

Cathodoluminescence and minor elements in forsterites from extraterrestrial samples

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ABSTRACT

Forsterite with less than about 2% FeO in the carbonaceous (C3V, C3O, C2) and unequilibrated ordinary chondrites (UOC) shows cathodoluminescence (CL) hues ranging from red to purple to blue. Spectral scans of the light show that it is composed of two broad peaks for forsterites in the C3V, C3O, and UOC meteorites, one centered at about 458 nm (visible blue) and the other near 800 nm but extending into the visible red. The resulting color varies with relative intensities of the two peaks. CL of forsterite in C2 meteorites is distinctly different with a broad weak peak in the blue and a broad peak at about 723 nm in the red. These distinct spectral differences should allow a rapid method of assigning single forsterite grains such as those in deep-sea particles or in cosmic dust to a particular source or affinity.

Blue CL correlates with a high level of refractory minor elements including Al, Ca, Ti, and V, whereas red CL correlates with high Mn and Fe. Cr shows no obvious difference between the two colors. Scanning CL allows recognition of dramatic and complex textural features associated with these forsterites.

INTRODUCTION

Some minerals give off light, technically termed cathodoluminescence (CL), under electron bombardment. Many minerals can readily be identified just from their CL colors, e.g., quartz, Ca and Mg carbonates, apatites, and feldspars. Qualitative descriptions of CL in minerals, especially carbonates, using an electron probe were given by Long and Agrell (1965) and Smith and Stenstrom (1965), and Zinkernagel (1978) presented an extensive study of quartz CL with semiquantitative spectra. Because high levels of Fe quench CL in the visual range, luminescence in olivines, pyroxenes, micas, and amphiboles is rarely observed; however, nearly pure Mg olivine and (Mg,Ca) pyroxenes do show rather intense CL. Although these minerals are rare in terrestrial rocks, nearly pure forsterite and enstatite are common in the carbonaceous, unequilibrated ordinary, and enstatite chondrites, and CL has revealed significant textural features that probably cannot be seen by any other technique (Hutcheon et al., 1978; Leitch and Smith, 1982). Visual observation of CL is rather subjective, and descriptions of color or texture require quantitative representation. In this paper, various methods are described to illustrate CL in forsterite, and uses are suggested for quantitative CL in the primitive meteorites.

Forsterite in carbonaceous chondrites

A common mineral in the carbonaceous and unequilibrated ordinary chondrites is olivine with composition ranging from nearly pure forsterite ($\approx\text{Fo}_{99.8}$) to intermediate Mg-Fe compositions ($\approx\text{Fo}_{50}$) (e.g., Dodd, 1981).

Textural associations include single euhedral grains within the matrix, subhedral grains, crystal fragments, partial chondrules, and whole chondrules. McSween (1977) documented a correlation of the Mg/Fe ratio in olivine with texture. During determination of olivine compositions in deep-sea particles (DSP) (Steele et al., 1985a) and comparison with olivines from carbonaceous and unequilibrated ordinary chondrites, an unusual and apparently unique chemical signature in the nearly pure forsterites of both DSP and C-chondrites (Steele et al., 1985b) was recognized. This chemical signature is characterized by high levels of Al, Ti, and Ca. In addition, the forsterites in meteorites showed complex CL textures, the red and blue hues of which correlated with the unusual minor-element content.

Table 1 presents the ranges of minor-element levels generalized from data in Steele (in prep.) in the red and blue luminescing forsterites. Each entry represents the maximum range from all meteorites and greatly simplifies the distribution of analyses within particular meteorites or meteorite groups. Although Table 1 implies only two types of luminescing forsterite, it is the judgment of the observer whether a particular point is red or blue resulting in some overlap of assignment. Within group A oxides and group B oxides, there is a strong positive intercorrelation of concentrations. The group C oxides, although occurring in some terrestrial and meteoritic olivines, are generally below detection in the luminescing forsterites. It is not as yet certain whether individual meteorites or classes of meteorites have different ranges for particular elements (Steele, in prep.). Within individual single crys-

Table 1. Ranges of minor-element concentrations in luminescing forsterites from carbonaceous and unequilibrated ordinary chondrites*

Element	Blue	Red
Group A		
Al ₂ O ₃	1500-3600	300-2500
CaO	0.3-0.75	<0.6
TiO ₂	300-900	<700
V ₂ O ₃	40-150	(<40)
Group B		
Cr ₂ O ₃	800-3000	500-4500
MnO	<300	100-1600
FeO	0.2-0.9	0.9-2.0
Group C		
Na ₂ O	(<50)	(<50)
P ₂ O ₅	(<40)	(<40)
NiO	(<150)	(<150)

*numbers in parentheses represent 2 σ detection levels based on counting statistics.

tals of forsterite, the minor-element level varies and qualitatively correlates with the observed blue or red color.

Cathodoluminescence study

It was apparent that the CL color ranged from bright blue for the high trace-element levels to red as the total trace elements decreased and Fe and Mn increased. Above about 2% FeO, no visible CL is present. The CL color also varies with current density, as was seen when comparing visual observations for a focused beam in the electron probe with large-area (1 mm) CL photographs obtained in a CL microscope.

To correlate chemical changes with color variations, an electron probe (JEOL-733) was equipped with a light-dispersing spectrometer (Tracor Northern 6500 rapid scan spectrometer) allowing display of the CL spectrum. Details of this system are given in Appendix 1.

Spectra obtained from forsterites showing red CL and blue CL are illustrated in Figures 1b and 1c, respectively. Figure 1a is the background spectrum obtained with no electron beam and thus shows no features in the range 300 to 800 nm for which the detector system is sensitive. In contrast, areas luminescing red under visual observation show a broad peak partially in the visible range (Fig. 1b) but peaking in the near-infrared probably just beyond the 800 nm cutoff of the spectrometer. An olivine showing bright-blue visible CL gave the spectrum in Figure 1c, which is dominated by a broad peak centered at 458 nm (vertical cursor) near the center of the blue spectral range (424–491 nm). In addition, a weak broad peak similar to that of Figure 1b occurs at the red end of the spectrum. Many recorded spectra and others observed in real time showed that CL spectra of forsterite are composed of the above blue and red peaks, but combined in varying intensity to produce blue, purple, and red color as observed by eye. Figure 1d shows two spectra of pale-blue CL both obtained from the same area but the lower spectrum with a focused electron beam ($\sim 1 \mu\text{m}$) and the upper spectrum

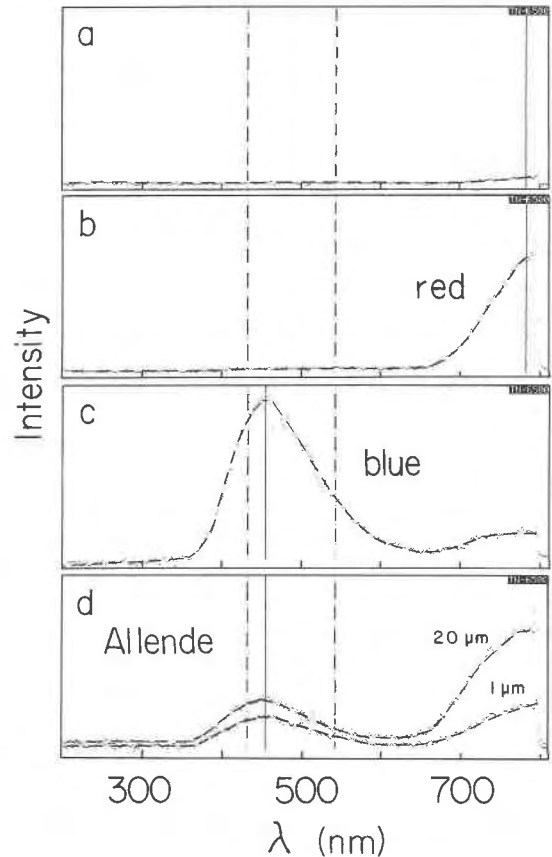


Fig. 1. (a) Luminescence spectra obtained with no electron beam which represents instrumental background; (b,c) spectra from red and blue areas, respectively, of Allende forsterite; (d) pale-blue area of Allende forsterite. The upper trace was obtained with a $\sim 20\text{-}\mu\text{m}$ beam and the lower with a $\sim 1\text{-}\mu\text{m}$ -diameter electron beam. Each spectrum was enhanced by a dashed line to aid reproduction.

with a beam of $\sim 20 \mu\text{m}$. We have noted qualitatively that as the current density decreases, the CL becomes more red; Figure 1d shows that this is due to a change in the intensity of the two broad peaks and not due to a change in wavelength of either. This is especially important because the wavelength remains constant and can be quantitatively compared; on the other hand, the intensities must be compared under identical beam conditions. All spectra presented here were obtained with a focused beam to minimize this variable.

The CL spectra of forsterites from a selection of meteorites are illustrated in Figure 2, and although only one spectrum is shown for each, a rapid survey was made for about 10 different grains using the real-time display capability of the system. Although relative intensities of the peaks vary, the position of the blue peak and shape and hence the projected position of the red peak remain constant. The spectrum from Vigarano (C3V) (Fig. 2a) is similar to Allende (C3V), although the vertical cursor marking the visual peak center is slightly different (456

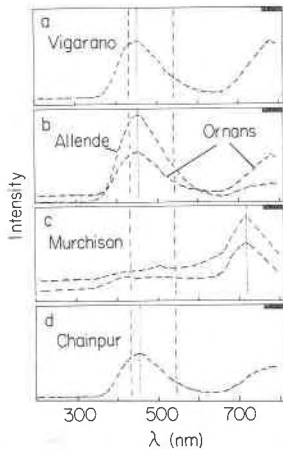


Fig. 2. Comparison of cathodoluminescence spectra from forsterites in different meteorites. (a) Vigarano C3V; (b) Allende C3V (high, blue; low, red) and Ormans C3O (low, blue; high, red); (c) Murchison C2; (d) Chainpur UOC.

nm) from that of Allende (458 nm) (Figs. 1c, 2b). A somewhat greater difference is shown on Fig. 2b where spectra for Allende and Ormans (C3O) are displayed. Relative to the cursor at 458 nm, the Ormans blue peak is estimated to occur about 450 nm. Although shifts in peak position can be recognized, changes in peak shape may also occur, but accurate description probably requires computer analysis.

We have noted that color photographs of C3 and C2 forsterites systematically differ in CL color; C3 forsterites range from blue to purple to red and C2 forsterites are dominated by red, orange, and yellow. The reasons for these differences were unknown especially since under a focused electron beam, C2 forsterites appear blue. The spectra shown in Figure 2c were obtained from two forsterites in Murchison (C2) and clearly show differences compared to C3 forsterites in that a red peak occurs at 723 nm (vertical cursor) and the blue peak is represented by a broad band extending from 400 to 650 nm. Although spectra were not obtained from other C2 meteorites, the common yellow and orange CL colors suggest that the spectra are basically similar to those of Figure 2c. Figure 2d shows a spectrum from Chainpur (UOC) that is like spectra of C3 forsterites; likewise, color photographs of UOC and C3 forsterites show similar CL colors.

Composition and cathodoluminescence

A correlation between the minor-element content of forsterite and the observed CL color was documented by Steele et al. (1985b), and to further illustrate the quantitative variation of color and to possibly correlate these changes with chemical changes, a traverse was made in an Ormans forsterite from the rim, which showed no CL, across a red zone and into the core, which showed bright-blue CL. Data were obtained for Al, Ca, Ti, Cr, Mn, and Fe concentrations at 13 points along this traverse and CL

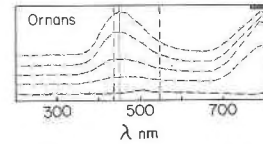


Fig. 3. Sequence of spectra from Ormans forsterite at 8- μ m intervals from nonluminescing (lower spectrum) to red and then to blue areas (upper spectrum). The individual spectra are displaced to avoid overlap.

spectra at 11 points but both encompassing 90 μ m. Because the compositions were determined at a different time than the CL spectra, there may be a slight relative positional error of less than 5 μ m. Figure 3 shows a sequence of CL spectra that were obtained at points 4–8 of the 11-point traverse. The first three points were in the blue core and are essentially identical to the upper spectrum of Figure 3, whereas points 9–11 from the edge of the grain are identical to the lower spectrum. The sequence of spectra from top to bottom thus represents the CL in steps of about 8 μ m. The upper spectrum is typical of blue CL, and in the sequence of spectra the blue peak gradually becomes less intense while the red peak remains constant until the bottom spectrum where it abruptly disappears, consistent with no CL at the edge.

The concentration profiles of the minor elements are shown on Figure 4. Superimposed on these profiles are the relative intensities of the red and blue CL peaks from each of the 11 spectra. From other similar scans as well as Figure 4, it is apparent that the blue CL in the interior of the forsterites is associated with high Al, Ca, and Ti and that these elements show a marked decrease across color boundaries. In contrast, Mn and Fe show low concentrations in the core and marked increases in the red and nonluminescing zones. The relation between the changes in the two groups of elements (groups A and B, Table 1) are not perfectly inversely correlated in that where the changes in group A occur, no change occurs in the group B elements (see Fig. 4).

The intensity of the blue peak decreases gradually from the core to the rim and correlates with the variation in Al and Ca and possibly with Ti, although the larger errors will tend to mask details of the latter. The red peak correlates inversely with both Fe and Mn. Although the above correlations are rather obvious, the element causing the CL may not be apparent because of geochemical correlations and because elemental concentrations well below the detection limit of the electron probe may cause CL. Both Ti^{4+} and V^{3+} are known activators in insulators (White, 1975), and both Ti and V have been detected in the blue-luminescing areas of forsterites although their oxidation states are unknown. In synthetic forsterites grown from a V-bearing flux, all forsterites contain about 0.5% V_2O_5 and do luminesce blue (I. Steele, unpub. data), but quantitative spectral scans have not been obtained. Forsterites have also been grown with other minor elements including Ti^{4+} , Cr^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , and Zn^{2+}

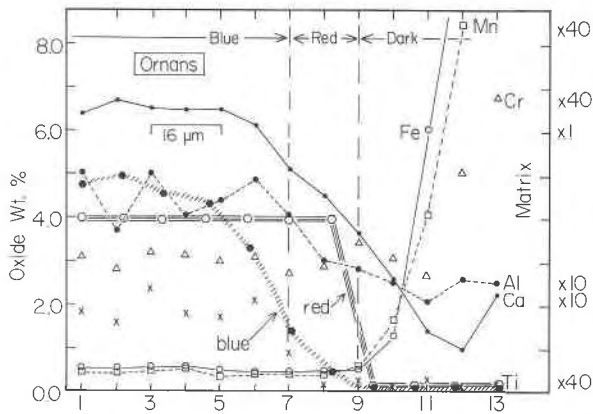


Fig. 4. Minor element variation along 90- μm traverse in Ornnans forsterite. Labels (1–13) on x -axis represent 13 equally spaced points along traverse. The core (left) shows blue CL, changing to red (center), and finally to no CL at boundary of grain with matrix. The peak height of the red and blue CL peaks on Fig. 3 are plotted for comparison with an arbitrary vertical scale.

in addition to V_2O_3 and compensating Li. All qualitatively show the same CL as forsterite containing only V with the exception of the Mn^{2+} -bearing forsterite which shows red CL. Until quantitative spectra are obtained, it is probably futile to assign the observed CL in the meteoritic forsterites to a specific activator. On the other hand, the red CL peak correlates well with both Mn and Fe and might best be assigned to Mn^{2+} , whereas the rapid disappearance of the peak might be due to the correlated rapid increase in Fe^{2+} , which is known to quench CL (White, 1975). Cr does not correlate with either the red or blue peak and thus probably does not have a large effect. One could conclude that for these meteoritic forsterites, the intensity of the blue CL correlates with the level of refractory minor elements, and likewise the intensity of the red anticorrelates with the concentration of Mn and Fe.

Applications of quantitative CL

Because the color of CL is associated with an element or group of elements as illustrated above, the distribution and qualitative concentration can be recognized by display of the CL of appropriate color. On a large scale, color photographs from a CL microscope serve this purpose but show all colors simultaneously. More specific information can be displayed by selecting a specific wavelength range of light by one of several methods: (1) use of filters in the CL microscope; (2) a phototube selective to particular wavelength ranges and used in scanning mode on a microprobe; (3) a device similar to the detector used in the present study but with the output of a group of diodes (wavelength range) modulating the intensity in scanning mode.

The textural information obtained from any of these schemes can be dramatic as, for example, the complex textures revealed in single crystals of forsterite (Fig. 5). In

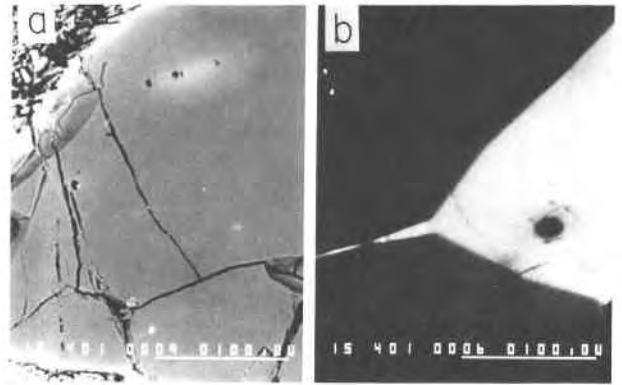


Fig. 5. Portion of Allende forsterite grain illustrated by (a) back-scattered electron image (BSE) and (b) scanning CL image. Whereas the BSE image shows an apparently homogeneous single crystal, the CL image shows a sharp boundary. Because the detector is sensitive only to blue, this boundary marks the change in minor-element content. Note also a sharp daggerlike protrusion into the nonluminescing margin. This protrusion is distinctly bluer than the core. The sharp, symmetrical boundaries of the blue core suggest crystallographic control during growth.

this case, the detector has a photocathode with a response in the blue about 100 times greater than in the red. Thus in scanning mode, the image displayed will be the distribution and relative intensity of the blue peak in Figure 1c.

Currently there is a great deal of speculation on the relation among extraterrestrial types of material including the various types of primitive meteorites, cosmic dust, deep-sea particles, and comets. Because olivine is the one phase abundant in most of these samples, it is possible to draw comparisons using the minor-element chemical signature of olivine. Thus Steele et al. (1985a) argued that deep-sea particles were related to some C2 meteorites because of a similar minor-element pattern of their forsterites. This was rather a tedious study, and the CL spectra may provide an alternative rapid means of relating olivines from various sample types. The spectral signature from deep-sea particles might allow a certain match with a particular meteorite type, but care must be taken in interpretation because the CL may be modified by heating, although in a refractory material such as olivine this should be minimal.

Possibly of greater interest is the relation of cosmic dust to known meteorites. The small size of these samples often precludes obtaining accurate compositional data. On the other hand, it should be relatively easy to obtain a CL spectrum because the samples may not need to be polished and contamination by other phases within the cosmic dust aggregates should not be a serious problem as CL is a surface effect.

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APPENDIX 1

The cathodoluminescence spectra shown herein were obtained using a Tracor Northern rapid scan spectrometer (TN-6500). Light was collected using a 1-mm diameter fiber optics probe at the focal point of the microscope objective on the JEOL-733 microprobe. The other end of the fiber optics probe was at the entrance slit of a 200-mm focal length TN-6048 fixed holographic spectograph (200 lines/mm). The spectrum (200-800 nm) was imaged on a 1-in.-diameter image intensifier (TN-6122). This in turn was fiber optic coupled to a Si photodiode array composed of 1024 25 μm \times 2.5 mm elements with a response range from 360 to 850 nm. The intensities from this array were stored and displayed in real time as 512 channels of information. For calibration, the detector was simply directed at a fluorescent light, and the Hg lines at 435.8 and 546.1 nm, which appeared as sharp peaks, provided known reference lines. These positions appear as the dashed vertical lines on each spectrum.