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RAPID COMMUNICATIONS

Complex quartz growth histories in granite revealed by scanning cathodoluminescence techniques

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Abstract

A scanning electron microscope based cathodoluminescence technique utilizing a novel collector system reveals complex internal heterogeneities within granitic quartz grains. The technique overcomes the low intensity and limited variation in cathodoluminescence generated by quartz, which hamper conventional cathodoluminescence analysis. Detailed images of zoning patterns in quartz are comparable to those observed in minerals such as feldspar, and attributed to a combination of progressive growth, boundary layer effects and mineral–melt disequilibria produced during fluctuations in melt composition and temperature during the crystallization interval. We attribute such mineral–melt disequilibria to open system, mixing behaviour in the granite plutons sampled.

1. Introduction

Internal heterogeneities and zoning within quartz are normally invisible to conventional optical microscopy and rarely documented by quantitative analysis. Cathodoluminescence (CL) microscopy, which images photons emitted when a sample is irradiated by an electron beam, has been applied successfully to distinguish detrital quartz grains from their diagenetic overgrowths in sedimentary rocks (e.g. Smith & Stenstrom, 1965; Marshall, 1988). However, the weak luminescence and only miniscule intracrystalline variability in igneous quartz, combined with the limited spatial resolution of conventional optical CL systems, has meant that details of growth histories of quartz in granite, a phase which typically accounts for one third of such rocks, are greatly limited. In this paper we outline results of applying a recently established technique to the study of quartz grains which combines the imaging attributes of a specially adapted scanning electron microscope with CL methodology. The high resolution of the system can distinguish minor intracrystalline variations in CL which reveal complex zoning. In our samples, we attribute such zoning patterns to a combination of progressive growth, boundary layer effects and episodes of mineral–melt disequilibria resulting from fluctuations in melt composition and temperature during the crystallization interval. In turn, we relate such process to open system behaviour within host plutons. It is not our aim in this paper to provide a detailed explanation of the underlying, complex causes of variable luminescence in quartz, a matter which remains the subject of some debate (e.g. Waychunas, 1988; Marshall, 1988; Fisher, Hayes & Stoneham,1990; Gorton, Walker & Burley, 1996), but to demonstrate the application of the technique to geological investigations and provide some insight into the wealth of data that can be achieved from such studies.

2. Cathodoluminescence imaging

2.a. Imaging techniques

Structural and/or chemical variations within crystals, which may relate to crystal growth zones, can be identified by spatial variations in wavelength and intensity of cathodoluminescence (e.g. Waychunas, 1988; Marshall, 1988; Finch, 1992). However, because quartz, exhibits little intracrystalline variability and typically luminesces only weakly, and because most conventional CL apparatus lacks the ability to scan or undertake spectroscopic analysis, little detail is commonly afforded from CL studies of this very common and important mineral. In this study, images were obtained from quartz grains using a JEOL JSM-840 scanning electron microscope (SEM) running at an accelerating voltage of 20 kV, fitted with an Oxford Instruments retractable Mono-CL detector. A parabolic mirror (placed under the pole-piece) above the sample, symmetric around the electron beam axis, enabled a high proportion of the small photon flux generated to be collected and directed to a photomultiplier tube for polychromatic imaging or through a scanning monochromator to select a particular narrow waveband (Fig. 1). This system has a significantly enhanced collection efficiency (*c.* 80%) for emitted photons compared to conventional CL (*c.* 1%), allowing even the low signal levels generated by quartz to be significantly raised above background noise while the scanning technique allows repeated frame integration to further increase signal to noise ratios. Increased signal collection also enables smaller probe currents to be used than are common in conventional flood gun systems, thereby enhancing spatial resolution (≤1 μm) and reducing electron beam damage to samples. The combination of improved collection, scanning facility and focused beam therefore avoids inherent problems for detailed image aquisition associated with conventional systems (Marshall, 1988). The instrument (Fig. 1) has the facility to generate both polychromatic (all wavelengths) and monochromatic (i.e. a selected narrow waveband) images and spectra. All images used in this study are polychromatic, which reveal the variation in total CL intensity. We have also carried out monochromatic imaging of individual narrow wavebands and compared the relative intensity of emission. In our study, the igneous quartz grains, in common with synthetic silica, mainly luminesce in blue wavelengths (cf. Waychunas, 1988; Gorton, Walker & Burley, 1996).

The three photomicrographs in Figure 2a–c show part of the same quartz grain and illustrate the potential of the SEM–CL technique. Figures 2a (transmitted light) and 2b (backscattered electron image) clearly pick out the quartz grain boundary but do not reveal any internal features of the grains. In contrast,

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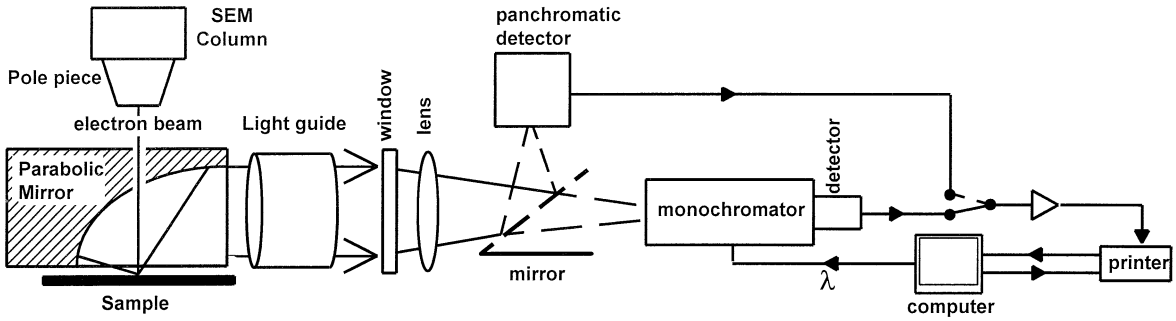


Figure 1 Schematic illustration of instrumentation used to acquire scanning cathodoluminescence images.

Figure 2c (SEM–CL image) reveals a brighter core region to the grain and darker mantle resulting from variations in total luminescence emitted from different parts of the grain.

2.b. Possible causes of CL variation

Quartz luminesence typically occurs in both blue and red wavelengths. Red emissions have been ascribed to minor Na and OH impurities (Waychunas, 1988). Blue luminesence is present in synthetic quartz with very low impurity levels, indicating that it is intrinsic feature of the quartz itself (Waychunas, 1988). The root cause of *variable* CL emission within a crystal (both in terms of different wavelengths, their relative intensities, and overall emission) from materials such as quartz is more problematic, and has not been unequivocably established, but could result from one or a combination of mechanisms (Waychunas, 1988; Marshall, 1988; Fisher, Hayes & Stoneham, 1990; Gorton, Walker & Burley 1996). Possible contributary factors include the presence of minor chemical impurities (e.g. Al, Na, OH) acting either directly changing CL characteristics as a result of chemical variation, or indirectly causing defects in the crystal lattice; trapped electron hole pairs; or oxygen vacancies. Alternatively, non-compositionally controlled lattice defects might themselves effect CL variation.

Trace element concentrations within the quartz grains in this study are below electron microprobe detection limits, but ion microprobe (SIMS) analyses (Table 1) do reveal some compositional variation. Aluminium and titanium, both suggested CL activators in quartz (Marshall, 1988), are the main trace elements present. Al substitutes for Si in tetrahedral sites in quartz accompanied by charge compensation through incorporation of cations (Dennen, Blackburn & Quesada, 1970), including Na^{+} and Ca^{2+} which show a positive correlation with Al in our samples. Fe, Mn, Ca and Na, also considered potential activators and/or inhibitors (e.g. Marshall, 1988), occur in very low concentrations. The observed systematic co-variation on a grain scale might indicate some possible link between trace element concentration and CL signal. Other workers have reported similar Al zoning in quartz and systematic variations in Al content between bright and dark zones in CL images (I. Henderson, Univ. Leeds, unpub. data). The variable intensity of luminescence in image 1 (Fig. 2c) could therefore relate to minor, possibly Al controlled, compositional variation. Systematic elemental variation parallel to crystal growth zones in minerals commonly results from changes in crystallization conditions and melt composition during growth. Alternatively, the variations in trace element abundance and luminescence may be simply coincidental and crystal lattice defects related to growth rate may be playing an important role. Whatever the precise cause, we interpret the parallelism between bands showing variation in CL intensity and facets of the crystal as recording crystal growth stages. In turn, we attribute these differing growth stages to indicate minor changes in crystal composition or structure which developed during growth.

3. Complex zoning patterns from quartz grains in granite

Samples illustrated in this study were collected from the south-west granite complex of Jersey (Channel Islands, UK). Textural evidence (Pembroke & D'Lemos, 1996), including complex growth patterns in feldspars, resorbed and pseudomorphed grains, mixed feldspar populations and small-scale modal and textural heterogeneity, all indicate that magma mixing was an important process in the petrogenesis of these felsic plutonic rocks (cf. Wager *et al*. 1965; Hibbard, 1991).

Image 2. Image 2 (Fig. 2d), obtained using the SEM–CL technique, displays numerous alternating brighter and darker bands mainly concentrated in the outer 300 microns of the grain. Individual bands are parallel to crystal facets and range between 5 and 30 microns across. Often, there is a gradational transition in luminescence from weak to stronger, followed by an abrupt return to weak luminescence. The patterns are reminiscent of fine-scale oscillatory zoning commonly

Table 1. Selected elemental concentrations (ppm) in two quartz grains

Grain A (Image 2)	Q10 (core)	Q11	Q12	Q13	Q14	Q15	Q16 (rim)
Al	97.8	90.4	96.5	109.0	92.2	86.2	95.4
Ti	94.5	94.3	82.6	78.9	80.6	69.7	71.5
Mg	1.1	1.5	0.9	0.9	0.9	8.2	0.9
Fe	5.8	4.3	1.5	3.6	3.4	3.2	1.8
Mn	0.3	0.2	0.2	0.2	0.2	0.2	0.3
Ca	2.5	2.2	2.0	2.7	2.0	2.2	3.9
Na	2.3	1.9	2.2	2.3	2.0	2.1	1.9
Grain B (Image 4)	Q3 (core)	Q4 (core)	Q5 (core)	Q6 (rim)	Q7 (rim)	Q8 (rim)	Q9 (rim)
Al	92.8	196.0	205.0	86.2	88.6	96.1	86.6
Ti	90.9	84.7	87.0	83.6	77.7	65.2	81.1
Mg	0.9	1.0	1.3	1.6	1.5	0.8	0.8
Fe	1.0	5.7	6.6	3.6	6.6	1.8	0.7
Mn	0.2	0.3	3.0	0.2	0.2	0.2	0.2
Ca	2.9	3.7	3.9	2.0	2.3	3.0	2.6
Na	3.3	4.7	5.4	2.3	2.4	3.2	2.8

Determined by Cameca ims-4f ion microprobe using an O- primary beam (10 keV accelerating voltage, 20 nA primary beam current) and spot size of approximately 3040 mm. Analyses were performed for Na23, Mg24, Al27, Ca40, Ti48, Fe54 and Mn55. V51 and Cr52 abundances were below detection. Data normalized to an Si value of 4.67 x 105 ppm and calibrated against glass standard NBS610. Typical errors = 1–5 % at 5 ppm levels, 0.1–0.3 % at 100 ppm levels. Analyses 10–16 (grain A) represent a core-to-rim traverse.

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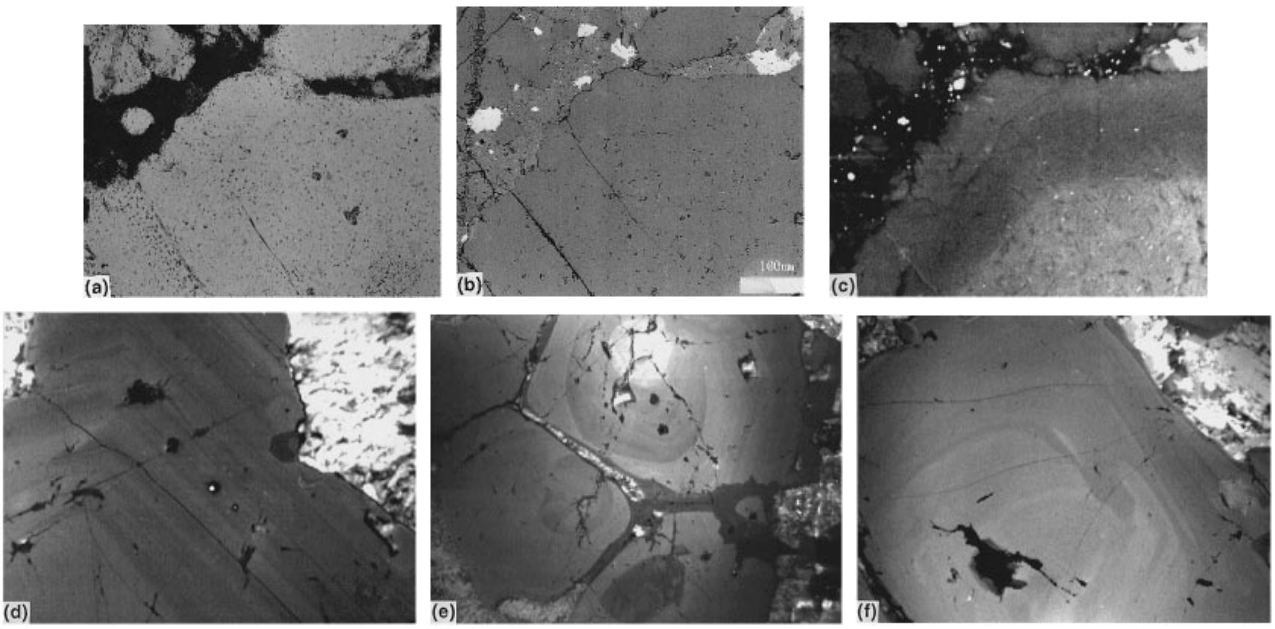


Figure 2. (a–c) Comparative images of the outer portion of a quartz grain in a granite using (a) cross-polarized transmitted light, (b) backscattered electron imaging and (c) scanning cathodoluminescence (image 1). The internal variation in tone shown by the quartz grain using scanning CL relates to different intensities of luminescence (mainly in blue wavelengths) resulting from minor, optically undetectable variation in composition/structure of the quartz grain. Field of view long axes = 0.5 mm. (d) Image 2. Scanning CL image showing sub-parallel oscillatory growth zones in the outer 300 micron portion of a quartz grain from granite. Minor imperfections and non-parallelism of some zones result from local variation in growth rate, while rhythmic pattern results from small changes in boundary layer composition due to relative crystal growth–boundary layer diffusion rates. Growth zones abut against adjacent feldspar (brightly luminescing, upper right). This occurred when the growing grain contacted with the feldspar along part of its boundary causing parts of the crystal to cease growth, while other parts continued outward growth. Field of view long axis = 0.7 mm. (e) Image 3. Scanning CL image of quartz grains in granite revealing distinct core and mantle structure. The cores to some grains are sub-rounded and faint internal growth zones are truncated by the core–mantle boundary. The mantle shows oscillatory growth zones. The features result from initial growth of the quartz grain, partial resorption (dissolution) during a period of disequilibrium, then further growth to form the mantle. The weakly luminescing outermost rim to each grain comprises quartz which luminesces in the red wavelengths and may have formed under sub-solidus conditions. Brightly luminescing areas within grains result from mineral inclusions. Field of view long axis = 5.9 mm. (f) Image 4. Scanning CL image of granitic quartz grain showing complex convolute core–mantle boundary. Truncation of core growth zones, and irregular nature of boundary, result from partial resorption of a quartz xenocryst within an enclosing granitic melt due to disequilibrium. Field of view long axis = 0.9 mm.

observed in many minerals. Such cyclicity and repetition is indicative of geochemical self-organization (Sibley *et al*. 1976; Pearce & Kolisnik, 1990) where crystal growth leads to a shift in boundary layer composition, leading either to incorporation of other elements or in restricted growth, in turn resulting in punctuated growth. Growth is resumed when diffusion within the boundary layer allows the melt composition to return to the liquidus. This takes place during periods of only minor variation in bulk melt chemistry. The fine oscillatory zoning continues to the outer part of the crystal. Where the crystal has impinged upon, and become moulded around, a neighbouring grain (a feldspar), the growth zones continue to mimic the quartz facets, and are clearly unrelated to the final grain shape. Minor truncations and discontinuities are visible at edges. These probably result from slight differences in growth rates of different faces and local self-organization (cf. Pearce & Kolisnik, 1990).

Image 3. The grains shown in Figure 2e exhibit dark, weakly luminescent core regions, sharply bounded by slightly curvilinear surfaces which separate them from brighter luminescing mantles. The abrupt change from the core to the mantle indicates a marked change in composition or structure. The core region in the upper grain contains a number of slightly lighter (more luminescing) regions, similar to those in image 2. These apparently represent oscillatory zoning which is truncated by the mantle. The presence of internal discontinuities 'cross cut' by outer zones is strong evidence that the mantle formed later and that original grain boundaries have undergone resorption (dissolution). Such boundaries tend to be gently curved and the majority of resorption has been concentrated along crystal edges where the melt–crystal surface area ratio would have been greatest. Similar patterns have been observed in feldspars interpreted as resulting from juxtaposition of the grain with a melt with which it is not in equilibrium (cf. Donaldson, 1985; Pearce & Kolisnik, 1990). We hence interpet the growth history revealed by image 3 as resulting from two distinct periods of growth under differing magma conditions. Initial growth gave rise to a core, which after a period of peripheral dissolution was followed by mantle growth.

The grains are rimmed by a narrow zone of distinctly less luminescent material. Monochromatic imaging over a range of selected wavelengths, and small area spectral analysis of these rims and also transgranular fractures, show that they mainly luminescence in red wavelengths contrasting with the mainly blue luminescence of the main body of the grains. We attribute them to low temperature, sub-solidus alteration. The mantle of the large grain exhibits weak oscillatory zoning with growth zones paralleling the growing crystal surface. At the right side of the grain, the oscillatory growth zones terminate abruptly against the grain rim. The most likely explanation for this

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feature is that the growing grain impinged on another during growth, so that no further growth took place along this face.

Image 4 . The grain depicted in Figure 2f shows a markedly lobate boundary between a brightly luminescing core and darker mantle. The boundary truncates internal zoning and apparently records a period of resorption. High aluminium contents were recorded in the irregular core of the grain (Table 1). The large variations in aluminium content, coupled with disequilibrium textures indicating periods of dissolution indicate that this quartz grain grew in two stages and in contact with melts of different composition. If elevated aluminium contents in quartz reflect growth at high temperature, as suggested by Dennen, Blackburn & Quesada (1970), then the core of the grain formed in equilibrium with a higher temperature magma, and later either came into contact with a melt of different composition or began to dissolve due to adiabatic melting on decompression to be followed by crystallization of a lower temperature mantle.

4. Discussion

The SEM–CL images reveal internal heterogeneity in granitic quartz grains interpreted as arising from compositional and/or related structural variation. The form of the zoning patterns clearly relate to episodic crystal growth and sporadic dissolution. We consider the patterns to result from primary igneous rather than sub-solidus recrystallization processes since quartz grains grown at low temperatures (particularly from hydrothermal solutions) mainly luminesce in red wavelengths whereas those studied here predominantly luminescence in the violet to blue spectrum, typical of cores of detrital grains in sediments and igneous grains in general (e.g. Smith & Stenstrom, 1965). Furthermore, the patterns produced are closely analogous to those observed in igneous feldspars (e.g. Pearce & Kolisnik, 1990) in that the growth patterns and truncations observed between zones are consistent with outward growth from a core or resorption at a crystal–liquid interface, rather than solid-state replacement or recrystallization from the rim inward.

Wide zones with transitional boundaries (e.g. Fig. 2) are attributed to progressive changes in melt composition or temperature through time. This could have been induced through fractional crystallization of the melt, or perhaps quasi-continuous open system addition of melt. The regular oscillatory zoning observed is attributed to punctuated growth of a grain growing under near-equilibrium conditions but where growth is largely controlled by diffusion within the boundary layer, i.e. due to local chemical self-organization. The sluggish diffusivity of Al_2O_3 and SiO_2 in granitic melts may be an important influence here.

Abrupt and marked zone boundaries in quartz grains indicate significant variations in melt composition and/or temperature during the crystallization interval, and are likely to have been environment-controlled rather than due to local self-organization. Erratic temperature fluctuations are unlikely since the plutons are large (greater than tens of cubic kilometres) and would hence cool at slow, continuous rates. Often in granites, marked zonation patterns in feldspars are attributed to the transport of the feldspar grains into a different environment, either during ascent or due to convection within the pluton or magma mixing (e.g. Anderson, 1984; Hibbard, 1991). A similar xenocrystal origin seems likely for the growth patterns in several quartz grains illustrated here. Quartz grains crystallizing in equilibrium became mixed with new magma leading to disequilibrium with their host and resorption. In some cases, physical transport of the crystal into new melt is unlikely because textural evidence indicates that significant solidification and development of a crystal framework had taken place, preventing crystal movement, prior to resorption. In such cases it is more likely that disequilibrium was induced by melt infiltration into the developing crystal mush (cf. D'Lemos, 1992; Petford *et al.* 1996). Both processes can be attributed to open system mixing processes in which magma is progressively added to the pluton during pluton construction (e.g. Pembroke & D'Lemos, 1996).

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