

## Cathodoluminescence of coexisting plagioclases, Boehls Butte anorthosite: CL activators and fluid flow paths

CLAUDIA I. MORA

Department of Geological Sciences, University of Tennessee, Knoxville, Tennessee 37996, U.S.A.

KARL RAMSEYER

Geologisches Institut, Universität Bern, Baltzerstrasse 1, 3012 Bern, Switzerland

### ABSTRACT

Cathodoluminescence (CL) petrography and luminescence spectra of coexisting plagioclases from the regionally metamorphosed Boehls Butte anorthosite permit rapid visual distinction of complex plagioclase intergrowths and fine-scale, retrograde fluid flow features that are nearly invisible in transmitted light. Calcic plagioclase (An<sub>87-97</sub>) exhibits bright yellow luminescence, whereas intermediate plagioclase (An<sub>39-65</sub>) is green. Luminescence spectra indicate that red emissions are sensitive to anorthite content, shifting from 687 to 744 nm over the range An<sub>94</sub>–An<sub>38</sub>. Green peak positions are less sensitive, with shorter wavelength emissions in anorthite (540–548 nm), compared with coexisting andesine (549–561 nm). The Mn<sup>2+</sup> contents correlate well with the intensities of the peak at 540–560 nm, suggesting that Mn<sup>2+</sup> is an effective CL activator in plagioclase at levels as low as 19 ppm. Fe<sup>2+</sup> acts as neither a sensitive activator nor important quencher. Very weak Fe<sup>3+</sup>-activated peaks (680–745 nm) but variable Fe<sup>3+</sup> abundance (23–2504 ppm) suggest that most Fe<sup>3+</sup> is present in a minute, coexisting phase such as hematite. Anorthite inclusions in andesine megacrysts have significantly different CL peak positions and intensities than granoblastic, polygonal anorthite forming thin laminae in the anorthosite. Plagioclase occurring in association with the laminae shows CL evidence of dissolution and replacement and of grain fragmentation accommodating dilation. The laminae are inferred to have been foci of retrograde fluid circulation through the anorthosite that resulted from rapid uplift of the Boehls Butte region after the peak of regional metamorphism.

### INTRODUCTION

Cathodoluminescence (CL; electron-excited luminescence) has been used for more than 20 yr to examine compositional variations, replacement, and growth phenomena in sedimentary rocks (cf. Marshall, 1988; Barker and Kopp, 1991). The majority of these studies have employed qualitative evaluation of CL colors and petrographic analysis of compositional zonation or mineral intergrowths that may be exclusively visible in CL. Much additional information can be gained by spectral analysis of the CL. Spectral analysis permits identification of the activator elements, resolution of complex spectra (those containing more than one activator element), and quantitative comparison of CL in different samples.

In this study, we examine the CL petrography and luminescence spectra of plagioclases from the regionally metamorphosed Boehls Butte anorthosite, northern Idaho. This unusual anorthosite contains two or three compositionally distinct, coexisting plagioclases. The origin of the coexisting plagioclases is controversial, but may be due to shear differentiation of a single, igneous plagioclase (Juras, 1974) or a complex history of intrusion, assimilation, and metasomatic alteration of the anorthosite (Nord, 1973; Goldberg, 1983; Hietanen, 1963, 1984).

Plagioclases formed under different conditions may show different CL emission characteristics, depending on trace-element uptake during growth or recrystallization. Careful textural description of the anorthosite, combined with CL spectral analysis, may therefore help to constrain the origin or postcrystallization history of the unusual feldspar assemblage. To help interpret the CL emissions, we have identified luminescence activators by combining trace-element analysis and measurement of the luminescence spectra.

The CL activators in many rock-forming minerals are sensitive to recrystallization and fluid-rock interaction, thus CL petrography has largely unexplored potential to identify fluid flow through metamorphic rocks. Recent studies have used CL in calcite to illuminate prograde metamorphic processes (Yardley and Lloyd, 1989) and retrograde metamorphic processes (Morrison and Valley, 1988; Mora and Valley, 1991) and to distinguish fine-scale structures, such as healed microcracks, that are not typically visible with transmitted light (Smith and Stenstrom, 1965; Sprunt and Nur, 1979; Padovani et al., 1982). CL petrography may be particularly useful to identify fluid pathways through relatively nonreactive or monomineralic rock types, such as quartzites and anorthosite. We have examined the anorthosite for CL zo-

nation, alteration, and microstructures that may indicate flow paths of prograde or retrograde metamorphic fluids through the anorthosite body.

### THE BOEHLS BUTTE ANORTHOSITE

The samples described here were collected in the regionally metamorphosed, Proterozoic Boehls Butte anorthosite. The anorthosite is exposed in an uplifted block, surrounded by regionally metamorphosed metasediments of the Belt Supergroup and Cretaceous-Tertiary plutons of the Idaho batholith (Fig. 1). At least two episodes of regional metamorphism have affected the anorthosite, with late Cretaceous M2 metamorphism of the upper amphibolite facies (700–720 °C, 8–10 kbar) followed by nearly isothermal decompression accompanying rapid, early Tertiary uplift of the batholith (cf. Grover and Rice, 1988; Ziegler and Rice, 1991). Stable isotope compositions in the anorthosite and surrounding metasediments indicate that the study area was locally affected by retrograde hydrothermal or meteoric alteration (Mora and Valley, 1988, 1991).

The Boehls Butte anorthosite contains various combinations of two or three plagioclases that are compositionally distinct: andesine ( $An_{34-48}$ ), labradorite ( $An_{50-70}$ ), and bytownite-anorthite ( $An_{82-98}$ ). Representative plagioclase compositions are given in Table 1. For this study, we examined two common examples of the textural varieties of anorthosite that are distinguished in the Boehls Butte area. The first is massive anorthosite characterized by andesine megacrysts (up to 20 mm) containing inclusions ( $\leq 0.2$  mm in length) of bytownite-anorthite (Fig. 2A). The host crystal and calcic inclusions are sometimes in the same crystallographic orientation. Aggregates of 0.1–0.2 mm, granoblastic, polygonal anorthite crystals occur in thin layers (laminae, up to 3 mm wide) throughout the rock (Figs. 2A, 2C). A third plagioclase,  $An_{60-69}$ , is found in a small number of massive anorthosite samples occurring as twinned or untwinned crystals of 2–5 mm. The second example is sheared anorthosite, characterized by grain-size reduction of massive anorthosite assemblages; few megacrysts remain in these samples (Fig. 2G). More complete petrographic and compositional details of the anorthosite are given elsewhere (Hietanen, 1963; Nord, 1973; Walker and Mora, 1990).

Plagioclase ( $\pm$  quartz) veins (10–30 cm in diameter) locally intrude anorthosite in the study area. These veins contain a single coarse-grained plagioclase ( $An_{28}$ ) and are probably associated with Cretaceous-Tertiary plutonism in the general area. We have examined the CL of one plagioclase-rich vein to compare it with anorthosite samples, which are inferred to have a significantly different origin and geologic history.

### METHODS

Plagioclase was examined on an improved CL microscope (Ramseyer et al., 1989), with an energy of 30 keV and a beam-current density of  $0.3 \mu A/mm^2$ . Lumines-

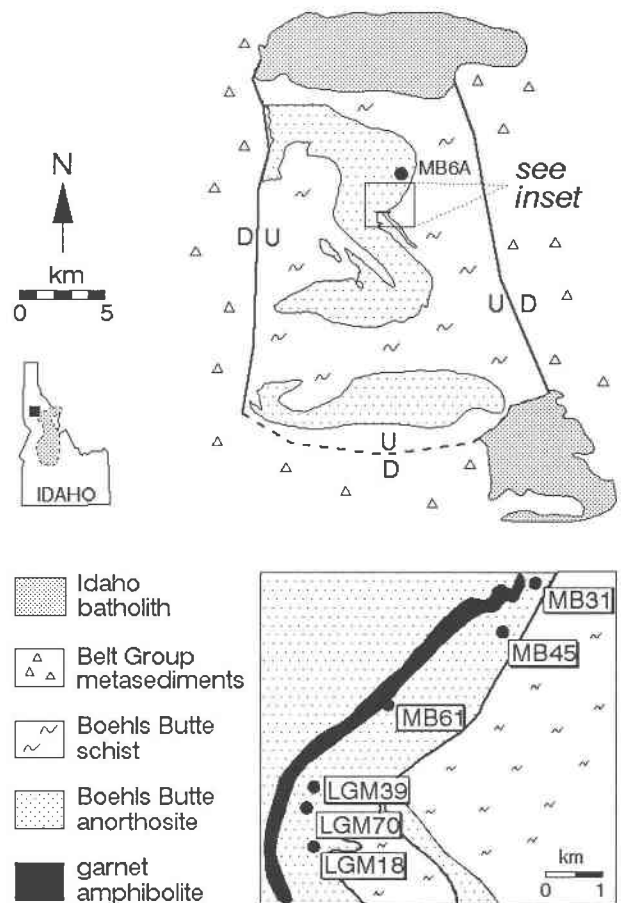


Fig. 1. Generalized geologic map of the Boehls Butte anorthosite and vicinity (after Hietanen, 1984) showing sample locality MB6A; inset shows other sample localities.

cence photomicrographs were recorded on Ektachrome 400 color transparency film, developed at 800 ASA. Luminescence colors are described according to their appearance under visual observation. The CL spectra between 370 and 860 nm (10 nm resolution) were recorded from a 200- $\mu m$  spot using a PTI model 01-001 monochromator equipped with a Hamamatsu R928 photomultiplier. The monochromator was linked to the CL microscope by a flexible optic fiber bundle. The spectra were corrected for the spectral response of the instrument, which has been previously determined by means of a calibrated tungsten lamp. Peak intensity is given as a function of photons emitted at a given wavelength.

Quantitative analyses of major elements in plagioclase were made on a Cameca SX-50 electron microprobe at the University of Tennessee with an accelerating potential of 15 kV and a beam current of 15 nA. The mole fraction of anorthite is reported in Table 1. The low concentrations of CL activators in plagioclase, as well as the  $Fe^{3+}/Fe^{2+}$  ratios, cannot be accurately measured on the electron microprobe. Therefore, separates of plagioclases having compositions of  $An \geq 90$  or  $An \leq 50$  were made

TABLE 1. Plagioclase compositions and peak positions and intensities of cathodoluminescence emissions, Boehls Butte anorthosite

SPL no.	Type*	$X_{An}$ **	Mn (ppm)	Fe <sup>2+</sup> (ppm)	Fe <sup>3+</sup> (ppm)	Position†	Position	Position			
<b>Massive anorthosite</b>											
MB6A	M	40.8	25	942	78	—	558(4.4)	743(2.8)			
	F-M	39.1/60.1				—	—	—			
	I	93.3				—	—	—	542(13.8)	687(4.6)	
	L	92.1				—	—	—	—	—	
MB31	M	42.6	43	572	589	—	561(5.3)	735(6.2)			
	F-M	41.8				—	—	—	553(6.3)	733(2.2)	
	I	90.6				100	471	2504	—	540(36.2)	687(3.5)
	L	94.1							—	—	—
LGM39	M	39.4	34	688	39	—	558(5.0)	738(3.4)			
	I	92.4				—	—	—	546(18.0)	689(3.8)	
	L	97.3				—	—	—	—	—	
MB45	M	39.1	19	512	40	446(0.8)	557(3.4)	730(2.4)			
	I	90.7				410(0.9)	540(11.8)	705(2.2)			
	L	95.0				412(0.8)	540(15.0)	687(2.5)			
<b>Sheared anorthosite</b>											
LGM18C	M	43.8	27	690	23	—	555(8.3)	743(3.6)			
	I	—				60	1422	1140	—	550(27.0)	—
	L	94.3				—	—	—	—	549(24.6)	740(3.1)
LGM70	M	39.6	60	723	144	—	550(19.3)	744(3.6)			
	F-M	65.5				—	—	—	397(0.8)	549(19.5)	720(2.2)
	I	91.0				—	—	—	—	—	—
	L	86.7				—	—	—	408(1.1)	545(61.3)	—
<b>Plutonic vein</b>											
MB61	C	28.0	12	290	117	387(7.2)	545/564(4)	740(10.6)			

Note: Major element composition determined by electron microprobe, trace elements determined by wet chemistry on separates containing all plagioclase types having either  $X_{An} \leq 50$  or  $X_{An} \geq 90$ .

\* Plagioclase occurrence where M = megacryst, F-M = fine-medium grained plagioclase without inclusions, I = inclusions in megacryst, L = granoblastic-polygonal grains in laminae, C = single plagioclase phase.

\*\* Values of  $X_{Or}$  are 0.3–0.8 in megacrysts, 0.0–0.1 in calcic plagioclases.

† Positions of CL peaks are given in nanometers and intensities (given in parentheses) are peak height values of the corrected spectra.

using heavy liquids, and trace amounts of Mn<sup>2+</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup> were analyzed by wet chemistry (J. Husler, analyst). Fe<sup>2+</sup> was determined by dissolution and titration, Mn<sup>2+</sup> and Fe<sub>tot</sub> were determined by atomic absorption. The abundance of Fe<sup>3+</sup> was determined by difference.

#### CATHODOLUMINESCENCE PETROGRAPHY

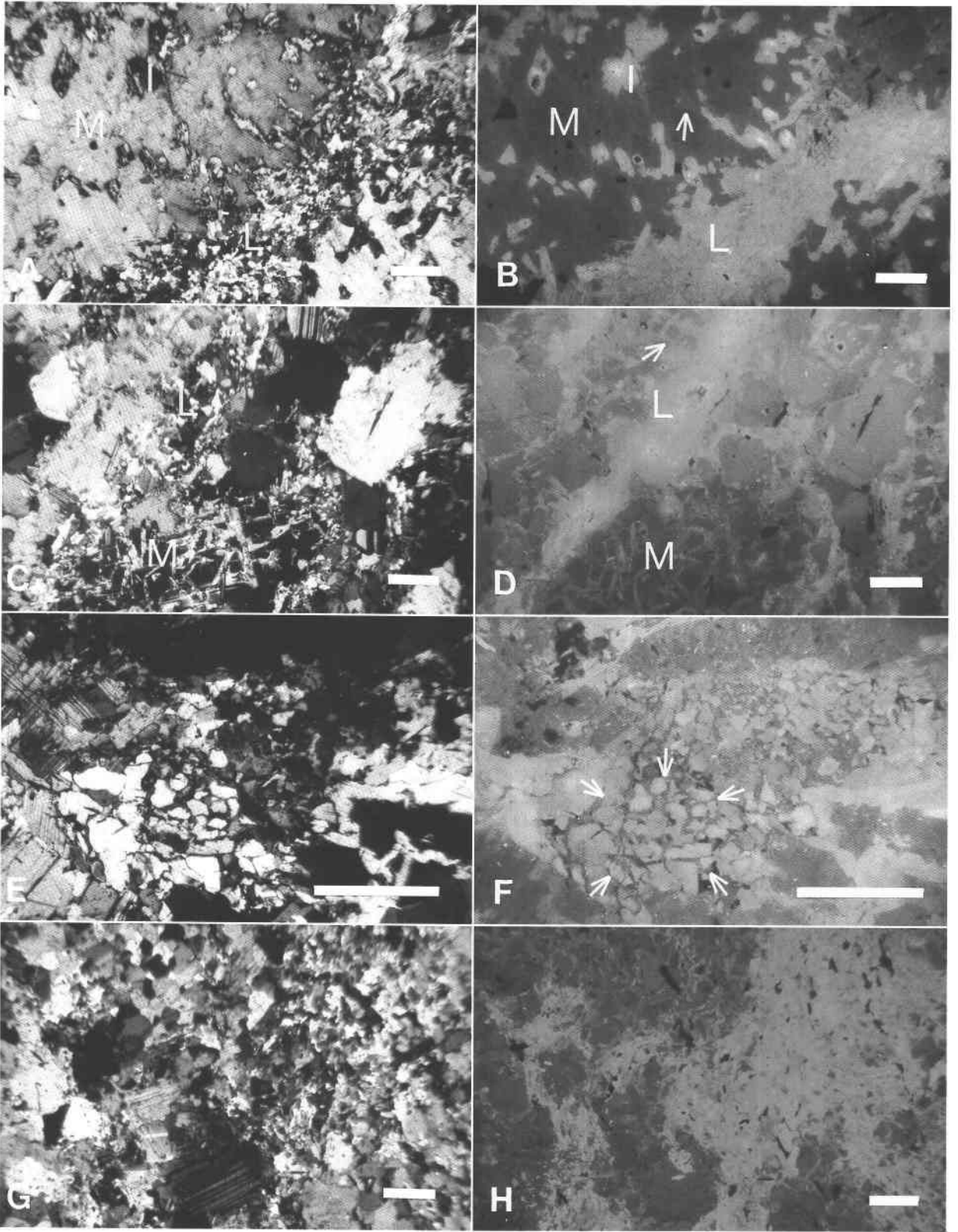
All plagioclases in the Boehls Butte anorthosite exhibit cathodoluminescence, with the color largely a function of plagioclase composition. Representative CL photomicro-

graphs are shown in Figure 2. Calcic plagioclase (An<sub>87–97</sub>) is readily distinguished by its yellow CL color; intermediate plagioclase (An<sub>39–65</sub>) has a green to green-yellow color (Fig. 2B). By comparison, a more sodic plagioclase sample (An<sub>28</sub>) that occurs in veins intruding the anorthosite (Table 1) has a dull green-blue color. The different colors permit rapid visual distinction of the plagioclase phases, complex plagioclase intergrowths, and compositional zonation.

Zones in CL color are observed in both plagioclase

Fig. 2. Transmitted light (left) and cathodoluminescence (CL; right) photomicrographs of the Boehls Butte anorthosite; all CL photomicrographs taken under identical operating conditions. Scale bar is 500  $\mu$ m; (A), (B) Massive anorthosite (sample MB31) showing green andesine (An<sub>38</sub>) megacryst (M) and yellow anorthite (An<sub>90–99</sub>) occurring both as inclusions (I) in megacryst and small granoblastic, polygonal grains in laminae (L). Patchy CL colors in the megacryst (arrow) may indicate zoned distribution of CL activators. The grain boundaries between host megacryst and inclusions are sharp, arguing against exsolution and coarsening as a mechanism to produce the coexisting plagioclases. The megacryst appears embayed by anorthite in the lamina, suggesting dissolution along its grain boundary. The CL is slightly zoned within the lamina, having brighter yellow CL toward the center. (C), (D) Megacryst (M) and lamina (L) in

massive anorthosite (sample MB31). Note the variability of CL intensity within the lamina; this is not the result of differences in major-element content (Ca, Na) of plagioclase. Note also the CL zonation of plagioclases near the lamina and the very fine, diffuse fractures emanating from the lamina (arrow). (E), (F) Lamina within massive anorthosite (MB45). Note the apparent fragmentation of grain (arrows) within lamina; fragmentation appears to have occurred by dilation, with little rotation of the grain fragments. (G), (H) Complex of CL color distribution within sheared anorthosite (LGM70). The CL of medium-grained, intermediate plagioclase is strongly zoned. Aggregates of granoblastic, polygonal anorthite engulf several large plagioclase grains at the bottom center and appear almost anastomosing in the left portion of the photomicrograph.



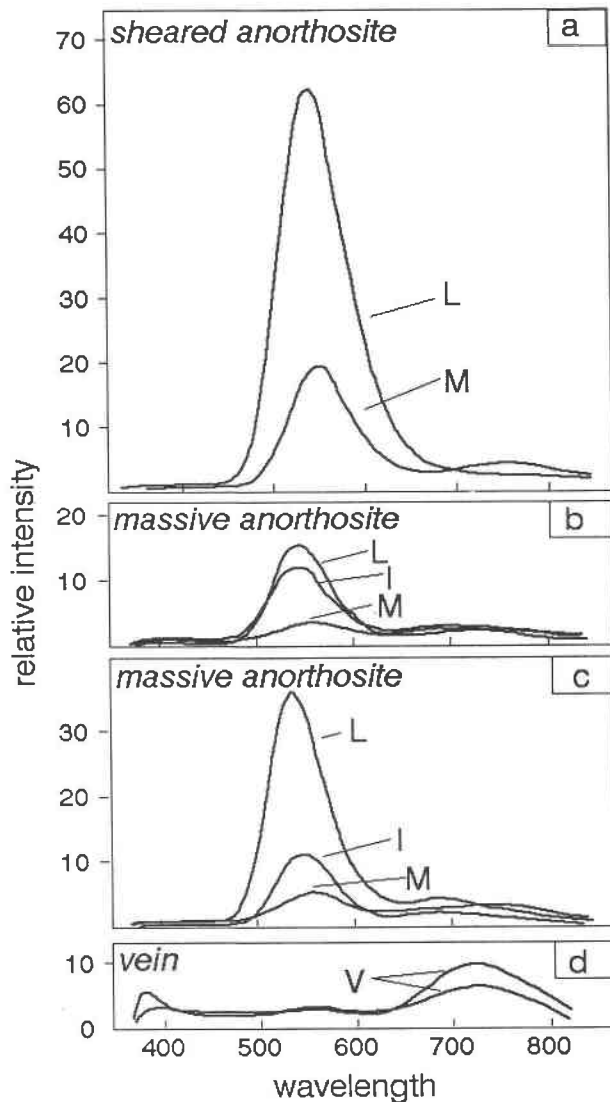


Fig. 3. Spectra of cathodoluminescence colors from plagioclase. All spectra are corrected for the instrumental response. Luminescence spectra from andesine megacrysts (M), anorthite inclusions in megacrysts (I), and anorthite in laminae (L) found coexisting in the Boehls Butte anorthosite [(a) sample LGM70, (b) MB45, and (c) MB31]; (d) Oligoclase-andesine plagioclase from plagioclase-rich vein intruding the anorthosite (V) is shown for comparison.

phases. Andesine megacrysts may exhibit subtle, patchy zonation but generally are not strongly zoned. The CL color change between host megacrysts and calcic inclusions is sharp. Zonation is more prevalent in fine- to medium-grained andesine occurring in contact with anorthite-bearing laminae (Figs. 2D, 2H). The andesine becomes increasingly yellow toward the grain boundaries. Granoblastic, polygonal anorthite within laminae are zoned; however the zonation affects the laminae as a whole, rather than individual grains within these structures. Typically, a brighter yellow is concentrated at the

center of the laminae (Fig. 2D); however a few examples have yellow concentrated at laminae edges (Fig. 2F).

Numerous factors govern CL zonation in plagioclase. Zonations formed during crystallization may be homogenized or disturbed during high-grade regional metamorphism. Those formed by dissolution and reprecipitation may be inferred from concave or embayed crystal faces and other replacement features, such as patchy coloration, and may occur only locally within the anorthosite. Strong CL zonations in the anorthosite are limited to granoblastic, polygonal plagioclases within or near the very fine laminae (Figs. 2D, 2H). Other dissolution and replacement effects, such as embayment of megacrysts by calcic plagioclases (Fig. 2B), are concentrated along these layers. These observations suggest that the incorporation and distribution of CL activators in the plagioclases have been mainly affected by recrystallization accompanying fluid flow along the laminae.

Microscopic structures, some of which are virtually invisible in transmitted light, are visible upon CL examination of the Boehls Butte anorthosite. These structures include (1) diffuse streaking or fracturing extending perpendicularly from the laminae (Fig. 2D), (2) fragmentation of calcic plagioclase grains within the laminae, with slight rotation of some of the fragmented grains (Fig. 2F), and (3) very fine brittle fractures (0.1–0.3 mm) that cross-cut plagioclase megacrysts and laminae (Fig. 2F). All of these features, as well as CL zonation along laminae in the anorthosite, appear to be superimposed on existing minerals, suggesting that they formed after metamorphic recrystallization of the anorthosite.

#### LUMINESCENCE SPECTRA

An objective measurement of luminescence color can be made by examining the positions and intensities of peaks in the emission spectra. In general, plagioclase spectra are characterized by three bands: 420–460, 550–570, and 680–750 nm (cf. Marshall, 1988). The CL spectra were measured in the range 370–860 nm (10-nm resolution) for three samples of Boehls Butte anorthosite (Figs. 3a–3c); these spectra were recorded under the same operating conditions and are all directly comparable. The samples show a pronounced peak in the range of 540–570 nm, with minor peaks in the range 387–446 and 690–750 nm (Table 1). The lack of a prominent peak in the range 690–750 nm is notable, as this peak is often strong, or dominant, in terrestrial plagioclases (Sippel and Spencer, 1970; Geake et al., 1971). Weak red emissions in the Boehls Butte plagioclases may reflect relatively low  $f_{O_2}$  during anorthosite crystallization; weak or absent emissions in the near IR are characteristic of lunar plagioclases and have been ascribed to low  $f_{O_2}$  during plagioclase crystallization (Geake et al., 1973, 1977).

The main differences observed in the spectra are the intensity of the green peak (540–570 nm) and the position of the red peak (690–750 nm). The relative intensities of the green peaks vary by up to a factor of 20. Megacrysts and inclusion-free crystals of intermediate

composition ( $An_{39-44}$ ) have the lowest intensity green peaks (M, I in Fig. 3). The highest intensities are measured for fine-grained, calcic plagioclase ( $An_{87-97}$ ) occurring in the thin laminae (L, Fig. 3). The CL spectrum for vein plagioclase ( $An_{28}$ ) is clearly different than the anorthosite plagioclase spectra, with almost no green peak and a relatively intense red peak (Fig. 3d). In this sample, a peak at approximately 380 nm was unstable during electron bombardment.

Differences in the color or intensity of CL in plagioclase may be controlled, in part, by plagioclase composition ( $X_{An}$ ), as it is likely that a divalent CL activator such as  $Mn^{2+}$  substitutes for  $Ca^{2+}$ , and  $Fe^{3+}$  for tetrahedrally coordinated  $Al^{3+}$ , in plagioclase (Geake et al., 1971, 1973, 1977; Telfer and Walker, 1975, 1978). The dependence of the red peak position on  $X_{An}$  has been previously reported (30-nm range, Sippel and Spencer, 1970; 60-nm, Geake et al., 1973; 100-nm, Telfer and Walker, 1975), although the green peak has been reported to be relatively insensitive to An content ( $\leq 10$ -nm; Geake et al., 1973). Our study differs from these previous studies in that naturally occurring plagioclases from a single occurrence are examined, rather than a suite of unrelated terrestrial and synthetic samples. Figure 4 shows the relationship of CL wavelength and plagioclase composition in the Boehls Butte plagioclases. Spectral response-corrected data reported by Telfer and Walker (1975) are shown for comparison; peak positions reported by Geake et al. (1973) are uncorrected and therefore cannot be included in this diagram. The data confirm the sensitivity of the red peak to anorthite content, with the peak position ranging from 687 nm for plagioclase of  $An \geq 90$  to 744 nm for  $An_{38}$  (Fig. 4). There is a significant difference between the red peak position in anorthite inclusions (average  $An_{91}$ ; 701–705 nm) and anorthite in laminae (average  $An_{94}$ ; 687 nm) that may not only be due to the slight compositional difference. Other factors that can affect the red peak position include the structural state of the plagioclase and the tetrahedral site occupancy of the activator (Telfer and Walker, 1978; Boroznovskaya et al., 1982). The position of the green peak appears to be slightly sensitive to plagioclase composition, with calcic plagioclase associated with shorter wavelength luminescence (540–548 nm) compared with more sodic compositions (549–561 nm; Fig. 4). Thus, increasing anorthite content in plagioclase results in red and green peak shifts toward shorter wavelengths.

The intensity of CL peaks is principally governed by the concentration of the activator element in the plagioclase. Peak intensity is related to the concentration of the activator, up to a maximum concentration of approximately 1 mol% for  $Mn^{2+}$  and 1.5 mol% for  $Fe^{3+}$  (Telfer and Walker, 1975); above this level of concentration, the activator may become self-quenching. Subtle variations in the activator content, resulting from differences in the environment of formation or recrystallization of the grain, may thus affect the CL color and spectrum. To this extent, it is interesting to note that the intensity of the green

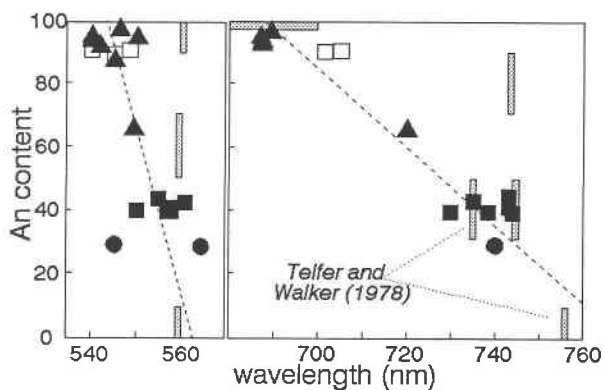


Fig. 4. Cathodoluminescence wavelengths of green (left) and red (right) peaks vs. plagioclase composition in mole fraction anorthite. Filled squares = plagioclase megacryst, open squares = inclusions in megacrysts, triangles = plagioclase in laminae, circles = plagioclase from plutonic vein. The positions of both peaks are sensitive to plagioclase composition; linear correlation coefficient  $r = -0.77$  for green peak,  $-0.97$  for red peak. Previous experimental data on synthetic or natural plagioclase are shown for comparison.

peak in granoblastic, polygonal anorthite occurring in laminae is significantly greater than the peak intensity in anorthite inclusions in megacrysts. These samples have  $Mn^{2+}$  and  $Fe^{3+}$  contents significantly below levels at which self-quenching is predicted (Table 1). Together with differences in the red peak position noted above, the intensity data suggest that the two types of anorthite formed or recrystallized in environments containing significantly different concentrations of activators.

#### CATHODOLUMINESCENCE ACTIVATORS

Examination of CL spectra in natural and synthetic plagioclases have identified elements that can cause cathodoluminescence in plagioclase; lattice defects resulting from shock damage may also cause CL (Sippel and Spencer, 1970). The following elements behave as CL activators:  $Ce^{3+}$  (wavelength = 355 and 490 nm),  $Eu^{2+}$  (420, 470 nm),  $Cu^{2+}$  (420 nm),  $Ti^{4+}$  (450–460 nm);  $Ti^{4+}$  may only act to enhance intrinsic CL),  $Mn^{2+}$  (550–570 nm), and  $Fe^{3+}$  (680–750 nm) (Geake et al., 1971, 1972, 1973; Laud et al., 1971; Mariano et al., 1973; Mariano and Ring, 1975; Telfer and Walker, 1975). It is uncertain whether  $Fe^{2+}$  behaves as a CL activator (550–570 nm, Mariano et al., 1973) or quencher element (Geake et al., 1972, 1973). The  $Mn^{2+}$ ,  $Fe^{2+}$ , and  $Fe^{3+}$  contents of Boehls Butte plagioclases are given in Table 1. Intermediate plagioclases ( $An \leq 50$ ) contain low abundances of  $Mn^{2+}$  and moderate amounts of  $Fe^{2+}$  ( $\leq 60$  ppm and 512–979 ppm, respectively; Table 1). Coexisting calcic plagioclases ( $An \geq 90$ ; granoblastic, polygonal anorthite and anorthite inclusions in megacrysts) were not mechanically separable) contain similar amounts of  $Fe^{2+}$  and approximately two times as much  $Mn^{2+}$ . The  $Fe^{3+}$  abundances (23–2504 ppm) and  $Fe^{3+}/Fe^{2+}$  ratios (0.03–5.3) are much less predictable. Anorthite separates contain four to six times as much

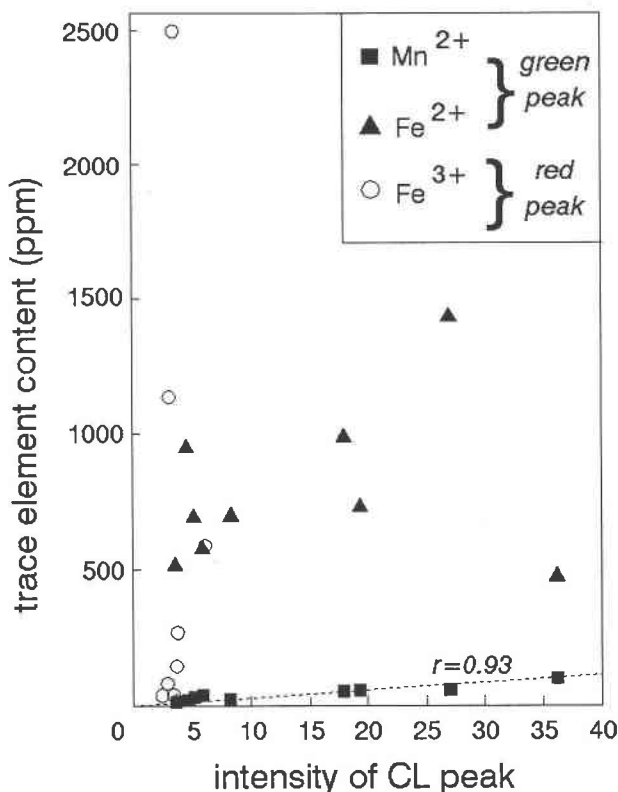


Fig. 5. Trace-element content vs. CL peak intensities. The excellent correlation between peak intensities and  $\text{Mn}^{2+}$  content suggests  $\text{Mn}^{2+}$  is an activator at concentrations as low as 19 ppm.  $\text{Fe}^{2+}$  acts as neither an activator nor quencher of green CL emissions up to 1422 ppm. Very large  $\text{Fe}^{3+}$  contents show no correlation with  $\text{Fe}^{3+}$ -activated red CL emissions, suggesting that most  $\text{Fe}^{3+}$  is present in a separate phase.

$\text{Fe}^{3+}$  as coexisting intermediate plagioclase in massive anorthosite; this factor is 50 times in sheared anorthosite (Table 1). By comparison with the anorthosite samples, vein plagioclase contains less  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  (12 and 290 ppm, respectively; Table 1) and has an  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio of 0.40. The trace element contents are all within the range reported for high-grade metamorphic plagioclases (Smith and Brown, 1988).

There is a strong correlation between  $\text{Mn}^{2+}$  content and peak intensities at 540–570 nm (Fig. 5); no correlation exists for  $\text{Fe}^{2+}$ . Thus,  $\text{Mn}^{2+}$  appears to be the dominant CL activator for this peak at concentrations as low as 19 ppm (Table 1), far lower than activation levels previously reported ( $\geq 100$  ppm, Mariano et al., 1973). The  $\text{Fe}^{2+}$  content has no apparent influence on the CL color or intensity. The relative intensities of the  $\text{Fe}^{3+}$ -activated red peaks (680–740 nm) in the Boehls Butte samples are small ( $I \leq 6.2$ ; Fig. 5; Table 1), despite  $\text{Fe}^{3+}$  contents as great as 2504 ppm. In fact, the most intense red peak is observed in vein plagioclase ( $I = 10.6$ ; Fig. 5) containing only 117 ppm  $\text{Fe}^{3+}$ . Because the anorthosite contains significantly less than a self-quenching level of  $\text{Fe}^{3+}$  (self-

quenching at 1–1.5 wt%, Geake et al., 1973; Telfer and Walker, 1975), it is likely that much of the measured  $\text{Fe}^{3+}$  is not incorporated in the plagioclase structure but is instead present in a phase such as hematite. Large amounts of  $\text{Fe}^{3+}$  in anorthite (Table 1) may reflect oxide precipitation or plagioclase alteration more than  $\text{Fe}^{3+}$  substitution for  $\text{Al}^{3+}$ . Anorthite in laminae forms the largest proportion of calcic plagioclase separates, suggesting a direct correlation between  $\text{Fe}^{3+}$  content and the laminae. For example, sample LGM39 (266 ppm of  $\text{Fe}^{3+}$ ; Table 1) contains predominantly megacrystic plagioclase, with few well-defined laminae. By comparison, sample MB31 contains more abundant laminae and  $\text{Fe}^{3+}$  (2504 ppm). Possible explanations for this result are examined in the following section.

#### RETROGRADE FLUID-ROCK INTERACTION

Any interpretation of the CL phenomena observed in this study must address several points. As a general observation, all of the plagioclases are luminescent, suggesting that all phases formed or were recrystallized at relatively high temperatures because authigenic and low grade metamorphic plagioclase rarely luminesces (Kastner, 1971). Other observations include (1) the occurrence of two distinct modes of anorthite (inclusions and in laminae), having different CL peak positions and intensities, (2) subtle CL zonation and embayment of andesine megacrysts along laminae, (3) variable  $\text{Fe}^{3+}$  contents, especially in calcic plagioclase separates, and (4) numerous brittle features such as the apparent dilational fragmentation of anorthite grains within laminae, diffuse fractures emanating from laminae, and very fine-scale fractures cross-cutting all phases in the anorthosite. These observations are best explained by retrograde fluid-rock interaction focused along laminae in the anorthosite. Recrystallization of anorthite accompanied fluid flow along these layers, resulting in changes in activator concentrations (peak intensities increased) and possibly changes in structural state (peak positions shifted). Alteration or oxide precipitation along these layers increased the overall abundance of  $\text{Fe}^{3+}$  in the laminae; possible changes in other trace elements mobilized by the hydrothermal fluid can also be inferred. The timing of fluid flow is inferred from the numerous brittle structures and the concentration of CL changes along the laminae. The rapid, nearly isothermal decompression of the Boehls Butte area from peak metamorphic pressures of 8–10 to approximately 3 kbar (Criss and Fleck, 1987; Grover and Rice, 1988; Ziegler and Rice, 1991) may have resulted in fluid circulation into the anorthosite during retrograde cooling. Stable isotope evidence for local, retrograde meteoric or hydrothermal alteration of Belt Supergroup metasediments and the Boehls Butte anorthosite has been previously reported (Taylor, 1969; Mora and Valley, 1988, 1991). In both cases, alteration was not widespread and pervasive but variably affects the rocks on a scale of millimeters to meters.

The results of this study highlight the usefulness of a detailed cathodoluminescence study to identify evidence

for fluid-rock interaction that can be virtually invisible during routine petrographic or whole-rock geochemical analysis. Indeed, except for stable isotope studies, retrograde fluid-rock interaction has been largely unrecognized in previous studies of the anorthosite (Hietanen, 1963; Nord, 1973; Juras, 1974; Goldberg, 1983). CL petrography helps to identify fluid pathways and to constrain the scale of fluid-rock interaction; these observations are useful guides to further geochemical studies. Clearly, cathodoluminescence petrography can be a powerful tool in studies of high-grade metamorphic rocks.

#### ACKNOWLEDGMENTS

Support for this work was provided by National Science Foundation grant EAR-8922638 (C.I.M.) and Swiss National Science Foundation grant 20-30854.91 (K.R.). We thank M. Owen and an anonymous reviewer for their comments on the manuscript.

#### REFERENCES CITED

- Barker, C.E., and Kopp, O.C. (1991) Luminescence microscopy and spectroscopy: Qualitative and quantitative applications. Society for Sedimentary Geology (SEPM) Short Course, 25, 195 p.
- Boroznovskaya, N.N., Lesonov, F.P., and Scherbakova, V.L. (1982) On the cathodoluminescence of Fe<sup>3+</sup> in calcic plagioclase. *Geokhimiya*, 9, 129–131 (in Russian).
- Criss, R.E., and Fleck, R.J. (1987) Petrogenesis, geochronology, and hydrothermal systems of the northern Idaho batholith and adjacent areas based on <sup>18</sup>O/<sup>16</sup>O, D/H, <sup>87</sup>Sr/<sup>86</sup>Sr, K-Ar, and <sup>40</sup>Ar/<sup>39</sup>Ar studies. U.S. Geological Survey Professional Paper 1436, 95–137.
- Geake, J.E., Walker, G., Mills, A.A., and Garlick, G.F.J. (1971) Luminescence of Apollo lunar samples. Proceedings of the Second Lunar Science Conference. *Geochimica et Cosmochimica Acta*, 3 (suppl. 2), 2265–2275.
- (1972) Luminescence of lunar material excited by electrons. Proceedings of the Third Lunar Science Conference. *Geochimica et Cosmochimica Acta*, 3 (suppl. 13), 2971–2979.
- Geake, J.E., Walker, G., Telfer, D.J., Mills, A.A., and Garlick, G.F.J. (1973) Luminescence of lunar, terrestrial and synthesized plagioclase, caused by Mn<sup>2+</sup> and Fe<sup>3+</sup>. Proceedings of the Fourth Lunar Science Conference. *Geochimica et Cosmochimica Acta*, 3 (suppl. 4), 181–189.
- Geake, J.E., Walker, G., and Telfer, D.J. (1977) The cause and significance of luminescence in lunar plagioclase. *Philosophical Transactions of the Royal Society of London*, A285, 403–408.
- Goldberg, S.A. (1983) Geochemical constraints on the origin of Proterozoic anorthosites, western United States, 191 p. Ph.D. thesis, University of Oregon, Eugene, Oregon.
- Grover, T.W., and Rice, J.M. (1988) Pressure-temperature evolution of aluminous schists in the Boehls Butte–Goat Mountain area, northern Idaho. Geological Society of America Abstracts with Program, 20, A160.
- Hietanen, A.H. (1963) Anorthosite and assorted rocks in the Boehls Butte quadrangle and vicinity, Idaho. U.S. Geological Survey Professional Paper 334-B, 78 p.
- (1984) Geology along the northwest border of the Idaho batholith, northern Idaho. U.S. Geological Survey Bulletin 1608, 17 p.
- Juras, D. (1974) The petrofabric analysis and plagioclase petrography of the Boehls Butte anorthosite, 132 p. Ph.D. thesis, University of Idaho, Moscow, Idaho.
- Kastner, M.A. (1971) Authigenic feldspars in carbonate rocks. *American Mineralogist*, 56, 1403–1442.
- Laud, K.R., Gibbons, E.F., Tien, T.Y., and Stadler, H.L. (1971) Cathodoluminescence of Ce<sup>3+</sup> and Eu<sup>2+</sup>-activated alkaline earth feldspars. *Journal of the Electrochemical Society*, 118, 918–923.
- Mariano, A.N., and Ring, P.J. (1975) Europium-activated cathodoluminescence in minerals. *Geochimica et Cosmochimica Acta*, 39, 649–660.
- Mariano, A.N., Ito, J., and Ring, P.J. (1973) Cathodoluminescence of plagioclase feldspars. Geological Society of America Abstracts with Programs, 5, 726.
- Marshall, D.J. (1988) Cathodoluminescence of geological materials, 146 p. Unwin-Hyman, Boston.
- Mora, C.I., and Valley, J.W. (1988) Channelized meteoric-hydrothermal alteration of the Boehls Butte and Bitterroot anorthosites, northern Idaho and Montana. *Eos*, 69, 1489.
- (1991) Prograde and retrograde fluid-rock interaction in Wallace Formation calc-silicates northwest of the Idaho batholith: Stable isotopic evidence. *Contributions to Mineralogy and Petrology*, 108, 162–174.
- Morrison, J., and Valley, J.W. (1988) Post-granulite facies fluid infiltration in the Adirondack Mountains. *Geology*, 16, 513–516.
- Nord, G.L., Jr. (1973) The origin of the Boehls Butte anorthosite and related rocks, Shoshone County, Idaho, 159 p. Ph.D. thesis, University of California, Berkeley, California.
- Padovani, E.R., Shirey, S.B., and Simmons, G. (1982) Characteristics of microcracks in amphibolite and granulite facies rocks from southeastern Pennsylvania. *Journal of Geophysical Research*, 87, 8605–8630.
- Ramseyer, K., Fischer, J., Matter, A., Eberhardt, P., and Geiss, J. (1989) A cathodoluminescence microscope for low intensity luminescence. *Journal of Sedimentary Petrology*, 59, 619–622.
- Sippel, R.F., and Spencer, A.B. (1970) Cathodoluminescence properties of lunar rocks. *Science*, 167, 677–679.
- Smith, J.V., and Brown, W.L. (1988) Feldspar minerals. Crystal structures, physical, chemical, and microstructural properties, vol. 1. Springer-Verlag, New York.
- Smith, J.V., and Stenstrom, R.C. (1965) Electron-excited luminescence as a petrologic tool. *Journal of Geology*, 73, 627–635.
- Sprunt, E.S., and Nur, A. (1979) Microcracking and healing in granites. New evidence from cathodoluminescence. *Science*, 205, 495–497.
- Taylor, H.P., Jr. (1969) Oxygen isotopic studies of anorthosites, with particular reference to the origin of bodies in the Adirondack Mountains, New York. In Y.W. Isachsen, Ed., *Origin of anorthosites and related rocks*, memoir 18, p. 111–134. New York State Museum and Science Service, Albany, New York.
- Telfer, D.J., and Walker, G. (1975) Optical detection of Fe<sup>3+</sup> in lunar plagioclase. *Nature*, 258, 694–695.
- (1978) Ligand field bands of Mn<sup>2+</sup> and Fe<sup>3+</sup> luminescence centres and their site occupancy in plagioclase feldspars. *Modern Geology*, 6, 199–210.
- Walker, K.D., and Mora, C.I. (1990) Mineralogy, cathodoluminescence, and stable isotope geology of the Boehls Butte anorthosite, northern Idaho. Geological Society of America Abstracts with Program, 22, A345.
- Yardley, B.W.D., and Lloyd, G.E. (1989) An application of cathodoluminescence microscopy to the study of textures and reactions in high-grade marbles from Connemara, Ireland. *Geological Magazine*, 126, 333–337.
- Ziegler, R.D., and Rice, J.M. (1991) Growth and resorption of garnet in polymetamorphic amphibolites from northern Idaho. Geological Society of America Abstracts with Programs, 23, A443.

MANUSCRIPT RECEIVED JANUARY 17, 1992

MANUSCRIPT ACCEPTED JUNE 18, 1992