Petrogenesis of plagioclase phenocrysts of Mount Etna, Sicily, with particular reference to the 1983 eruption: contribution from cathodoluminescence petrography

D. Stirling, A. M. Duncan*

Centre for Volcanic Studies, University of Luton, Park Square, Luton LU1 3JU, UK

J. E. Guest

Planetary Image Centre, University College London, London NW7 4SD, UK

AND

A. A. Finch

Dept. of Environmental Sciences, University of Hertfordshire, Hatfield AL10 9AB, UK

ABSTRACT

The cathodoluminescence (CL) characteristics of plagioclase phenocrysts in water-quenched lavas from the 1983 eruption of Etna have been investigated to examine the application of plagioclase CL to the study of magmatic processes. The phenocrysts have a green luminescent inner zone that is sharply bounded by a blue luminescent outer zone, with the boundary often coinciding with a concentric zone of glass inclusions.

Strong compositional differences between the green (An_{70}–An_{75}) and blue (An_{50}–An_{60}) luminescent areas are interpreted as the result of two phases of growth under differing conditions. The green luminescent cores are considered to be anorthite-rich cumulate crystals from a basic magma which have been disrupted by the injection of a more evolved melt, resulting in heterogeneous nucleation and crystallization of the outer blue luminescent zone. The relationship between the CL and the trace element contents of the plagioclase crystals is discussed.

KEYWORDS: cathodoluminescence (CL), plagioclase, Etna, magmatic processes.

Introduction

MOUNT Etna volcano, Sicily, is one of the most active volcanoes in the world and provides an opportunity to investigate the petrology of a dynamic magma system. The basaltic lavas of Etna are typically strongly porphyritic with abundant plagioclase phenocrysts. The plagioclase phenocrysts are strongly zoned and often possess concentric bands of inclusions; they show considerable evidence of resorption, and are compositionally heterogeneous (Cristofolini and

Tranchina, 1980; Cristofolini and Romano, 1982; Chester *et al.*, 1985). These features suggest that the plagioclase phenocrysts of any given lava are not simply the result of crystallization from a single magma under a specific set of conditions, but must have grown under varying conditions of temperature and pressure and/or have been derived from magmas of different composition.

The 1983 eruption of Etna was long lived and the quiescent, effusive nature of the activity along the fissure vent-system enabled easy access for observation and sampling (Guest *et al.*, 1987). Quenched samples of lava from the 1983 eruption were collected to investigate the state of crystallinity of the lava at eruption. The plagioclase

Editorial handling: A. M. Clark
* author for correspondence

phenocrysts have been studied using CL petrography, electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS) in order to gain a better insight into petrogenetic processes prior to eruption. The study of these quenched samples allows investigation of the features revealed using CL, which are wholly attributable to primary crystallization processes, as quenching eliminates post-crystallization processes such as ordering and metasomatism.

Analytical methods

Cathodoluminescence petrography

Three polished 60 μm thin sections of lavas from the 1983 eruption of Etna were studied using CL petrography. The samples were examined using a Technocyn Mk3 flood-gun cold-cathode luminoscope, mounted on a petrological microscope with a camera attachment. Working conditions were maintained at 550 to 600 μA and 14 kV, corresponding to a power density of 50 kWm^{-2}. Examination times of <5 min were favoured, to reduce the effects of sample heating which can cause degradation of the mounting media, particularly important for highly vesiculated samples.

Electron probe microanalysis

Electron microprobe analyses were carried out on polished and carbon coated thin sections. Cathodoluminescence photographs of areas of particular interest were used to select the location of the EPMA and SIMS analyses. Analyses were made using an EPSRC supported Cameca SX51 electron microprobe in the Department of Chemistry, University of Aberdeen. Analyses were made by wavelength-dispersive techniques and a PAP correction routine applied. An accelerating potential of 20 kV and 20 μA and a beam size of 10 μm was used. The spectrometers were calibrated for the elements Si, Al, K, Na, Ca, Mg, Mn, Ti and Ba using the following standards: albite (for Na), almandine garnet (Al, Mg and Fe), orthoclase (K), wollastonite (Si and Ca), benitoite (Ba and Ti) and rhodonite (Mn). Oxygen contents were estimated by stoichiometry.

Ion probe analysis

Secondary ion mass spectrometry (SIMS) analyses were performed on a Cameca ims-4f ion probe at the Department of Geology and Geophysics, University of Edinburgh. A polished thin section, with a 60 nm Au coating was analysed. The incident beam comprised $^{16}O^-$ ions accelerated at 14.5 kV with a beam current of 7 nA. The energy offset was 75 ± 20 eV. The minimum spot size was *c.* 700 μm^2 (30 μm diameter), corresponding to a power density of 100 kWm^{-2}. Secondary ions were accelerated into a mass spectrometer where counts of trace elements were ratioed to counts of ^{30}Si. The nuclides examined were ^{7}Li, ^{9}Be, ^{11}B, ^{24}Mg, ^{40}Ca, ^{47}Ti, ^{55}Mn, ^{56}Fe, ^{71}Ga, ^{74}Ge, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{138}Ba, ^{139}La, ^{140}Ce, ^{151}Eu, ^{153}Eu and ^{208}Pb and backgrounds were measured at mass 130.5. Counts at masses 60, 67, 68, 152, 154 were also taken to measure the amounts of ^{44}CaO, $^{40}Ca^{27}Al$, $^{40}Ca^{28}Si$, ^{136}BaO and ^{138}BaO species respectively. Default relative ion yields were used with these counts to estimate the contributions of potential interferences at the following masses: ^{56}Fe (interferences with ^{40}CaO and $^{28}Si_2{}^+$), ^{71}Ga (interferences with $^{44}Ca^{27}Al$ and $^{43}Ca^{28}Si$), ^{74}Ge (interferences with $^{44}Ca^{30}Si$) and ^{151}Eu and ^{153}Eu (interferences with ^{135}BaO and ^{137}BaO respectively). Samples were assumed to be free of Ni. Estimates of absolute concentrations were obtained using relative ion yields with respect to SRM 610 glass standard using further correction factors to accommodate the differences in the glass and feldspar matrices (R.W. Hinton, pers. comm., 1997). Final concentrations, after corrections, were obtained by scaling with respect to SiO$_2$ concentrations from corresponding EPMA data.

Mount Etna

Mount Etna dominates the eastern coastline of Sicily and provides one of the most extensive records in the world of documented historic eruptions. There are written statements of eruptions over 2000 years ago and an almost complete record of flank eruptions since 1500 AD (Chester *et al.*, 1985). Throughout the historic period the volcano has erupted lavas of a rather uniform, typically hawaiitic composition. From 1750 to 1983 the volcano has been in a broadly steady state with a mean eruption rate of 0.18 m^{3}s^{-1} (Hughes *et al.*, 1990) with flank eruptions occurring every few years (recent eruptions occurred in 1979, 1981, 1983, 1985, 1986, 1987, 1989 and 1991–3). Since 1983, Etna has shown increased output and it may be that the volcano is entering a new phase of activity.

Ground deformation studies indicate that significant high level storage of magma does not occur prior to eruptions (Murray and Guest, 1982; Chester et al., 1985). Local deformation up to two years prior to some flank eruptions supports dyke emplacement sometime before the start of an eruption.

These dykes did not contain sufficient magma to feed eruptions such as those of 1983 and 1991−3 and there must have been supply from depth during these eruptions. Indeed, in the 1991−3 eruption, microgravity measurements recorded no mass change over the dyke except towards the end of the eruption. Drainage of the dyke was therefore not taking place and erupted magma was being replenished as the eruption continued (Rymer et al., 1995). It is likely that larger eruptions are fed by batches of magma and Armienti et al. (1994) argue, on geochemical evidence, that the 1991−3 eruption was the result of a distinct magma pulse.

Deeper storage areas for magma have been revealed by an analysis of travel times of natural and artificially generated seismic waves below the volcano (Sharp et al., 1980). Sharp et al. (1980) interpreted these results in terms of a large ellipsoidal storage area at 20 km depth in the lower crust with magma occupying about 14% by volume in an inferred network of fissures. Primitive magmas generated in the mantle rise up and collect in the deep-seated lower crustal reservoir; fractionation of the magma involving predominantly mafic phases leads to less dense hawaiitic melts, which then ascend towards the surface (Guest and Duncan, 1981; Condomines et al., 1995). Seismic tomography has revealed low velocity bodies at around 6 km depth (Hirn et al., 1991), which may represent upper crustal reservoirs feeding the high-level plumbing system.

In the hawaiites and basic mugearites of the Alkalic Series, the plagioclase phenocrysts range in composition from An_{80} to An_{55} (Chester et al., 1985, Chap. 6) and the full range of compositions may be found in crystals coexisting in the same lava. This wide range in plagioclase composition within any one basalt sample may reflect fractional crystallization, although magma mixing may also play a part.

In the more evolved prehistoric lavas, mugearites and benmoreites, the plagioclase phenocrysts became more sodic and generally less abundant. As with the hawaiites, within any one sample there is a considerable range in the chemistry of the plagioclase phenocrysts. In the benmoreite lavas from the autoclastic breccia domes near Biancavilla, the plagioclase phenocrysts are typically andesine in composition, $An_{40}−An_{50}$. Some crystals have more calcic cores up to An_{65} and the outer rims of the phenocrysts and the microphenocrysts have compositions down to oligoclase of about An_{25}.

Plagioclase phenocrysts of the Alkalic Series of Etna are typically more calcic than the plagioclase phenocrysts in hawaiites and mugearites from other mildly alkaline suites such as Hawaii (Keil et al., 1972), Terceira, Azores (Self and Gunn, 1976) and Mauritius (Baxter, 1975). Tanguy (1978) suggests that the abundance of calcic-plagioclase in the Etnean lavas is due to the high CaO and Al_2O_3 content of the magma. Another possible factor is provided by the experimental work in the system Ab–An–H_2O by Johannes (1978) which has shown that the An-content of a plagioclase in equilibrium with a given melt composition will be higher for more hydrous conditions. In their study of the 1983 lavas, Trigila et al. (1990) demonstrate that the magma was relatively hydrous with 1.0−2.3 wt.% H_2O. It may be, therefore, that the high An-content of Etnean plagioclases is a function of the high pH_2O of the magma.

Plagioclase phenocrysts in the 1983 lavas

Lavas of the 1983 eruption

In the 1983 eruption the lava was erupted on the southern flank of the volcano at an altitude of 2250 m a.s.l. from the lower end of a relatively short fissure 750 m in length. The effusive nature of the eruptive activity provided an ideal opportunity for collecting quench samples of lava from the vent area. One quench sample (DK24) was collected from the active channel within 25 m of the vent and the other (DK8), from the flow front 4 km from the vent. Both samples were plunged into water. The lavas are of hawaiite composition, with ~40% plagioclase as phenocrysts and as laths within a fine-grained to glassy matrix. Clinopyroxene and olivine are also present as phenocrysts.

The 1983 eruption lasted 131 days, with a relatively low average effusion rate of ~8 m^3s^{-1} and produced a total of 80×10^6 m^3 of erupted material (Frazzeta and Romano, 1984). Despite its duration and the large volume of lava discharged, no significant petrochemical variation was observed during this eruption (Tanguy and

Clochiatti, 1984). On the basis of naturally occurring and experimental phase equilibria data from 1983 lava, thermochemical calculations support a model in which maximum crystallization of the ascending magma occurred between 85–225 MPa, corresponding to depths of 3–10 km, at a temperature range of 1096–1112°C (Trigila *et al.*, 1990).

The feldspars demonstrate intricate patterns of inclusions, indicative of a complex growth history. Plate 8 shows an example of the inclusion patterns observed. Often the inclusions are found in discrete concentric zones, corresponding to the growth zones. The inclusions are clear green glass quite distinct from the devitrified melt inclusions showing immiscible segregation in plagioclase phenocrysts of naturally cooled lava (Preston and Duncan, 1979). Analysis of the green glass inclusions shows them to be broadly similar in composition to the groundmass glass.

Cathodoluminescence petrography

Cathodoluminescence is the emission of light from a substance following its excitation by an electron beam. The application of CL to the study of igneous rocks is undergoing rapid development. Feldspars display broad band emissions in the blue, yellow and red regions of the visible spectrum with the luminescence observed by the naked eye, typically dependent on the presence and relative intensity of these three emission bands.

Cathodoluminescence petrography has proved particularly useful in the study of post-crystallization processes in plutonic igneous rocks, allowing rapid examination of the degree of metasomatism experienced (e.g. Finch and Walker, 1991; Rae and Chambers, 1988). Since post-crystallization processes have a significant influence on the CL characteristics of feldspars, interpretation of features resulting from a combination of both primary and post-crystallization processes can prove difficult. The application of CL to the study of quenched samples enables investigation of the textures that result solely from magmatic processes. This should help in distinguishing CL phenomena in igneous rocks relating solely to primary crystallization processes from those caused by sub-solidus re-equilibration or metasomatic alteration.

The CL petrography shows the plagioclase of the 1983 eruption to be characterized by two types of CL, shown in Plate 9. The majority of the phenocrysts have a green luminescent inner zone, with blue CL found in the outer zone and in the groundmass laths. The few phenocrysts that were found to be entirely blue luminescent are considered to be an artefact of the sample sectioning such that cores are not exposed.

The contact between the green and blue CL in the phenocrysts is very sharp and a concentric zone of inclusions often coincides with this boundary. It is notable that variations in the CL are apparent between different sets of twins, within both the green and blue zones of the phenocrysts. Because the CL results from emissions from the top 3 µm of the sample, it provides a truer representation of the crystal shape. Comparisons between the CL and PPL optical images can be seen in Plate 9a,b. The CL image shows the crystal marked X as having a clear euhedral margin whereas the optical image of the same crystal shows an irregular crystal outline which could be interpreted as evidence of resorption. It appears that the optical view is complicated by depth effects through the edge of a grain that has been cut obliquely. Cathodoluminescence therefore provides a simple method of determining the actual 2D crystal outline in thin section.

Chemical zonation

The composition of the zones in the plagioclase phenocrysts revealed using CL petrography was investigated using EPMA and SIMS. Six crystals from samples DK24 and DK8 were examined using EPMA with the location of point analyses selected to investigate the differences in composition between the green luminescent inner zone of the phenocrysts, the blue luminescent outer zone of the phenocrysts and the laths. The results show that there is a marked compositional discontinuity between the green and blue luminescent zones (Fig. 1 and Table 1). The green cores range in composition from An_{70} to An_{87}, while, the blue luminescent areas have compositions from An_{50} to An_{60}. An abrupt drop of 10–20% anorthite across the sharp boundary between the green and blue luminescent zones is found.

Cathodoluminescence characteristics can be considered as a representation of the bulk electronic properties of the material being studied. The luminescence results from excitation and electron recombination involving luminescent centres. These centres are often in the form of extrinsic element activators, whose presence
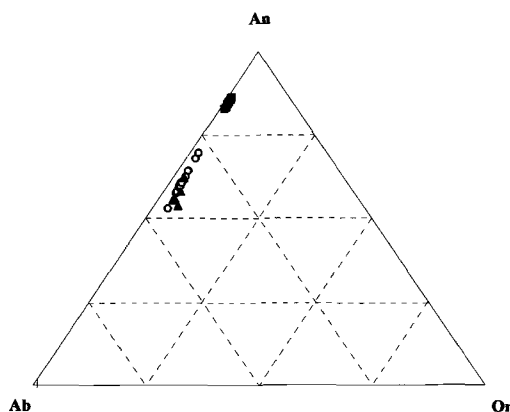
FIG. 1. Plot of plagioclase analyses for sample DK24. Squares: green luminescent inner zone of phenocrysts, circles: blue luminescent outer zone of phenocrysts, triangles: groundmass laths.

facilitates luminescence at a certain wavelength and intensity. Structural defects also provide effective luminescent centres, often attributed as responsible for intrinsic luminescence. Marfunin (1979), Marshall (1988), Redmond et al. (1992), and Krbetschek et al. (1997) provide discussions of luminescence mechanisms and spectroscopy in minerals. The influence of sample preparatory methods on the resultant luminescence is discussed by Townsend et al. (1999). Krbetschek et al. (1997) provides a good summary of the luminescent centres found in feldspars.

Low concentrations of activators are sufficient to activate CL, for example Geake et al. (1973) found 100 ppm Fe^{3+} generated red CL in synthetic plagioclase. SIMS provides a good tool for the investigation of trace element concentrations at the low levels necessary to activate CL. The high abundance of glass inclusions within the crystals made analysis of pure feldspar compositions difficult. Three point-analyses of green luminescent cores were made along with one confident analysis of purely blue luminescent feldspar. Discussion of the causes of CL in feldspars in the absence of quantitative spectral data is limited, however several observations can be made based on the SIMS data presented in Table 2.

Based on luminescence decay times, theoretical considerations and synthetic doping experiments, Geake et al. (1973) and Telfer and Walker (1978) attributed the green CL of plagioclase to

activation by Mn^{2+}. Mora and Ramsayer (1992) and Götze et al. (1999) also found a correlation between the green/yellow emission and the Mn content in natural plagioclase samples. The observed correlation of green CL with areas of highest anorthite content may indicate activation from a centre formed by substitution for Ca^{2+}. SIMS data indicate slightly higher Mn contents in the green luminescent regions (256 ppm in the green zone with 194 ppm in the blue zone), consistent with Mn^{2+} activation of green CL in plagioclase.

The origin of blue luminescence is a matter of some debate. Element activation by Ti^{4+} and Cu^{2+} (Mariano, 1973), Ga^{3+} (De St. Jorre and Smith, 1988) and Eu^{2+} (Mariano and Ring, 1975) have been suggested. Emissions from Sm^{3+}, Dy^{3+} and Nd^{3+} centres have also been identified in the CL spectra of plagioclase by Götze et al. (1999). The large number of different centres present in natural minerals makes the interpretation of the causes of the CL difficult, and currently no single element appears to be consistently responsible for blue luminescence in natural feldspars. Rae and Chambers (1988), working on the CL and mineral chemistry of alkali feldspars from the North Qôroq centre in south Greenland and Finch and Klein (1999), investigating the causes of CL in alkali feldspars, found no relationship between Ti, Ga and Eu concentrations and blue luminescence.

An increase in the Ti content was found in the blue zone (1346 ppm in the blue with 590 ppm in the green luminescent zone). Europium activation is not considered responsible for the blue CL in this case, as the concentrations of 1–2 ppm found are unlikely to activate luminescence. Gallium activation is also unsupported by this work with Ga contents being higher in the green luminescent region (82 ppm for the green luminescent areas with 70 ppm in the blue luminescent areas) and De St. Jorre and Smith (1988) considered Ga only to be an efficient activator in plagioclase at concentrations greater than 800 ppm.

Defect sites may be responsible for the broad blue band emission. Defects are difficult to characterize and are often postulated when luminescence cannot be accounted for by activation mechanisms. However, from studies of other semiconducting materials it appears that defect-related CL phenomena are highly efficient compared with element activation (Ozawa, 1990). Marfunin (1979), Speit and Lehmann (1982) and Petrov (1994) have identified a number of O^- hole centres in feldspars. The

TABLE 1. Representative EPMA analyses of plagioclase and glass from selected Etnean lavas

| | 1983 hawaiite lava | | | | Prehistoric hawaiite (AD1/65) | | | | | | Prehistoric benmoreite | | |
| | DK8 | | DK24 | | DK24 glass | | Reverse zoned | | Normal zoned | | | core | rim |
	core	rim	core	rim	inclusion	gr'mass	core	rim	core	rim	average	An rich	An poor
Na_2O	2.14	4.89	1.67	4.26	4.81	3.87	4.20	3.31	2.77	3.24	5.86	3.86	6.70
K_2O	0.15	0.63	0.11	0.40	2.62	3.97	0.29	0.21	0.13	0.21	0.60	0.19	2.23
CaO	16.45	11.07	17.30	12.35	8.80	6.66	12.18	13.67	14.71	14.15	8.90	13.20	5.32
Al_2O_3	34.58	29.64	35.24	30.89	16.87	16.86	31.25	32.67	33.62	32.71	26.06	29.87	22.80
SiO_2	46.20	52.59	44.82	51.15	45.61	47.76	51.27	49.08	47.96	48.77	57.39	51.76	61.26
MgO	0.06	0.07	0.04	0.08	3.62	2.88	0.06	0.06	0.04	0.06			
TiO_2	0.06	0.11	0.03	0.08	2.07	2.07	0.07	0.07	0.05	0.06			
FeO	0.70	0.74	0.69	0.74	10.75	10.46	0.00	0.00	0.00	0.00	0.61	0.66	0.07
MnO	0.01	0.01	0.02	0.03	0.23	0.26	0.09	0.04	0.05	0.02			
BaO	0.00	0.03	0.00	0.11	0.23	0.37							
Total	100.33	99.80	99.91	100.08	95.61	95.16	99.40	99.09	99.32	99.21	99.42	99.53	98.98

TABLE 2. SIMS analysis of a water quenched hawaiite lava from the 1983 eruption of Etna. Points 1, 2 and 3 are analyses of green luminescent plagioclase, point 4 is an analysis of blue luminescent plagioclase and point 5 is an analysis of the groundmass glass

Point	1	2	3	4	5
(ppm)					
Li	0.44	0.86	0.80	1.38	16.95
Be	0.38	0.29	0.35	0.57	5.94
B	2.29	2.48	7.88	5.63	47.52
Mg	108.64	74.86	86.86	102.98	4875.42
Ti	526.93	347.45	364.43	802.00	18022.54
Mn	260.90	256.86	252.48	194.92	8870.33
Fe	7754.46	7178.73	7335.58	6067.33	2155.33
Ga	52.93	55.20	55.68	41.77	139.57
Ge	8.05	6.77	6.75	6.99	48.03
Rb	1.27	0.91	0.76	1.76	89.19
Sr	3011.51	3245.96	3279.84	3478.03	1966.00
Y	0.72	0.39	0.34	0.29	51.95
Zr	4.04	0.65	0.24	0.37	634.76
Nb	0.99	0.17	0.02	0.11	151.82
Ba	354.37	235.85	309.37	782.66	1763.16
La	12.11	8.64	9.17	13.40	147.42
Ce	17.90	11.74	12.81	16.42	269.87
Pb	6.48	2.37	2.80	2.93	66.74
Eu	1.16	0.78	0.81	1.37	3.84

broad band nature of the blue emission, the rapid decay time of 6 μs and the detection of $Al-O^--Al$ and $Si-O^--Si$ centres, are considered by Finch and Klein (1999) to indicate an intrinsic defect-related cause for the blue CL in alkali feldspars. Another possibility is that the inclusion of certain elements causes modification of the structure as a result of structural distortion, facilitating blue CL. The role of Ti^{4+} in enhancing intrinsic luminescence has been suggested (Geake et al., 1973).

In summary, this work supports the role of Mn^{2+} in activation of the green CL of plagioclase feldspars. Work in progress on plagioclase crystals from the Gardar province, Greenland supports this suggestion, with electron paramagnetic resonance data (EPR) giving responses indicative of structural manganese in green luminescent plagioclase which is absent in blue luminescent plagioclase. While this work lends some support to the activation of blue CL by Ti, the role of Ti in plagioclase needs clarification. The observed variations in the CL between different sets of twins which have a uniform chemistry demonstrate anisotropy in the CL emission, indicating that it is insufficient to consider CL in terms of concentration thresholds for element activation alone.

In the present study the influence of the state of order (Finch and Klein, 1999) and hydrothermal processes (Finch and Walker, 1991; Rae and Chambers, 1988) are negligible, and therefore the CL reflects solely the conditions of crystallization. The observed variations in mineral chemistry between areas of contrasting CL can also represent concomitant variations in crystallization conditions that may influence the CL by other means. For example, the temperature and rate of crystallization and the water content of the magma may also be significant, particularly in terms of the mineral microstructure and defect concentration.

Petrogenesis

In the 1983 lavas, crystallization of anorthite-rich (An_{70-87}) green luminescent cores was followed by growth of the outer blue luminescent, less anorthite-rich zone (An_{50-60}). The onset of the blue luminescent zone often coincides with numerous glassy inclusions developing a sieve texture. The zones of glassy inclusions are developed parallel to the oscillatory zoning and Downes (1973), in a study of the petrography of the hawaiite lavas of the 1971 eruption of Etna, suggested that the glassy inclusions in the plagioclase phenocrysts formed from basaltic melt trapped during periods of rapid growth. The larger plagioclase phenocrysts in the 1991−3 lavas have fringes with abundant glass inclusions which Armianti et al. (1994) attribute to rapid growth, possibly due to undercooling during the ascent phase. Kuo and Kirkpatrick (1982) describe a skeletal texture in plagioclase crystals from mid-ocean ridge basalts and consider this to represent growth under conditions of considerable undercooling.

The abrupt change in chemical composition between the cores and outer parts of the plagioclase crystals suggests that undercooling for the 1983 magma of Etna may have come about through the mixing of magmas of contrasting temperature and composition. It is suggested, therefore, that this stage involved An-rich plagioclase crystals being incorporated into cooler more evolved basaltic melt. This led to the crystallization of the blue luminescent rims around the incorporated crystals, with a sharp drop of

An_{10-20} found across the boundary between the two zones. Crystallization of blue luminescent plagioclase laths then occurred in the final stages of crystallization prior to eruption. It is suggested that the anorthite-rich, green luminescent cores may represent cumulates, present in the magma conduit. These crystals were disrupted and incorporated into a more sodic melt causing a phase of rapid growth at the margins of the existing cores.

Other types of association of plagioclase phenocrysts occur in Etnean lavas reflecting their different mixing histories. In a prehistoric hawaiite (Duncan and Preston, 1985), rounded, partially resorbed plagioclase phenocrysts occur together with more euhedral lath-like crystals. The rounded plagioclase phenocrysts have a core composition between An_{60} and An_{61} and show reverse zoning with the outer part of the crystal being between An_{68} and An_{71}. The well-defined lath-like phenocrysts are normally zoned with interior compositions between An_{72} and An_{78} and a more sodic outer margin bertween An_{66} and An_{73}, similar in composition to the outer margins of the more anhedral crystals (Table 1). A possible mechanism to account for this association of plagioclase phenocrysts is the mixing of two chemically distinctive magmas, both containing plagioclase phenocrysts, to form a hybrid magma intermediate in composition and temperature compared with the initial liquids. The more sodic plagioclase crystals from the lower temperature melt will be superheated in the hybrid liquid and undergo resorption and become mantled by more anorthite-rich material than the core. Some of the normally zoned phenocrysts show a concentric zone of glassy inclusions formed through a mechanism of undercooling which is considered to be brought about by magma mixing. In a study of the trace element chemistry of 20th century lavas of Etna, Gyopari (1988) identified mixing in most eruptions. This would imply that small isolated pockets of magma might remain within the plumbing system for many years.

Discussion

Cathodoluminescence studies of quenched samples of lava provide a rapid means of recognising zonation in plagioclases that are wholly attributable to crystallization processes, often revealing a complex growth history. The true crystal outline is also readily observable using CL. The contrasting luminescence corresponds to a discontinuity in the mineral chemistry; green CL is found exclusive to the plagioclase cores of higher anorthite content, with lower anorthite contents represented by blue luminescence. Twinning is revealed in CL and highlights the importance of structural aspects in determining the nature of the CL observed.

The zoning and morphology of the plagioclase phenocrysts provide a valuable insight into the nature of the magmatic processes that operate prior to eruption. It is likely that a variety of styles of mixing have operated in the genesis of Etnean magmas, including both magma–magma mixing and magma–cumulate mixing.

In conclusion, cathodoluminescence can be an effective petrographic tool in studies of volcanic rocks. It is especially useful when considering the feldspar crystals, which are particularly sensitive to changes in pressure, temperature, volatile content and composition. Although the causes of luminescence in feldspars are not fully understood, the technique provides a very useful guide towards further mineral chemical studies and can readily reveal zonations difficult to recognise by other means. The study of quenched samples has simplified the interpretation of the CL by enabling the elimination of the effects of post-crystallization processes, thus providing grounds for a clearer understanding of the causes of CL in feldspars. The activation of green CL in plagioclase by Mn^{2+} (Geake *et al.*, 1973) is supported by this work. The cause of blue CL is more uncertain, with the role of Ti and *REE* in activating blue CL still uncertain. Detailed spectral analysis of the CL emissions and an improved knowledge of the nature and role of defects would contribute greatly to this issue.

References

Armienti, P., Pareschi, M.T., Innocenti, F. and Pompilio, M. (1994) Effects of magma storage and ascent on the kinetics of crystal growth. *Contrib. Mineral. Petrol.*, **104**, 594–608.

Baxter, A.N. (1975) Petrology of the Older Series lavas, Mauritius, Indian Ocean. *Bull. Geol. Soc. Amer.*, **86**, 1449–58.

Chester, D.K., Duncan, A.M., Guest, J.E. and Kilburn, C.R.J. (1985) *Mount Etna: The Anatomy of a Volcano.* Chapman & Hall, London, 404 pp.

Condomines, M., Tanguy, J.C. and Michand, V. (1995) Magma dynamics at Mt Etna: Constraints from U-Th-Ra-Pb disequilibria and Sr - Isotopes in historical lavas. *Earth Planet. Sci. Lett.*, **132**, 25–41.

Cristofolini, R. and Romano, R. (1982) Petrological features of the Etnean volcanic rocks. *Mem. Soc. Geol. It.*, **23**, 323–36.

Cristofolini, R. and Tranchina, A. (1980) Aspetti petrologici delle vulcaniti Etnee: caratteri dei fenocristalli isolati ed in aggregati (Petrological aspects of Etnean volcanics: characteristics of isolated phenocrysts and aggregates.) *Rend. Soc. It. Mineral. Petr.*, **36**, 751–73 (In Italian).

De St Jorre, L. and Smith, D.G.W. (1988) Cathodoluminescent gallium enriched feldspars from the Thor Lake rare-metal deposit, Northwest Territories, Canada. *Canad. Mineral.*, **26**, 301–8.

Downes, M.J. (1973) Some experimental studies on the 1971 lavas from Etna. *Phil. Trans. Roy. Soc. Lond.*, **A274**, 55–62.

Duncan, A.M. and Preston, R.M.F. (1985) Plagioclase phenocrysts and the Alkalic Lavas of Mount Etna: A contribution to the understanding of magmatic processes (abstract). In *IAVCEI 1985 Scientific Assembly: Potassic volcanism — Mount Etna volcano*, Catania.

Finch, A.A. and Klein, J. (1999) The causes and petrological significance of cathodoluminescence emissions from alkali feldspars. *Contrib. Mineral. Petrol.* (in press).

Finch, A.A. and Walker, F.D.L. (1991) Cathodoluminescence and microporosity from the Blå Måne Sø perthosite, South Greenland. *Mineral. Mag.*, **55**, 583–9.

Frazzetta, G. and Romano, R. (1984) The 1983 Etna eruption; event chronology and morphological evolution of the lava flows. *Bull. Volcanol.*, **47**, 1079–96.

Geake, J.E., Walker, G., Telfer, D.J., Mills, A.A. and Garlick, G.F.J. (1973) Luminescence of lunar, terrestrial, and synthesised plagioclase, caused by Mn^{2+} and Fe^{3+}. Proc. Fourth Lunar Science Conference, 3, *Geochim. Cosmochim. Acta suppl.*, **4**, 3181–9.

Götze, J., Krbetschek, M.R., Habermann, D. and Wolf, D. (1999) High resolution cathodoluminescence studies of feldspar minerals. In: Pagel, M., Barbin, V., Blanc, D. and Ohnenstetter, D. (Eds.) *Cathodoluminescence in Geosciences.* Springer Verlag (in press).

Guest, J.E. and Duncan, A.M. (1981) Internal plumbing of Mount Etna. *Nature*, **290**, 584–6.

Guest, J.E., Kilburn, C.R.J., Pinkerton, H. and Duncan, A.M. (1987) The evolution of lava flow fields: observations of the 1981 and 1983 eruptions of Mount Etna, Sicily. *Bull. Volcanol.*, **49**, 527–40.

Gyopari, M. (1988) *Temporal and spatial variations in the geochemistry and mineralogy of the younger historic lavas of Mount Etna, Sicily.* PhD thesis, Plymouth Polytechnic [now University of Plymouth, UK].

Hirn, A., Nercessian, A., Sapin, M., Ferrucci, F. and Wittlinger, G. (1991) Seismic heterogeneity of Mt Etna: structure and activity. *Geophys. J. Int.*, **105**, 139–53.

Hughes, J.W., Guest, J.E. and Duncan, A.M. (1990) Changing styles of effusive eruptions on Mount Etna since A.D. 1600. In *Magma Transport and Storage*, (M.P. Ryan, ed.). J. Wiley, pp. 385–406.

Johannes, W. (1978) Melting of plagioclase in the system Ab-An-H_2O and Qz-Ab-An-H_2O at pH_2O = 5 k bar, an equilibrium problem. *Contrib. Mineral. Petrol.*, **66**, 295–303.

Keil, K., Fodor, R.V. and Bunch, T.E. (1972) Contribution to the mineral chemistry of hawaiian rocks. II. Feldspars and interstitial material from Haleakala and West Maui volcanoes, Maui, Hawaii. *Contrib. Mineral. Petrol.*, **37**, 253–76.

Krbetschek, M.R., Gotze, J., Dietrich, A. and Trautmann, T. (1997) Spectral information from minerals relevant to luminescence dating. *Radiation Measurements*, **27**, 695–748.

Kuo, L.C. and Kirkpatrick, R.J. (1982) Pre-eruption history of phyric basalts from DSDP Legs 45 and 46: evidence from morphology and zoning patterns in plagioclase. *Contrib. Mineral. Petrol.*, **79**, 13–27.

Marfunin, A.S. (1979) *Spectroscopy, Luminescence and Radiation Centres in Minerals.* Springer. Berlin

Mariano, A.N. and Ring, P.J. (1975) Europium activated cathodoluminescence in minerals. *Geochim. Cosmochim. Acta*, **39**, 649–60.

Mariano, A.N., Ito, J. and Ring, P.J. (1973) Cathodoluminescence of plagioclase feldspars. *Abstracts with Programs*, **5**, 726. Geol. Soc. Amer. Boulder, CO.

Marshall, D.J. (1988) *Cathodoluminescence of Geological Materials.* Unwin Hyman.

Mora, C.I. and Ramsayer, K. (1992) Cathodoluminescence of coexisting plagioclases, Boel's Butte anorthosite: CL activators and fluid

flow paths. *Amer. Mineral.*, **77**, 1258–65.

Murray, J.B. and Guest, J.E. (1982) Vertical ground deformation on Mount Etna, 1975–1982. *Bull. Geol. Soc. Amer.*, **93**, 1166–75.

Ozawa, L. (1990) *Cathodoluminescence Theory and Applications*. VCH Publications (UK) Ltd.

Preston, R.M.F. and Duncan, A.M. (1979) Electron microprobe investigation of melt inclusions in plagioclase phenocrysts from Mount Etna. *Mineral. Mag.*, **43**, 181–3.

Rae, D.A. and Chambers, A.D. (1988) Metasomatism in the North Qôroq centre, South Greenland: cathodoluminescence and mineral chemistry of alkali feldspars. *Trans. R. Soc. Edinb: Earth Sciences.*, **79**, 1–12.

Redmond, G., Cesbron, F., Chapoulie, R., Ohenestetter, D., Roques-Carmes, C. and Schoerer, M. (1992) Cathodoluminescence applied to the microcharacterisation of mineral materials: A present status in experimentation and interpretation. *Scan. Microsc.*, **6**, 23–68.

Rymer, H., Cassidy, J., Locke, C.A. and Murray, J.B. (1995) Magma movements in Etna volcano associated with the major 1991–1993 lava eruption: evidence from gravity and deformation. *Bull. Volcanol.*, **57**, 451–61.

Self, S. and Gunn, B.M. (1976) Petrology, volume and age relations of alkaline and saturated peralkaline volcanics from Terceira, Azores. *Contrib. Mineral. Petrol.*, **54**, 293–313.

Sharp, A.D.L., Davis, P.M. and Grey, F. (1980) A low velocity zone beneath Mount Etna and magma storage. *Nature*, **287**, 587–91.

Speit, B. and Lehmann, G. (1982) Radiation defects in feldspars. *Phys. Chem. Min.*, **8**, 77–82.

Tanguy, J.C. (1978) Tholeiitic basalt magmatism of Mt. Etna and its relation with the Alkaline Series. *Contrib. Mineral. Petrol.*, **66**, 51–67.

Tanguy, J.C. and Clocchiatti, R. (1984) The Etnean lavas, 1977 - 1983: petrology and mineralogy. *Bull. Volcanol.*, **47**, 965–76.

Telfer, D.J and Walker, G. (1978) Ligand field bands of Mn^{2+} and Fe^{3+} luminescence centres and their site occupancy in plagioclase feldspars. *Modern Geology*, **6**, 199–210.

Townsend, P.D., Karali, T., Rowlands, A.D., Smith, V.A. and Vazquez Lopez, G. (1999) Recent examples of cathodoluminescence as a probe of surface structure and composition. *Mineral. Mag.*, **63**, 211–26. (This issue).
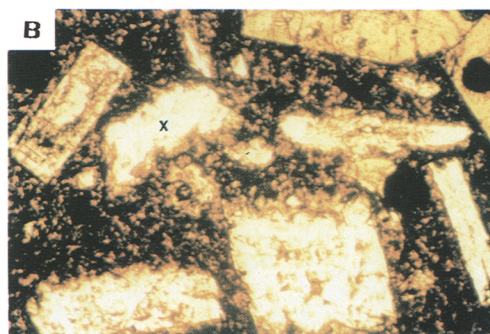
PLATE 8. PPL photomicrograph of a plagioclase phenocryst from the water quenched 1983 lava of Etna (sample DK5) showing a concentric zone of glass inclusions, indicated by tick marks.
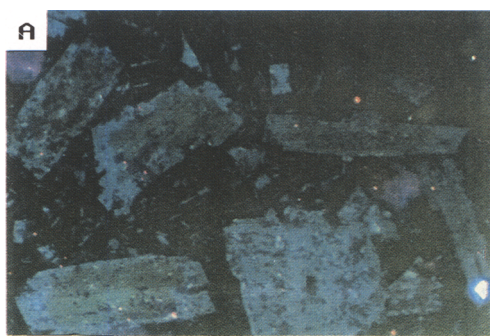
PLATE 9. (a) Cathodoluminescence photograph of a water quenched lava from the 1983 eruption of Etna (sample DK24), showing plagioclase phenocrysts with green luminescent inner zones, blue luminescent outer zones and blue luminescent laths in a non luminescent groundmass glass. Note variations in CL between the different twins. Excitation conditions of 550 μA and 14 kV were used, with 4 minutes exposure time on a 400 ASA fujicolour film. (b) Corresponding PPL photograph. Note the contrast in apparent crystal shape between the CL and PPL, for example at X.