

RESEARCH METHODS PAPERS

HOW TO OVERCOME IMAGING PROBLEMS ASSOCIATED WITH CARBONATE MINERALS ON SEM-BASED CATHODOLUMINESCENCE SYSTEMS

ROBERT M. REED¹ AND KITTY L. MILLIKEN²

¹ Bureau of Economic Geology, John A. and Katherine G. Jackson School of Geosciences, The University of Texas at Austin, Box X, University Station, Austin, Texas 78713-8924

e-mail: rob@alumni.utexas.net

² Department of Geological Sciences, John A. and Katherine G. Jackson School of Geosciences, The University of Texas at Austin, Austin, Texas 78712

ABSTRACT: On SEM-based cathodoluminescence systems (scanned CL), methods are needed to overcome image-quality problems caused by persistent luminescence of carbonate minerals. An effective solution to the persistence problem is to acquire images using only the shorter wavelengths, most easily done by using a broadband, short-wavelength (UV-blue range) filter. The filter used provides 80% to 90% transmissivity in the range of 385 to 495 nm and some transmissivity as low as 350 nm. The filter allows transmission of the relatively nonpersistent UV-violet luminescence present in most carbonates in the range of 350 to 425 nm, but blocks the common orange-red wavelength luminescence found in carbonates. The lack of imaging problems in subsequent images shows that persistent luminescence in carbonates is primarily in the orange-red wavelengths. Cathodoluminescence images produced using a short-wavelength filter are comparable in detail to those obtained from conventional light-microscope-based cathodoluminescence systems. In almost all examples, features visible in the orange-red wavelengths show corresponding variations in luminescence in the shorter wavelengths.

INTRODUCTION

SEM-based cathodoluminescence systems (scanned CL) afford higher magnifications, better detection of weak luminescence, detection of a broader spectrum of luminescence, and more stable operating conditions than do conventional, light-microscope-mounted CL systems. Scanned CL imaging of carbonate minerals, however, presents technical challenges that are more significant than those presented by similar imaging of most silicate minerals. These challenges relate to two aspects of carbonate CL: relative luminescence intensity and persistence of luminescence.

Luminescent carbonate minerals commonly emit brighter luminescence than most potentially associated silicate minerals (such as quartz). In a rock having a mixed silicate-carbonate lithology, this difference can create serious imaging problems. If contrast and brightness of the image are adjusted so that details are visible in silicate minerals, associated carbonate minerals may be too bright to image without loss of internal detail. If contrast and brightness are adjusted for observing the detail in carbonate minerals, silicate minerals commonly show little or no apparent luminescence. Differences in relative luminescence can also be a problem within zoned carbonates. This problem is not unique to scanned CL imaging: it is encountered in directly viewed, light-microscope-mounted CL systems as well.

Unique to scanned CL imaging, and the primary focus of this study, is the problem created by persistence of luminescence (phosphorescence). Marshall (1988, p. 24) noted that "some minerals have long phosphorescence and the CL of important cases such as calcite cannot be effectively studied on the SEM because of this." In some carbonate minerals, photoemission continues for considerable periods after cessation of electron-beam excitation. In a scanned CL system, a typical beam raster speed (200 μ s per pixel dwell time) may be slow relative to the decay time of the CL emission, resulting in simultaneous detection of light from different areas of the specimen. This simultaneous detection leads to bright streaking or smearing in the image parallel to the scan direction. The effect can severely degrade image quality (Fig. 1A), and it makes it difficult to use scanned CL on most samples containing luminescent carbonate minerals.

INSTRUMENTATION

Scanned CL images were produced using an Oxford Instruments MonoCL2 detector and PA-3 amplifier attached to a Phillips XL30 SEM. This system uses a retractable parabolic mirror and a photomultiplier tube to collect and amplify luminescence (Kearsley and Wright 1988). For the images shown here, the CL detector was being run in panchromatic mode either with or without a filter. The SEM was operated at either 15 or 20 kV and at large sample currents. The spot size used was

larger than that typically used for secondary electron imaging on an SEM and was more typical of the settings recommended for EDS mapping (setting 6.3 on the XL30). Emission currents ranged between 50 and 125 μ A. Photomultiplier voltages on the PA3 amplifier ranged from -625 V (for dominantly silicate lithologies) to -725 V (for dominantly carbonate lithologies). Samples were positioned 1 to 1.5 mm beneath the bottom of the CL mirror assembly. Samples discussed here are polished thin sections coated with a layer of carbon 25 to 30 nm in thickness, although polished rock slabs can be examined as well. Experiments using interpixel delay were conducted on a JEOL T330A using an Oxford Instruments PanaCL detector and 4pi Analysis beam control and image acquisition software.

APPROACHES

Several techniques have been tested for imaging carbonate minerals using scanned CL, with varying degrees of success. Each has its own merits and problems.

Dwell Time and Interpixel Delay

An approach to overcoming imaging problems associated with persistence of carbonate luminescence in SEM systems was previously proposed by Lee (2000). He showed that increased dwell time (the amount of time that the beam remains on a particular spot) during imaging can produce nondegraded images of carbonates using scanned CL. Very long dwell times (3,200 μ s per pixel) produced detailed and clear images of zoned calcite (Lee 2000).

The main problem associated with an approach based solely on increased dwell time is the increased time necessary to produce a single image. For a 1,024 \times 760 pixel image, a dwell time of 3,200 μ s per pixel results in an image-collection time of approximately 46 minutes (Fig. 1B). For studies requiring large numbers of images—microfracture analysis studies, for example (Gomez et al. 2001)—such an image-collection time is prohibitive. In addition, long dwell times result in significant beam damage of the specimen.

A carbonate scanned CL method, which has proven less effective than extremely long dwell times, involves a digital imaging system that allows interpixel delay (a pause between imaging one pixel and the next). The idea is that the pause between pixels will overcome the persistence problem and allow panchromatic imaging. Interpixel delays of as much as 800 μ s (maximum supported by imaging software) were tested. As with long dwell times, these delays significantly increase imaging time for images of any size. Whereas interpixel delay was found to decrease persistence problems, even 800- μ s delays were not long enough to remove the problem entirely. However, for these images the dwell time used was only 232 μ s per pixel. Imaging combining both interpixel delay and longer dwell times could conceivably overcome some of the problems associated with these approaches but would still require significantly long times for each image. This approach has not been pursued further because the digital imaging software associated with our newer and more advanced CL system does not support interpixel delay.

Limited Wavelength Imaging

Our most successful approach has been to acquire images of only the shorter wavelength CL emissions, which is done most easily by inserting a broadband, short-wavelength (UV-blue) filter between the mirror and the photomultiplier tube. Walker (2000) noted that long luminescence decay times (ms) are characteristic of common activator ions and short times (μ s) are characteristic of less-common activators and intrinsic luminescence. Intrinsic luminescence in carbonates is known to occur in the UV-violet range. Images created using only the shorter wavelength parts of the emission spectrum do not manifest smearing or streaking (Fig. 1C), whereas images taken without using a filter (Fig. 1A) do show degradation because of persistent luminescence. Using a red filter to examine a carbonate sample having persistent luminescence yields results similar to those of the nonfiltered example. It would

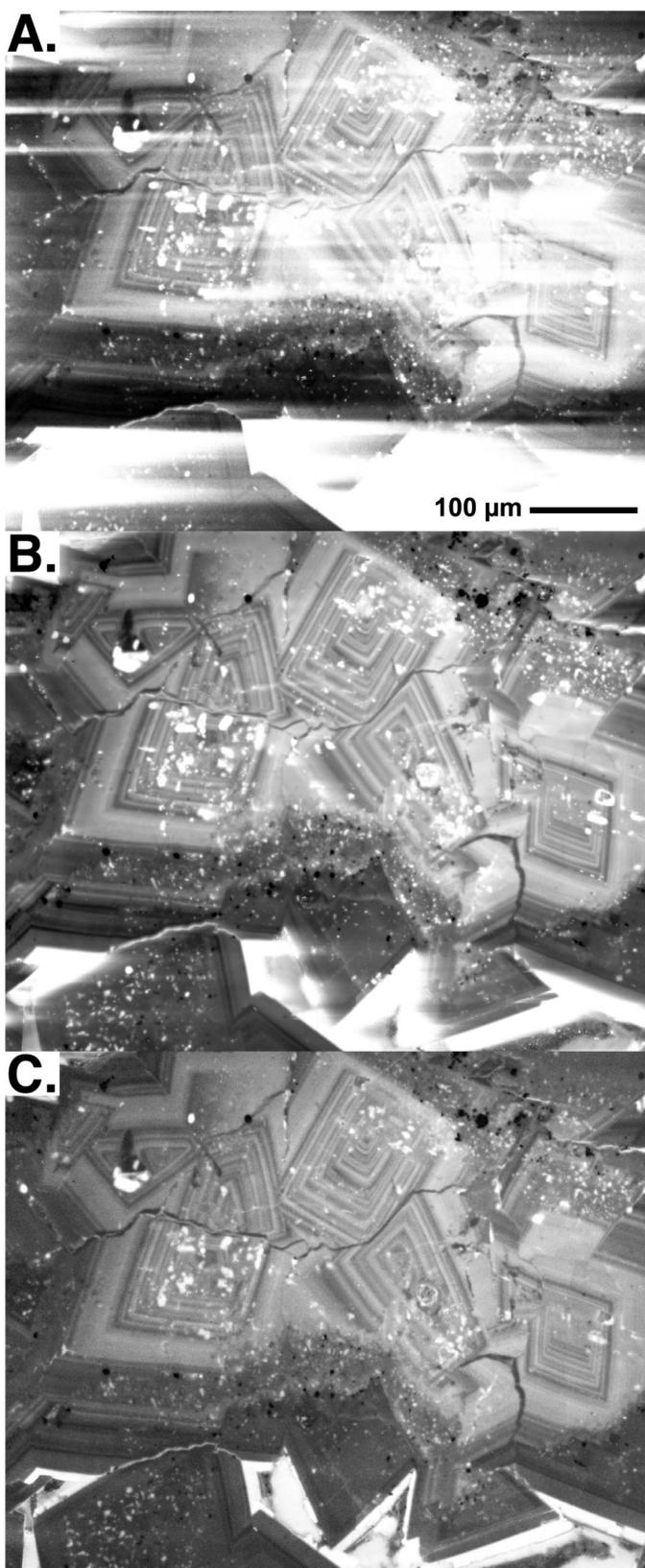


FIG. 1.—Micrographs showing a single area of dolomite rock imaged at several different SEM-CL settings. **A)** Area in panchromatic CL with streaking owing to persistent luminescence; dwell time of $400\ \mu\text{s}$ leading to an image acquisition time of ~ 6 minutes at 20 kV. **B)** Same area, still in panchromatic CL, but using the $3,200\text{-}\mu\text{s}$ dwell time recommended by Lee (2000). Persistence problems are almost

therefore appear that the longer, red-orange wavelength emissions of carbonate minerals are primarily responsible for persistent luminescence, whereas the ultraviolet-violet luminescence in carbonates does not appear to be strongly persistent. When the wavelengths examined are limited to the ultraviolet to blue range, an image comparable in detail to a conventional CL image is typically produced (Figs. 1C, 2A, 3A).

The UV-blue filter used is the CA-500-F produced by the Corion Corporation. This filter provides 80% to 90% transmissivity in the range of 385 to 500 nm (Fig. 4). A secondary transmissivity peak is present in the range of 800 to 850 nm. However, these wavelengths are outside the peak “red” luminescence range of carbonates (Marshall 1988) and therefore do not contribute significantly to images of carbonates that are produced.

When imaging silicates using a scanned-CL detector, we have most commonly used dwell times of approximately $200\ \mu\text{s}$. In some rare cases in which particularly clear images are desired, $400\text{-}\mu\text{s}$ dwell times are used. In carbonate imaging, it has been observed that $400\text{-}\mu\text{s}$ dwell times are the minimum necessary to produce images having acceptably low levels of noise (Figs. 1C, 2A, 3A, 5B, 6), with some images requiring $800\text{-}\mu\text{s}$ dwell times (Fig. 5A). Shorter dwell times lead to images that lose detail owing to increased noise. At 400- and $800\text{-}\mu\text{s}$ dwell times, $1,024 \times 760$ pixel images take approximately 6 or 12 minutes, respectively. Increased dwell times for carbonate minerals are probably necessitated by the decreased signal-to-noise ratio brought about by using only part of the available spectrum, as compared with a panchromatic image on the same system.

Using a limited portion of the luminescence spectrum does add to one inherent problem with scanned CL imaging. At low magnifications, the parabolic mirror used to channel luminescence into the photomultiplier tube is more efficient near the center of the image area. This situation creates differential illumination of the sample, expressed as a brighter area near the center of the image and darker corners. The problem is generally minor in panchromatic imaging. However, the increased contrast adjustment necessitated by the lower luminescence levels when a UV-blue filter is used in imaging intensifies the problem. To compensate for the uneven response of the mirror, image processing software such as Adobe® Photoshop® can be used to make localized intensity adjustments to the digital images.

Although images shown here were collected on a monochromator-equipped CL system operating in panchromatic mode, the short-wavelength filter technique should be equally effective on panchromatic CL systems. Use of a UV-blue filter to limit the wavelengths being imaged is a mechanically simple and relatively low cost approach that can be used with most scanned CL systems. Alternatively, a monochromator system could be used to limit the imaged wavelengths, although total photon intensity would be reduced relative to the broadband UV-blue filter. In a test of this method, SEM operating conditions for monochromator-filtered images were the same as those used for UV-blue-filter images. The monochromator was set to the peak of the violet luminescence, and monochromator slits were opened to their maximum widths (10 mm). The type of monochromator grating used has a considerable effect on the quality of a monochromator-filtered image. An optimal grating for carbonate imaging would have a low ruling density and a blaze wavelength of 400 nm. We have tested two monochromators, both with blaze wavelengths of 500 nm and one with a ruling density of 1200 lines/mm (standard equipment) and one with a ruling density of 150 lines/mm. In both cases, the monochromator technique required a higher contrast setting on the CL amplifier than was required when using the UV-blue filter, and the higher ruling-density monochromator also required a higher setting on the photomultiplier tube. The image acquired with the lower ruling-density monochromator was of significantly higher quality than the higher ruling-density image. In both cases, the images that have been acquired using the monochromator as a filter were of lower quality than the images acquired of the same areas using the UV-blue filter, although the images acquired with the lower ruling-density monochromator were acceptable.

Other Techniques

Another technique, which we have tested on sandstones, involves removing carbonate minerals by acid etching. This approach works only on predominantly silicate

←

eliminated, but image acquisition time was 48 minutes. **C)** Same area imaged using short-wavelength (UV-blue) filter. Dwell time of $400\ \mu\text{s}$ at 20 kV; acquisition time of ~ 6 minutes. Variation in luminescence intensity is due primarily to variations in the amount of iron in the dolomite. Because some of the brighter areas also have small amounts of Fe, however, there is another factor contributing to the luminescence variation. Sample courtesy of PEMEX.

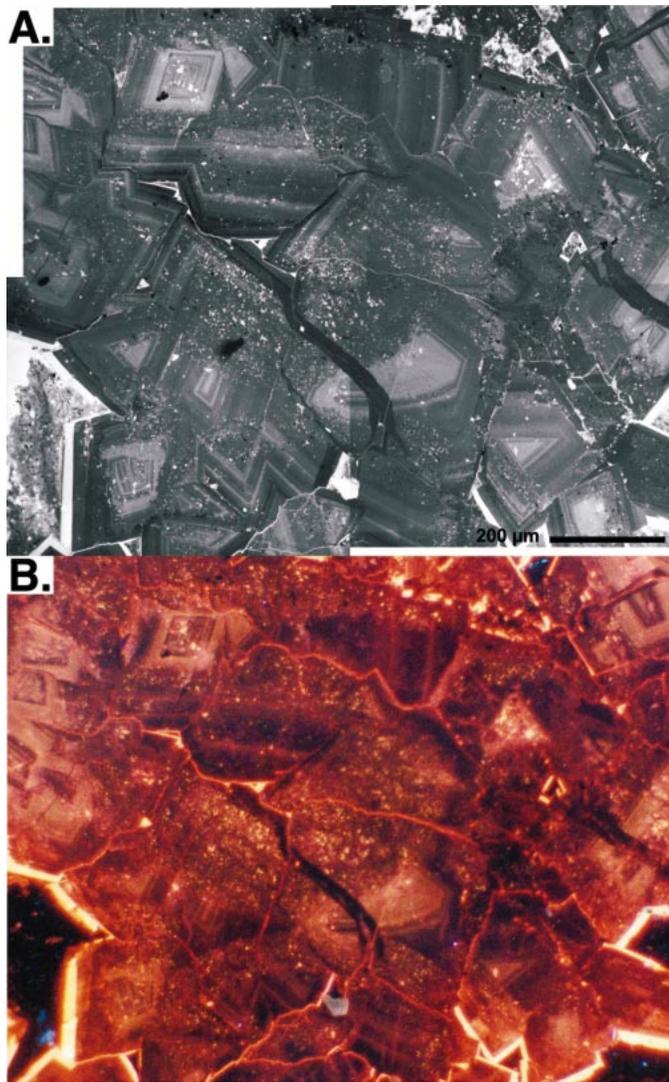


FIG. 2.—Comparison of scanned CL image versus conventional CL (Technosyn®) image of a fractured dolomite with strongly zoned crystals. **A**) Scanned CL image mosaic acquired using UV-blue filter. Image shows zoned dolomite crystals cut by fractures filled with nonluminescent (black) ferroan dolomite. Dwell time of 400 μ s; acquisition time was \sim 6 minutes, at 20 kV. **B**) Conventional CL image acquired using Technosyn® system operating at \sim 15 kV. Image area and scale are approximately the same as in Part A. Note similarity of zoning and fracturing seen in each. Sample is the same dolomite as in Figure 1.

samples having only small amounts of HCl-soluble carbonate, such as sandstones that have minor calcite cement. In samples of the Dakota Sandstone from the Greater Green River Basin, the calcite cement was highly luminescent and created significant problems with CL imaging. A polished thin section was immersed in 10% hydrochloric acid and left until the cessation of effervescence. The sample was then carbon-coated and examined normally. The highly luminescent calcite had been dissolved, and CL imaging of the silicate minerals was no longer impeded. This technique would not be useful for carbonate rocks, nor would it be recommended for sandstones in which carbonate cement is essential to the structural integrity of a sample. Although this method has significant drawbacks, it is nevertheless a fast and effective method of dealing with calcite luminescence problems in sandstones in which quartz is the primary imaging target.

Digital image manipulation using image-processing software, such as Adobe® Photoshop®, can resolve some problems related to both persistent luminescence and relative intensity differences between minerals. Superposition of images acquired at different brightness and contrast settings works for mixed carbonate-silicate lithologies. Stacking two images in different layers, erasing parts of one, and then merging the two layers together has proven a useful technique. Attempts to use image-pro-

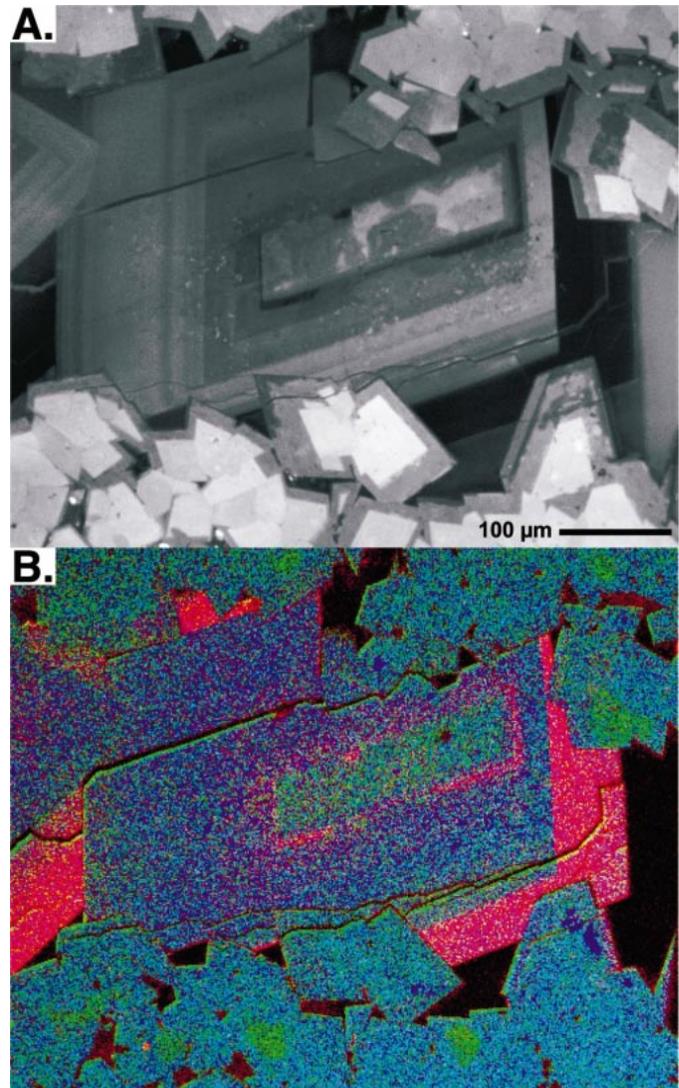


FIG. 3.—Synkinematic to postkinematic ferroan dolomite bridging a partly open fracture in a dolomite rock. **A**) Scanned CL image acquired using UV-blue filter. Note strong zoning, which correlates closely with the iron content in the dolomite. Darker areas have more iron. Dwell time of 400 μ s at 20 kV. **B**) Composite, false-color, EDS element map of a slightly larger area than shown in Part A. This image is constructed from three separate gray-scale intensity maps; red is Fe, green is Mg, and blue is Ca. Sample is from Ordovician Ellenburger Formation, Barnhart field, Reagan County, Texas, U.S.A., and the sample depth is 2,778.56 m.

cessing software to remove or reduce streaking caused by persistent luminescence in panchromatic images have been less successful, the result being mere reduction of the streaking. Such reduction is useful primarily in panchromatic images in which only one or two small spots of persistent luminescence are present. Areas marred by persistent luminescence are selected, the selected areas are feathered, and the contrast and brightness of the areas are adjusted independently of the rest of the image. Care should be taken that the image manipulation process does not end up taking longer than it would to deal with the persistence problem by acquiring a long-dwell-time panchromatic image according to the method of Lee (2000).

DISCUSSION

An obvious question, which arises from using only a limited wavelength of the CL emissions, is whether the images produced show the same detail as would be available in a panchromatic image. An answer has proven somewhat difficult to determine precisely. The persistence problem that makes it necessary to undertake the limited-wavelength images also makes it difficult to constructively compare full-

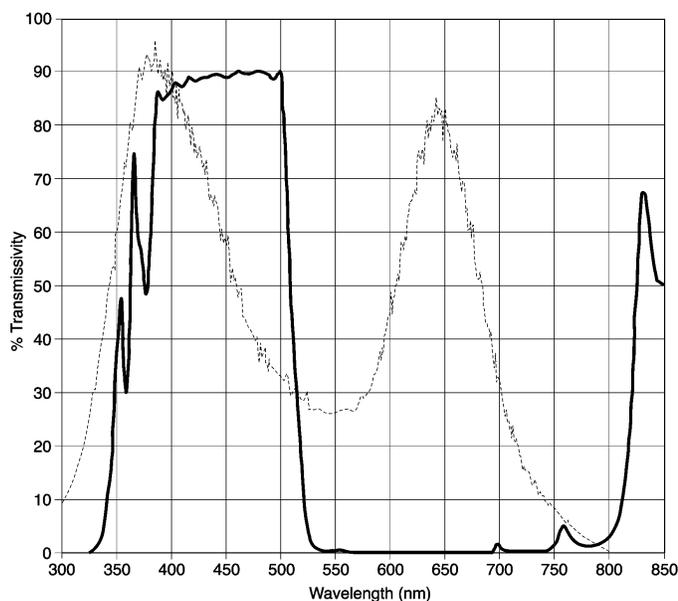


FIG. 4.—Graph of intensity versus wavelength showing spectral response of short-wavelength filter used in this study (solid line). Filter is the CA-500-F, manufactured by Corion Corporation, who also conducted the transmissivity testing. Also included on the graph are the CL spectra for a typical dolomite sample (dashed line), showing the presence of two separate luminescence peaks, one in the UV-violet range and one in the orange-red range. Dolomite used is an outcrop sample of the Permian Clear Fork Formation from West Texas, U.S.A

wavelength versus UV-blue imaging. When UV-blue CL images of carbonates are compared with panchromatic scanned CL images, the UV-blue images typically show all the features seen in panchromatic scanned CL (Fig. 1). UV-blue scanned CL images typically show detail that is comparable to that of panchromatic conventional CL images of the same area (Fig. 2). Some loss of contrast, but not detail, occurs in scanned CL relative to conventional CL if carbonates having distinct luminescence color variations, rather than distinct luminescence intensity variations, are examined.

Much of the control on carbonate CL variations in longer wavelengths seems related to changes in concentration of activator ions, which appear to have less impact on shorter wavelength emissions. If the primary source of short-wavelength CL in carbonates is intrinsic luminescence, then why do the variations correlate well with long-wavelength variations? Habermann et al. (1998) stated that intrinsic luminescence in the range of ~ 420 nm is quenched by Fe^{2+} . We have done a limited number of combined CL and EDS studies of dolomites that suggest that variation in Fe does correlate with variation in short-wavelength luminescence (Fig. 3B). However, it is also possible that these luminescence changes are due to a trace element that is covariant with Fe.

Our attempts to image carbonates using scanned CL confirm previous reports (Walker et al. 1989; Habermann et al. 1998) that many carbonate sample areas that appear “nonluminescent” in conventional CL do have faint luminescence. There are two probable reasons for this result. One is that the MonoCL2 detector is sensitive to wavelengths of 185 to 850 nm. The approximate range for visible light is 400 to 700 nm. Studies of the luminescence spectra of carbonate minerals have shown a common luminescence peak in the range of 350 to 425 nm (cf. Marshall 1988). Much of this peak falls outside the visible range but is within the sensitivity range of our CL detector and would be included in a panchromatic CL image. In addition, the use of a photomultiplier allows detection of light levels that are too faint to be registered by the human eye. Many of these “nonluminescent” carbonates can be effectively imaged using scanned CL without long dwell times or a short-wavelength filter. The luminescence intensity of these carbonates is much weaker than that of typical quartz grains, and the luminescence occurs primarily in the UV-violet range.

Carbonate Cement in Sandstones

In our experience, most carbonate cement in sandstones is only weakly luminescent (most Fe-bearing calcite and most ankerite) or apparently nonluminescent (siderite). Many of these weakly luminescent carbonates have little or no persistent

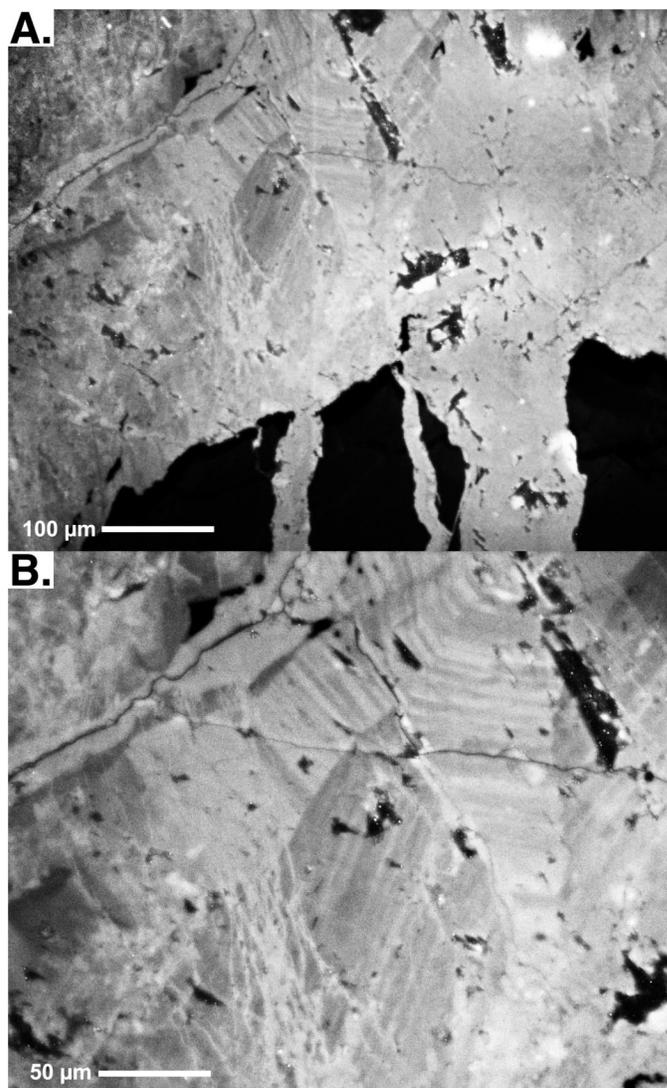


FIG. 5.—Scanned CL image of zoned, calcite-filled fractures in serpentinized peridotite. **A)** Low-magnification view shows at least two generations of fracturing. Nonluminescent areas are primarily serpentine. Dwell time of $800 \mu\text{s}$; acquisition time was ~ 12 minutes at 20 kV. **B)** Higher-magnification view of calcite fracture fill, showing secondary fractures also filled with calcite. Dwell time was $400 \mu\text{s}$ at 20 kV. Sample is acoustic basement from the Iberia Abyssal Plain, Site 899, Leg 149, of the Ocean Drilling Program.

luminescence and, hence, create no problems for scanned CL. Many sandstones containing carbonate cements that we have examined do not require special scanned CL imaging techniques. Problems have been encountered, however, with some calcite and many nonferrous dolomite cements. In some samples, one generation of carbonate cement will have persistent luminescence and another will not.

Utilizing a limited wavelength of CL emissions can be useful in some carbonate-cemented sandstones. In one example of a sandstone containing localized dolomite cement, use of a blue filter produced acceptable images (Fig. 6), whereas panchromatic imaging produced a significantly degraded image. In the case of luminescence of quartz cement, however, some information is lost when the red wavelengths are not imaged.

ACKNOWLEDGMENTS

Dr. Stephen E. Laubach of the Bureau of Economic Geology provided the impetus for developing a technique for doing scanned CL on carbonate rocks and provided an early review of this paper. The authors thank Gordon Watt, Thomas Dunn, and David Budd for insightful reviews. Development of carbonate scanned CL tech-

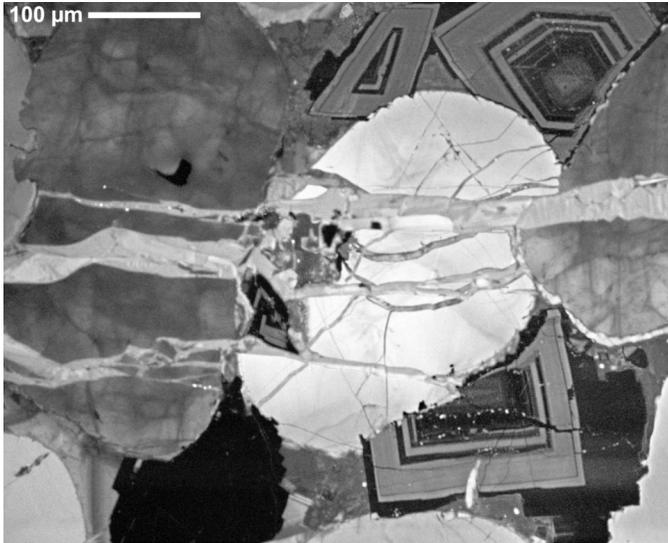


FIG. 6.—Scanned CL image, acquired using UV-blue filter, of a partly dolomite-cemented sandstone from the Ordovician Bromide Sandstone of the Anadarko Basin, Oklahoma, U.S.A. Despite the lack of red luminescence, structures within both quartz and dolomite are visible. Dwell time was 400 μ s at 15 kV. Where fractures cut quartz grains they are filled with quartz; where they cut dolomite they are filled with dolomite. Sample depth is 3,960.9 m

niques has been supported by a group of industry sponsors (Fracture Research and Application Consortium), by Department of Energy Contract No. DE-AC26-98BC15105, and by the University of Texas System and Goldrus Production Company through the University Lands Joint Advanced Recovery Initiative. Some images used in this paper are of samples provided by PEMEX and Goldrus Production Company. Publication authorized by the Director, Bureau of Economic Geology.

REFERENCES

- GOMEZ, L., GALE, J., RUPPEL, S., AND LAUBACH, S., 2001, Fracture characterization using rotary-drilled sidewall cores: an example from the Ellenburger Formation, West Texas, *in* The Permian Basin: Microns to Satellites, Looking for Oil and Gas at All Scales: West Texas Geological Society, Fall Symposium, WTGS publication 01-110, p. 81–89.
- HABERMANN, D., NEUSER, R.D., AND RICHTER, D.K., 1998, Low limit of Mn^{2+} -activated cathodoluminescence of calcite: state of the art: *Sedimentary Geology*, v. 116, p. 13–24.
- KEARSLEY, A., AND WRIGHT, P., 1988, Geological applications of scanning electron cathodoluminescence imagery: *Microscopy and Analysis*, September, p. 49–51.
- LEE, M.R., 2000, Imaging of calcite by optical and SEM cathodoluminescence: *Microscopy and Analysis*, September, p. 21–22.
- MARSHALL, D.J., 1988, *Cathodoluminescence of Geological Materials*: Boston, Unwin Hyman, 146 p.
- WALKER, G., 2000, Physical parameters for the identification of luminescence centres in minerals, *in* Pagel, M., Barbin, V., Blanc, P., and Ohnenstetter, D., eds., *Cathodoluminescence in Geosciences*: Berlin, Springer-Verlag, p. 23–39.
- WALKER, G., ABUMERE, O.E., AND KAMALUDDIN, B., 1989, Luminescence spectroscopy of Mn^{2+} centres in rock-forming carbonates, *in* Vaughan, D.J., ed., *Spectroscopic Studies of Minerals: Principles, Applications and Advances*, *Mineralogical Magazine*: v. 53, part 2 (370), p. 201–211.

Received 19 February 2002; accepted 10 August 2002.