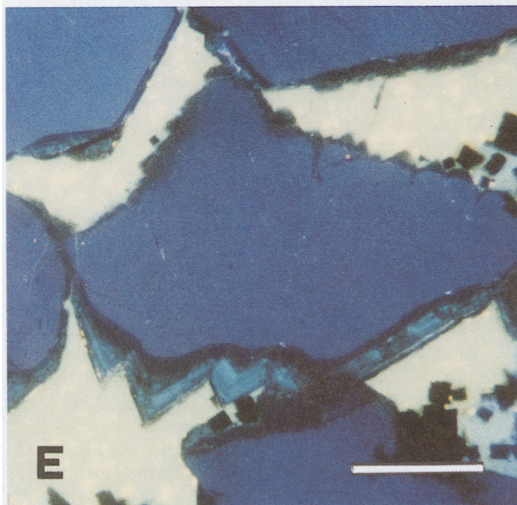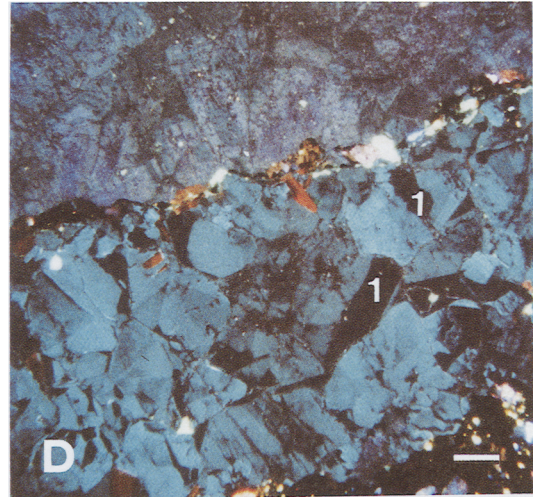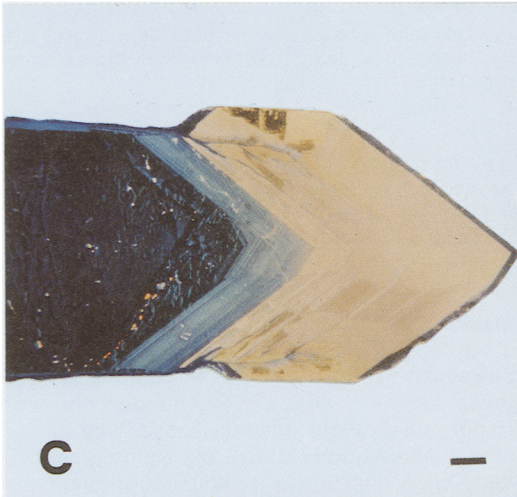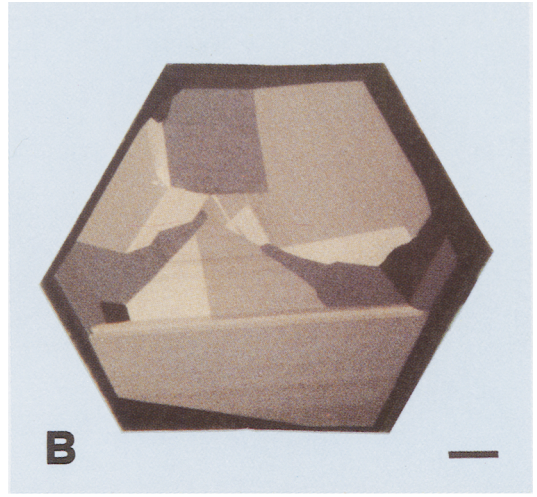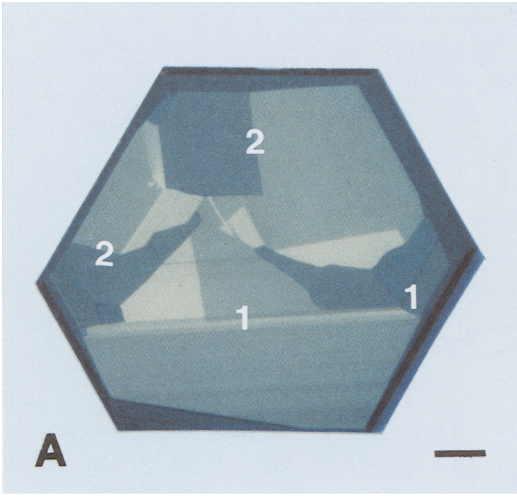
Luminescence colours of α-quartz

SiO$_2$ crystallized as α-quartz, a low-temperature polymorph, exhibits a variety of different luminescence colours. The most common colours of α-quartz are blue, blue–green, bottle-green and brown (Plates 1 and 2). Yellow, pink, violet and red (Plates 1 and 2) luminescence colours are also observed in α-quartz, but are restricted to special occurrences. Non-luminescent α-quartz is less common than suggested by the literature; commonly luminescence can be demonstrated by a high-sensitivity cathodoluminescence microscope (Ramseyer *et al.*, in prep.).

Short-lived and brown luminescence colours and intensity distributions are commonly patchy or zoned. The luminescence patterns produced represent either growth directions (Ramseyer, 1983), twinning planes or areas with a high density of lattice defects (Ramseyer and Mullis, in prep.). Luminescence zones are either sharply defined (Plate 1c) or transitional (Matter and Ramseyer, 1985, Plate 4c).

Short-lived violet, blue, blue–green, bottle-green and pink luminescence colours decay over different time intervals. Time–intensity plots for the blue ($\lambda_{max} = 440$ nm) and for the bottle-green ($\lambda_{max} = 500$ nm) luminescence colour are shown in Fig. 1. The intensity of both bottle-green and blue luminescence colours falls off rapidly within 30 and 45 seconds of electron bombardment respectively. After this initial drastic drop in the luminescence intensity, a much smaller loss in intensity can be observed with time. Intensity decay at short wavelengths is commonly accompanied by a marked increase in luminescence intensity in the yellow-red range (Fig. 2a and b). Time-resolved luminescence spectra at the beginning of, as well as after 4 and 11 minutes of continuous electron bombardment are shown in Fig. 2a and b. The resulting luminescence colours after prolonged electron exposure are different shades of reddish brown (Plate 1b). Alteration of the luminescence in α-quartz is caused by electron bombardment, but similar effects may also be produced by α-radiation and neutron bombardment (Ramseyer *et al.*, in prep.).

PLATE 1. Short-lived luminescence colours in α-quartz. Scale bar is 250 μm. (*a*) Short-lived blue-green luminescence colour (for spectral analysis see Fig. 2*a*) from an idiomorphic vein quartz crystal cut perpendicular to the *c*-axis. Variability in luminescence intensity permits recognition of growth zonations (1) and regions with different growth directions (2). (*b*) Luminescence micrograph from same quartz crystal but after 2 minutes of continuous electron bombardment. The spectrum of this induced brown luminescence colour is shown in Fig. 2*a*. (*c*) Yellow luminescing (for spectral analysis see Fig. 2*c*) sceptre quartz developed as an overgrowth on a prismatic core cut parallel to the *c*-axis, exhibiting a short-lived dark- and light-blue luminescence. The growth in the blue luminescent areas of the crystal is mainly perpendicular to the rhombohedral faces whereas in the yellow luminescent areas, growth is preferentially perpendicular to the prism face. (*d*) Short-lived luminescence colours: bottle-green (lower part) and zoned blue-green (upper part) luminescent fracture quartz. The bottle-green luminescing fracture quartz exhibits clearly defined non-luminescent areas (1) in some crystals. (*e*) Porous quartzarenite cemented by syntaxial quartz over-growths. The detrital dark blue luminescent quartz grains are locally overgrown by zones of blue-green and non-luminescent quartz cement showing a preferential growth perpendicular to the rhombohedra. (*f*) Quartzarenite with red luminescent quartz, both as fracture filling and cement surrounding detrital grains. This photo was taken through an analyser and thus represents only one specific polarization direction of the luminescence light. (*g*) Same field of view as (*f*), but with a 90° rotation of the analyser. Positions marked by white arrows show an apparent local fall in intensity of red luminescence compared with Plate 1*f* due to polarization effects.
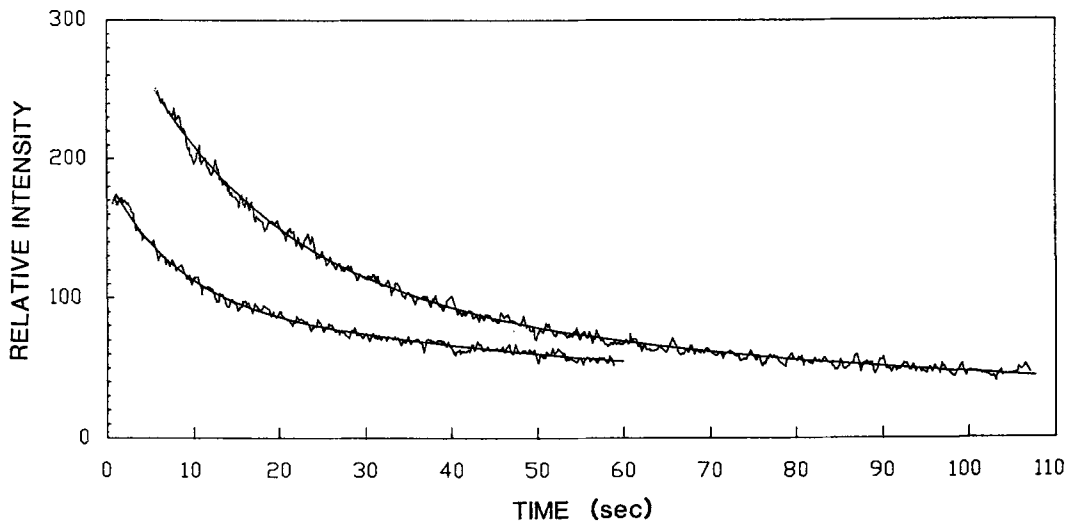
FIG. 1. Time-dependent exponential intensity decay of short-lived luminescence colours: blue (upper trace) and bottle-green (lower trace). The matching curves are those of the exponential decay function given in the text using the parameters from Table 1.

## Occurrence of natural and induced luminescence colours

Blue, blue–green and bottle-green luminescence colours are most common in authigenic quartz overgrowths developed around detrital quartz grains in sandstones (Plates 1e, 2a and f). These colours are also frequently observed in idiomorphic quartz crystals from fractures and veins (Plates 1a and c) and in quartz fracture cements (Plate 1d).

Normally, the luminescence colour distribution is not homogeneous over the whole α-quartz crystal, but forms distinct zones that are either perpendicular to the growth direction (Plate 1a, c and e) or separated by twinning planes (Plate 1a). Furthermore, the short-lived luminescence colours may be replaced along small-scale fractures by a brown colour (Plate 2f).

Different shades of brown luminescence are generally present in authigenic quartz cement which crystallized either subsequently to (Plate 2e) or during (Plate 2f) intense small-scale deformation of the rock. The same phenomenon was described by Dietrich and Grant (1985) in syntectonically-grown quartz fibres. In addition, a dark brown luminescence colour is commonly observed in polygonal quartz subgrains crystallized during plastic deformation (Matter and Ramseyer, 1985, Plate 2a). A similar brown colour is also commonly exhibited by drusy quartz that has grown rapidly (Mullis, 1982) or in quartz domains containing a high density of lattice defects (Ramseyer and Mullis, in prep.). Brown luminescence colour

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PLATE 2. Short-lived luminescence colours in α-quartz. Scale bar is 250 μm. (a) Medium grained quartz-sandstone with pore-filling quartz cement (1). The well-rounded detrital quartz grains (2) exhibit a blue to pink luminescence colour whereas the authigenic quartz cement shows short-lived, mottled, dark blue luminescence. (b) Pore-filling kaolinite (k) in a lithic arkose with volcanic rock fragments (1) and highly-fractured quartz grains (2). The fractures in the detrital quartz grains (generated by overburden pressure) are now cemented with non-luminescent quartz (white arrows). (c) Anhydrite-cemented quartzarenite with short-lived yellow luminescing quartz replacing fibrous anhydrite. The short-lived dark blue luminescence of anhydrite (1) exhibits a growth pattern and is similar to the short-lived dark blue luminescence colour in quartz (Plate 2b; Ramseyer *et al.*, in prep.). (d) Short-lived pink and blue luminescence colours in α-quartz occupying interstices and fibres of a former anhydrite nodule respectively. (e) Dark brown luminescing quartz cement (1) forming overgrowths on well rounded detrital quartz grains (2). These overgrowths pre-date deformation of the rock. (f) Quartzarenite with two generations of authigenic quartz cement. The first bottle-green luminescing generation (1) is followed by a brown, syntectonically-precipitated generation (2) of quartz cement. The first cement generation (1) shows hair-like syntectonic streaks of brown luminescence colour (white arrows).
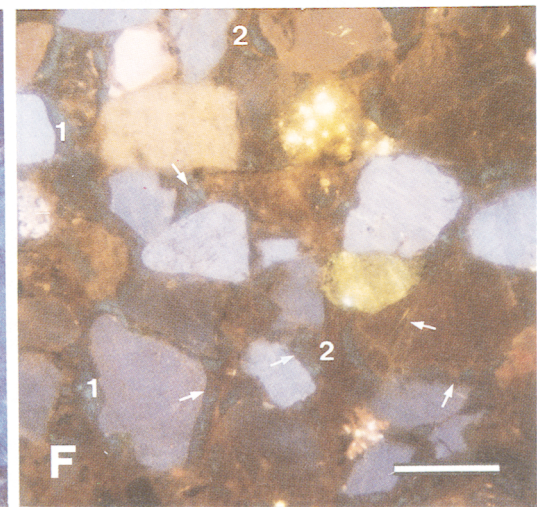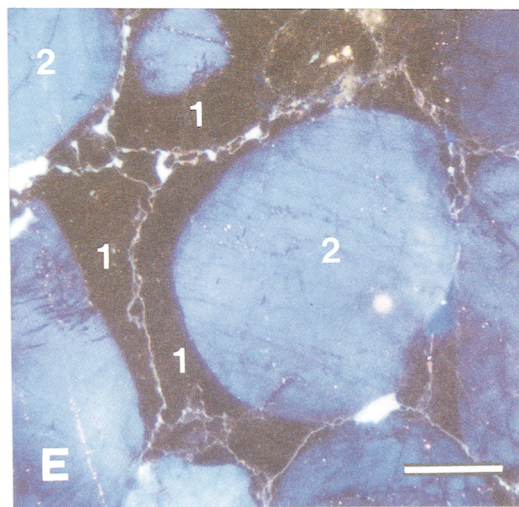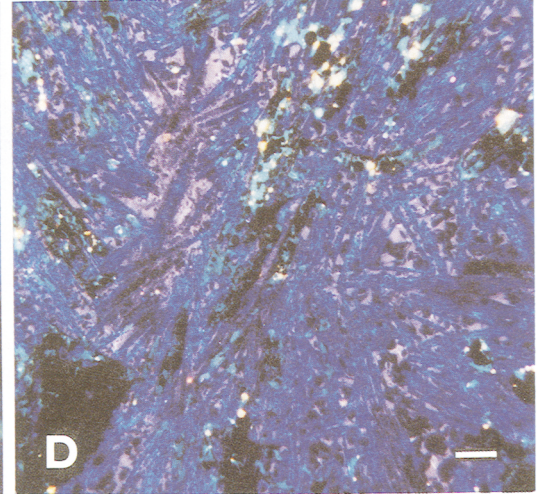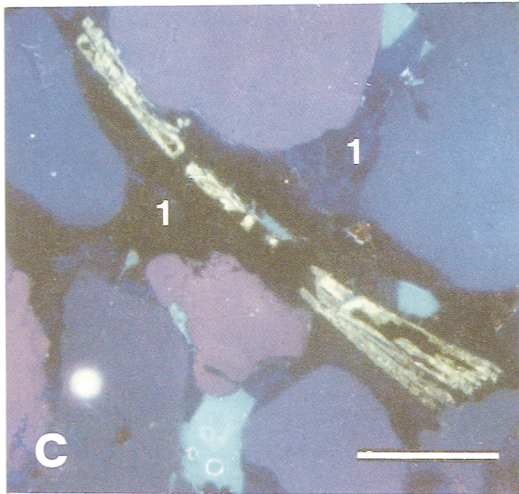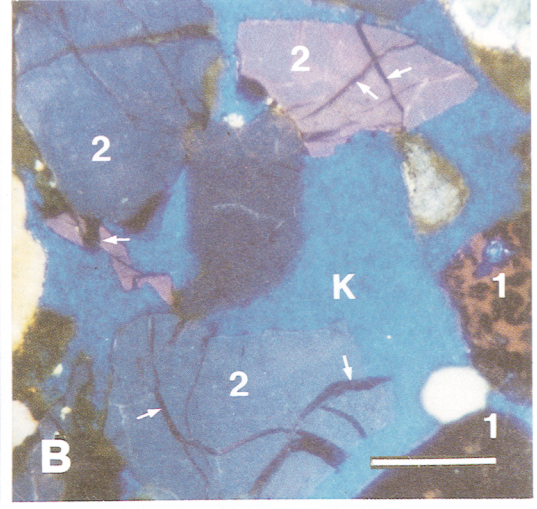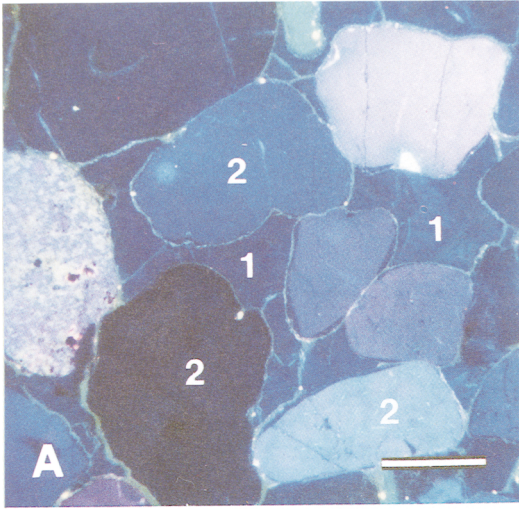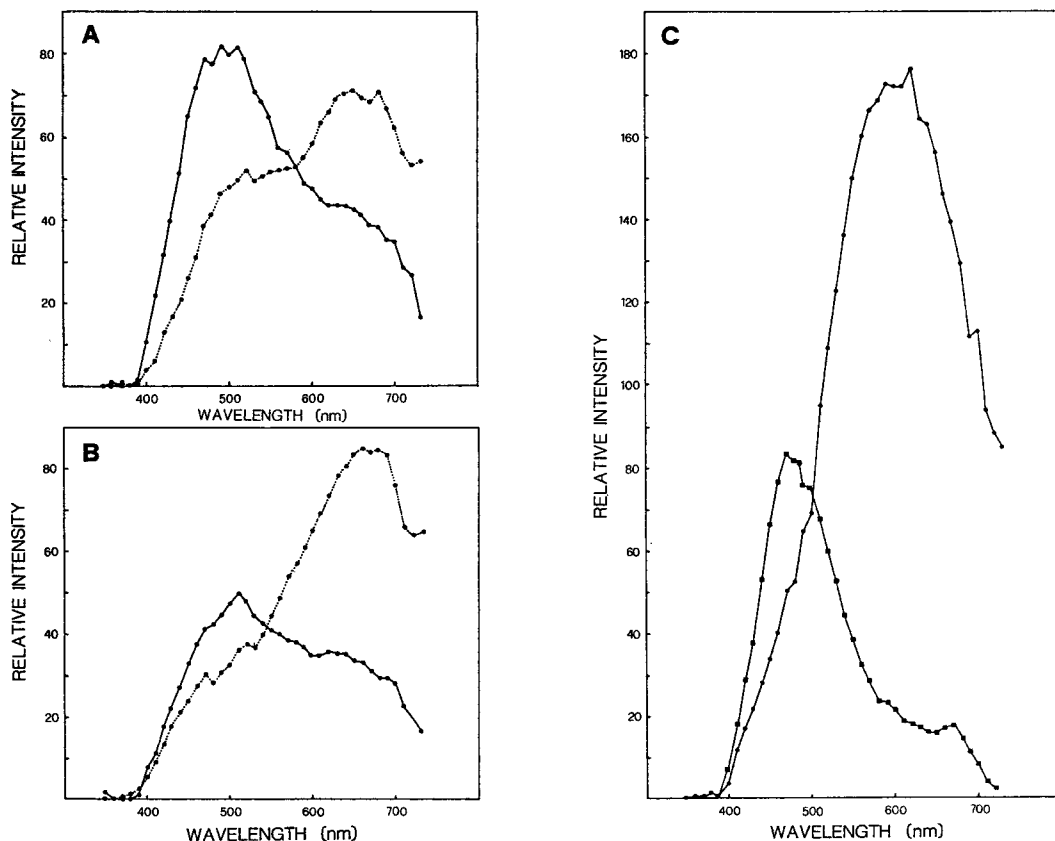
FIG. 2. Spectra of short-lived luminescence colours: blue–green (A), bottle-green (B), blue (C, squares) and yellow (C, dots). Dotted curves denote luminescence spectra taken after 4 minutes (A) and 11 minutes (B) of continuous electron bombardment respectively. All spectra shown are corrected for instrumental intensity response.

haloes are commonly observed in detrital quartz within a range of 28 ± 8 μm around zircon inclusions. These haloes result from α-radiation (Ramseyer et al., in prep). A similar effect can be induced by electron bombardment, where the thickness of colour alteration matches the penetration depth of electrons. Iron- or gallium-doped α-quartz crystals, produced in hydrothermal experiments also exhibit a brown luminescence colour.

Non-luminescent α-quartz occurs rarely, either as distinct growth zones, as patches within luminescent quartz overgrowths (Plate 1e), or as fracture fillings in rocks and individual grains (Plate 1d). Non-luminescent α-quartz is also found as an anhydrite replacement (Plate 2d).

The natural occurrence of yellow, pink and red luminescence colours in α-quartz is very restricted. A yellow luminescence colour is common in α-quartz replacing sulphate minerals (Plate 2c), in quartz formed under fumarolic conditions and in amethyst crystals with sceptre habit (Plate 1c). A red luminescence colour was noted in α-quartz formed by devitrification of ignimbrites (Matter and Ramseyer 1985, Plate 1e). Red luminescing quartz was observed as hair-like fracture fillings within and around detrital quartz grains in sandstones adjacent to volcanic sills and dykes, such as shown on Plate 1f.

The only example of pink luminescence colour in α-quartz found to date occurs occupying the interstices between short-lived blue luminescing α-quartz crystals which may be interpreted as anhydrite replacements (Plate 2c).

Origin of luminescence colours in α-quartz

Despite numerous studies, the origin of the cathodoluminescence colours in α-quartz is still not resolved. The phenomenon has been attributed

to the presence of trace elements (Claffy and Ginther, 1959; Pott and McNicol, 1971; Mitchell and Denure, 1973; Sprunt, 1981), to lattice ordering (Zinkernagel, 1978), to the occurrence of defect centres (Sippel, 1971; Mitchell and Denure, 1973; Jones and Embree, 1976; Koyama *et al.*, 1977; Gee and Kastner, 1980) or to an intrinsic property of the SiO_4^{2-} tetrahedron (Hanusiak and White, 1975; Trukhin and Plaudis, 1979). The trace amounts of elements (other than silica and oxygen) incorporated in α-quartz, as well as the charge-compensating exchange of silica by aluminium or iron with hydrogen, lithium, sodium or potassium, and the additional lack of oxygen, are the main reasons for the difficulty in determining the origin of α-quartz luminescence.

An attempt was made to resolve the origin of luminescence in α-quartz using the cathodoluminescence microscope built by Ramseyer (1983). Luminescence behaviour of α-quartz was investigated after heating, electro-diffusion and electron bombardment.

Brown luminescence colour. Zinkernagel (1978) related the brown luminescence colour of quartz to the degree of lattice order. This supposition was based on the natural occurrence and the artificial production of brown luminescing quartz. Zinkernagel stated that the brown luminescence colour represented a stage of ordering intermediate between the disordered violet luminescent and the ordered non-luminescent quartz. He also suggested that quartz with this degree of ordering is typical of metamorphic, slowly cooled quartz. However, this explanation fails to account for (1) the alteration in luminescence colour caused by high-energy radiation, (2) the alteration in luminescence characteristics induced by continuous electron bombardment, and (3) the results of heating experiments.

The alteration depth of the luminescence colour during artificial electron (Plate 1*a* and *b*) or natural α-particle bombardment (Plate 2*c*) depends primarily on the penetration depth of these particles in quartz. This is demonstrated by the natural 28 ± 8 μm alteration zone surrounding zircon inclusions in quartz (Ramseyer *et al.*, in prep.) and by the alteration depth of the luminescence caused by continuous electron bombardment (Ramseyer, 1983).

Heating experiments with quartz crystals exhibiting an artificial brown luminescence colour revealed that, after heat treatment, the intensity of the brown colour decreased substantially in comparison with that of untreated samples (Ramseyer and Mullis, in prep.). The lower intensity of the brown luminescence after thermal treatment ($> 600\,°C$) implies that the brown luminescence

colour is not the result of elevated temperature and is, therefore, not indicative of tempering. Evidence supporting this is given by Sprunt *et al.* (1978) in their study of the Johnson Spring Formation, where greenschist-grade quartz luminesces in a rusty red and amphibolite-grade quartz in a blue–violet colour.

In the special case of quartz crystals containing a high amount of aluminium (> 500 ppm), a natural or artificial brown luminescence colour (Ramseyer and Mullis, in prep.) was not observed. The visible luminescence colour of these aluminium-rich quartz crystals is different for low and high beam current densities. At the high beam current densities used by all the commercially available cathodoluminescence microscopes or electron microprobes, a blue luminescence colour is generated. In contrast, at the low beam current densities ($\leqslant 0.4$ μA/mm^2) of the Berne instrument, these aluminium-rich quartz crystals are either non-luminescent or exhibit a short-lived dark-blue luminescence colour. However, quartz with a low amount of aluminium (< 500 ppm) luminesces either blue, blue–green, bottle-green, yellow, brown, pink or red or is non-luminescent at low beam current densities, and exhibits a rusty-red colour due to radiation damage when excited with a high beam current density.

The most likely cause of the brown luminescence colour is damage to the quartz lattice induced by particle bombardment. Artificially produced lattice dislocations or formations of unpaired, non-bonding electrons are probably responsible for the brown luminescence colour in quartz. Siegel and Marrone (1981) recorded the formation of the 650 nm photoluminescence peak in quartz after exposure to a cobalt-60 radiation source. This they interpreted as the effect of dangling non-bridging oxygen ions generated by irradiation of the quartz lattice. Their interpretation is further supported by the occurrence of the brown luminescence colour in (1) quartz crystals grown during separation of a gaseous phase after pressure release (Mullis, 1982), (2) quartz crystallized during deformation (Plate 2*f*), or (3) quartz with mechanically induced lattice defects at rock fractures. The fact that these defects are randomly distributed in the quartz lattice may explain the broad nature (half width = 150 nm) of the 650 nm peak (Fig. 2*a* and *b*) and the lack of polarization of the brown luminescence light.

Short-lived blue, blue–green and bottle-green luminescence colours. The most typical characteristic of these two short-lived luminescence colours is their continuous decline in intensity during electron bombardment, as discussed above and shown

in Fig. 1. The intensity decay can be described by the following equation,

$$I(t) = I_1 * e^{-t/T_1} + I_2 * e^{-t/T_2}$$

where $I(t)$ is the intensity at time t and I_1 and I_2, and T_1 and T_2 represent the zero intensity and the decay constant of the first and second decay process respectively. The decay constants for the blue and bottle-green short-lived luminescence colours, summarized in Table 1, are different for the faster process, but the same within experimental error for the slower decay process. Intensity decrease during electron bombardment is, as mentioned earlier, restricted to the penetration depth of the exciting electrons and is matched by an increase in the yellow–red range of the spectrum.

Table 1. Parameters of the best-fit dual exponential decay function for short-lived bottle-green and blue luminescence colours. Zero intensity (I_1, I_2) and decay constant (T_1, T_2) are given in seconds.

COLOUR	I_1	T_1	I_2	T_2
BOTTLE-GREEN	90.4	7.9	95.5	109.8
2σ-error	±3.3	±0.6	±3.8	±10.5
BLUE	212.6	16.3	102.4	126.7
2σ-error	±4.6	±0.8	±6.3	±11.1

The bottle-green and probably the blue and blue–green luminescence light is linearly polarized with a plane of polarization parallel to the crystallographic c-axis of the quartz.

Ramseyer (1983) noted that the short-lived bottle-green luminescence colour in a syntaxial quartz overgrowth cement could be enhanced by heating the sample for one week at 700 °C. Furthermore, the short-lived luminescence colour which was destroyed during electron bombardment can be restored by heating the quartz for one day at 500 °C (Ramseyer and Mullis, in prep.). This behaviour of the short-lived cathodoluminescence colours is the opposite effect as known from thermoluminescence, where heating destroys and particle bombardment regenerates the luminescence. The recovery of the short-lived luminescence colour by heat treatment is restricted to areas which exhibited a short-lived luminescence colour before the treatment. These experiments reveal that thermal treatment alone is not the cause of the short-lived blue and bottle-green luminescence. These colours are, therefore, due to an inherent property of the quartz crystal.

Electrophoresis experiments have shown that interstitial ions present in the quartz lattice can diffuse along lattice channels parallel to the c-axis

(Brunner *et al.*, 1961). Quartz crystals subjected to this treatment and cut parallel to the c-axis reveal, under luminescence, a transitional zone between brown and bottle-green luminescing regions (Fig. 45 in Ramseyer, 1983). This zone exhibits a bell-shaped form convex towards the negative potential.

Zinkernagel (1978) stated that short-lived luminescence colours in quartz produced in the laboratory were unrelated to the composition of the aqueous solution from which they grew. Also, the oxygen vacancy defect centre seems not to be responsible for the bottle-green or the blue luminescence colours, as this centre produces a strong luminescence signal only in the ultraviolet range at 260 nm (Jones and Embree, 1976). Similarly, the known intrinsic luminescence centre of the SiO_4^{-} tetrahedron, responsible for a peak in the blue range at 447–465 nm, does not match the short-lived nature of the bottle-green and blue luminescence colour (Hanusiak and White 1975; Trukhin and Plaudis, 1979).

In summary, the effects of the various treatments discussed above on the behaviour of the short-lived blue and bottle-green luminescence colours are best explained by luminescence centres which are related to interstitial cations in the channels parallel to the c-axis of the quartz lattice. Additional support for this interpretation are the results of Remond *et al.* (1979), who assume that intensity decrease during continuous electron bombardment is produced by ionization-enhanced diffusion of luminescence centres.

Yellow luminescence colour. The yellow luminescence colour (Plates 1*c* and 2*c*) is also short-lived, as indicated by the decrease of intensity during electron bombardment. However, the linearly polarized yellow luminescence light has a plane of polarization perpendicular to the crystallographic c-axis of quartz. This orientation is in contrast to the short-lived blue and bottle-green luminescence colours. Heat treatment of yellow luminescing α-quartz whose luminescence intensity had been reduced by electron bombardment, for one hour at 600 °C restored the original luminescence colour and intensity.

Yellow luminescing authigenic α-quartz is observed in amethyst crystals, in quartz grown during fumarolic activities and in quartz replacing sulphates crystallized from slightly acidic oxidizing solutions containing sulphate and/or ferric iron. It appears, therefore, that the origin of the yellow luminescence in authigenic α-quartz is related to trace elements incorporated during crystallization from oxidizing solutions. However, the observation by Pott and McNicol (1971) of a red luminescence colour with peaks at 695

and 727 nm in quartz containing ferric iron (0.01 to 0.1% Fe^{3+}) suggests that ferric iron is not the primary cause of yellow luminescence.

Red luminescence colour. The only occurrences of red luminescing α-quartz were observed in devitrified ignimbrites (Plates 1*d* and *e* in Matter and Ramseyer, 1985) and fracture fillings in sandstones close to basalt intrusions (Plate 2*f*). The main characteristics of the red luminescence colour are its long-lived character and the linearly polarized nature of the luminescence light. The plane of polarization of the luminescence light is, as in the case of the yellow luminescence colour, perpendicular to the crystallographic *c*-axis of the quartz (Plate 2*f*).

Heating red luminescing α-quartz for one hour at 600 °C produced only a decrease in luminescence intensity and had no effect on the luminescence colour. Moreover, the red luminescence colour was still present even after $1\frac{1}{2}$ hours of continuous electron bombardment. Sprunt (1981) and Pott and McNicol (1971) concluded that ferric iron in trace amounts in the quartz lattice causes a red luminescence colour with a broad double-peak at 645 nm and at 725 nm.

Conclusions

The study of luminescence of authigenic α-quartz using an improved cathodoluminescence microscope enables the photographic and spectrometric recording of very faint luminescence colours. The distribution of the luminescence colours reveals growth zonations, twinning patterns, fractures in quartz grains and detrital grain shapes as well as syntaxial quartz cements.

Three main categories of luminescence colours are distinguished on the basis of their stability and intensity behaviour during electron bombardment: (1) short-lived, rapidly-fading violet, blue, blue-green, bottle-green and yellow luminescence colours; (2) long-lived brown luminescence colours with increasing intensity; and (3) long-lived, red luminescence colour with an approximately stable intensity.

The short-lived violet to yellow cathodoluminescence colours appear to be related to cations located either in the channels parallel to the *c*-axis or in silicon sites within the quartz lattice.

The long-lived brown luminescence colour is produced by lattice defects (nonbonding Si–O) and the red colour reflects trace amounts of ferric iron (Pott and McNicol, 1971; Sprunt, 1981).

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