CAMBRIDGE

Cambridge University Press
978-0-521-85878-6 - Application of Cathodoluminescence Imaging to the Study of Sedimentary Rocks
Sam Boggs and David Krinsley
Excerpt
More information

1

Introduction

Many minerals emit radiation, referred to as **luminescence**, when bombarded by an energy source. Emissions are commonly in the visible range; however, ultraviolet (UV) and infrared (IR) emissions may also occur (Marshall, 1988, p. 1). Luminescence is given different names depending upon the energy source: e.g., bombardment by high-energy UV photons generates photoluminescence; a beam of energetic ions produces ionoluminescence; X-rays generate radioluminescence; and bombardment by high-energy electrons produces cathodoluminescence (Pagel *et al.*, 2000a). **Cathodoluminescence** refers to emission of characteristic visible (and UV) luminescence by a substance that is under bombardment by electrons, where the cathode is the source of the electrons. Note: the word cathodoluminescence is often abbreviated to CL.

The phenomenon of luminescence was recognized as early as the seventeenth century (Leverenz, 1968); however, systematic observations and discussion of cathodoluminescence did not take place until around 1965 (e.g., Smith and Stenstrom, 1965). Early cathodoluminescence studies were carried out with a cathodoluminescence microscope, which is fundamentally a petrographic microscope to which some kind of cathode gun is attached. Subsequently, the electron-probe microanalyzer and, especially, the scanning electron microscope have been utilized to generate high-resolution, high-magnification cathodoluminescence images (Chapter 3).

Early applications of cathodoluminescence to geological materials included observations of the CL characteristics of both carbonate and silicate minerals, particularly quartz and feldspars. Many investigators noted, for example, that some carbonate minerals display zoning in CL images, which was not visible in other kinds of images. A particularly noteworthy observation was made by Sippel (1968), who pointed out that

CL provides a means of distinguishing between secondary quartz, which is nonluminescent (or poorly luminescent), and primary or detrital quartz, which displays luminescence.

Interest in cathodoluminescence and its applications to geological materials has escalated sharply since these early studies. Several books have been published that deal in some way with cathodoluminescence (listed below), and hundreds of research papers have also been published. We now recognize that CL imaging can be applied effectively to a number of geological problems, including sedimentological problems. Cathodoluminescence techniques have proven to be particularly useful in provenance analysis of sandstones and shales and in study of diagenesis in both siliciclastic and carbonate sedimentary rocks. Published observations on the CL characteristics of sedimentary materials are widely scattered in the literature. In this book, we attempt to bring together material from diverse published sources, as well as from our own research, to provide a comprehensive treatment of the application of cathodoluminescence imaging to a range of geological problems involving sedimentary rocks.

Books dealing with cathodoluminescence microscopy and spectroscopy

Barker, C. E. and O. C. Kopp (eds.), 1991. *Luminescence Microscopy and Spectroscopy: Qualitative and Quantitative Applications*, SEPM Short Course, 25 (published by the Society for Sedimentary Geology, Tulsa).

> A multi-author volume that covers both fundamentals (limited) and applications of cathodoluminescence. Topic coverage includes applications to carbonate rocks, sandstones, oil shales and coals, diagenetic minerals, petroleum geology, and ore deposits.

Gorobets, B. S. and A. A. Rogozhin, 2002. *Luminescent Spectra of Minerals: Reference Book,* Moscow, RPC VIMS.

> Translated from the Russian by B. S. Gorobets and A. Girnis. Not widely available.

Götze, J., 2000. Quartz and silica as guide to provenance in sediments and sedimentary rocks. In *Contributions to Sedimentary Geology*, **21** (published by Schweizerbart'sche Verlagsbuchhandlung, Stuttgart).

Cambridge University Press
978-0-521-85878-6 - Application of Cathodoluminescence Imaging to the Study of Sedimentary Rocks
Sam Boggs and David Krinsley
Excerpt
More information

This short monograph provides a comprehensive treatment of the characteristics of quartz, including cathodoluminescence, as provenance indicators. Includes color plates of CL images.

Götze, J., 2000. Cathodoluminescence microscopy and spectroscopy in applied mineralogy. Ph.D. Thesis, Technische Universität Bergakademie Freiberg.

This thesis covers the basic principles of cathodoluminescence; CL characteristics of quartz, feldspars, and zircons; and various applications, particularly applications to industrial materials.

Marfunin, A. S., 1979. *Spectroscopy, Luminescence and Radiation Centers in Minerals*. Berlin, Springer-Verlag.

This book covers various kinds of spectroscopy, including luminescence spectroscopy and luminescence centers. No direct application to sedimentary geology.

Marshall, D. J., 1988. *Cathodoluminescence of Geologic Materials,* Boston, Unwin Hyman.

This volume is an excellent book that provides a useful introduction to cathodoluminescence techniques and applications to geological materials. It has fairly limited coverage of applications to sedimentary rocks.

Ozawa, L, 1990. *Cathodoluminescence: Theory and Applications,* Tokyo, Kodansha.

The focus is on commercial applications of the principles of cathodoluminescence. The book contains no discussion of geological materials.

Pagel, M., V. Barbin, P. Blanc, and D. Ohnenstetter (eds.), 2000. *Cathodoluminescence in Geosciences,* Berlin, Springer-Verlag.

This work is another useful multi-author volume. It is an outgrowth of a conference on cathodoluminescence applications held in Nancy, France in 1996. All of the papers in the book are by conference participants. It is an excellent, up-to-date book; however, only a few of the papers deal specifically, and in detail, with application to sedimentary rocks.

Redmond, G., L. Balk, and D. J. Marshall (eds.), 1995. *Luminescence*, Scanning Microscopy Supplement 9, Proceedings of the 13th Pfefferkorn Conference, Scanning Microscopy International, Chicago.

This volume contains twenty-four papers, ten of which deal with mineral luminescence, eight with semiconductors, and six with experimental techniques. Cathodoluminescence is the focus of ten papers; however, only two of these discuss applications to sedimentology (carbonate rocks).

Yacobi, B. G. and D. B. Holt, 1990. *Cathodoluminescence Microscopy of Inorganic Solids,* New York, NY, Plenum Press.

This book focuses on application of cathodoluminescence techniques in the assessment of optical and electronic properties of inorganic solids, such as semiconductors, phosphors, ceramics, and minerals. Although it contains useful information about the fundamentals and techniques of cathodoluminescence, it contains no discussion of applications to geological materials.

Zinkernagel, U., 1978. *Cathodoluminescence of Quartz and its Application to Sandstone Petrology,* Stuttgart, Schweizerbart'sche Verlagsbuchhandlung.

An early book that describes cathodoluminescence imaging by using a CL attachment to a light microscope. It focuses on CL color as a tool for provenance analysis and other applications.

Cambridge University Press
978-0-521-85878-6 - Application of Cathodoluminescence Imaging to the Study of Sedimentary Rocks
Sam Boggs and David Krinsley
Excerpt
More information

PART 1

Principles and instrumentation

The theoretical underpinnings of cathodoluminescence are complex and not fully understood. It is necessary, however, to develop some understanding of the causes of cathodoluminescence and the instrumentation required to generate cathodoluminescence images before moving on to discuss the application of CL to study of sedimentary rocks. Chapter 1 is a general introduction to the phenomenon of cathodoluminescence and

Scanning electron microscope equipped with a cathodoluminescence detector.

includes brief descriptions of some relevant books that deal with cathodoluminescence microscopy and spectroscopy. Chapter 2 provides an introduction to the fundamental causes of CL and the factors that affect the nature and intensity of CL emissions. Chapter 3 describes the instruments and techniques currently available for CL imaging and related analyses.

Cambridge University Press
978-0-521-85878-6 - Application of Cathodoluminescence Imaging to the Study of Sedimentary Rocks
Sam Boggs and David Krinsley
Excerpt
More information

2

Cathodoluminescence and its causes

Introduction

When a crystal such as quartz or feldspar is bombarded by a stream of high-energy electrons in a scanning electron microscope or other suitable instrument, photons (“particles” of light) are emitted, a phenomenon called cathodoluminescence (CL). Much is known about the origin of CL in artificial crystals because of their economic importance in the manufacture of television screens, computer monitors, and the like. Although less is known about the origin of CL in naturally occurring minerals, the fundamental causes of CL emissions are moderately well understood.

To visualize the factors responsible for CL emissions, it is useful to consider atoms in crystals in terms of the band theory of solids. Energy states of electrons in crystals depend upon whether the electrons are bound in particular atoms (inner-shell electrons) or are delocalized. Delocalized electrons are electrons that are not associated with individual atoms or identifiable chemical bonds, but are shared collectively by all the constituent atoms or ions of a substance. Delocalized electrons have wave functions (in quantum mechanics, a complex function of time and position) that in effect traverse the entire crystal. Individual atoms have discrete energy states that are associated with the orbits of shells of electrons in the atom. When atoms are spaced far apart, as in a gas, they have very little influence upon each other. By contrast, atoms within a solid, such as quartz or feldspar, have a marked effect upon other atoms in the crystal (atomic orbitals combine to form molecular orbitals). Because of the very large number of atoms that interact in a solid material, the energy levels are so closely spaced that they form bands.

Cambridge University Press
978-0-521-85878-6 - Application of Cathodoluminescence Imaging to the Study of Sedimentary Rocks
Sam Boggs and David Krinsley
Excerpt
More information

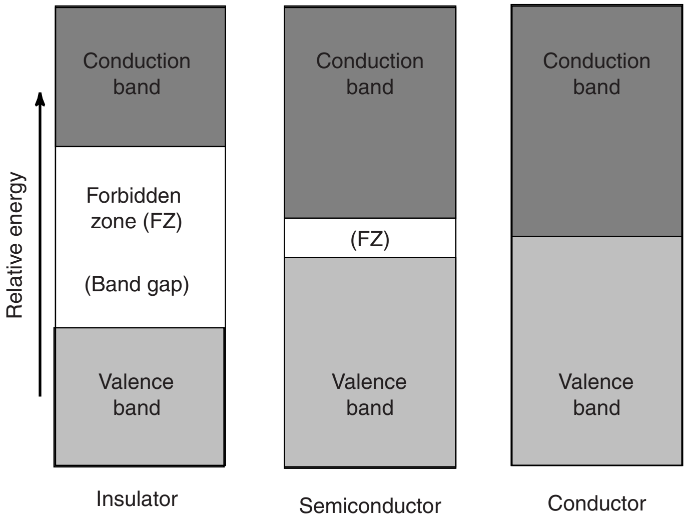

Fig. 2.1. Illustration of energy bands in minerals. Note that insulator minerals such as quartz have a wide band gap, semiconductors have a narrow band gap, and conductors have essentially no band gap.

That is, the close proximity of atoms in a solid causes the discrete energy levels of individual atoms to broaden into **energy bands**.

These energy bands are commonly designated as the **valence band** and the **conduction band** (Figure 2.1). The valence band, which has lower energy than the conduction band, is analogous to the highest *occupied* molecular orbital in a molecule and the conduction band is analogous to the lowest *unoccupied* molecular orbital in a molecule. Electrons in the conduction band are easily removed by application of an electric field. If a material has a large number of electrons in the conduction band, it acts as a good conductor of electricity. The lower-energy valence band contains a series of energy levels containing valence electrons. Electrons in this band are more tightly bound to the individual atom than are the electrons in the conduction band; however, the electrons in the valence band can be moved to the conduction band with the application of energy. In the case of cathodoluminescence, this energy is supplied by bombardment with high-energy electrons. There are more bands below the valence band, but they are not important to the understanding of CL theory and will not be discussed.

In insulators, such as quartz, a forbidden zone exists between the valence band and the conduction band, which is referred to as the **band**

Cambridge University Press
978-0-521-85878-6 - Application of Cathodoluminescence Imaging to the Study of Sedimentary Rocks
Sam Boggs and David Krinsley
Excerpt
More information

gap. Electrons do not reside permanently in the forbidden zone; however, they can travel back and forth through it. The band gap is quite wide in insulators. It is much narrower in semiconductors, and is absent in conductors, as shown in Figure 2.1.

Fundamental causes of cathodoluminescence

In insulator minerals, all electrons are present in the lower-energy valence band; that is, the conduction band is empty. If sufficient energy is applied to the mineral, electrons can be promoted from the valence band to the conduction band, leaving behind a so-called "hole." (Figure 2.2B). Holes can be visualized as positive charges with the effective mass of an electron. Once energized electrons are in the conduction band, they remain only a very short time before they lose energy and return to the valence band. In an ideal crystal, nothing would be present in the band gap to hinder the return of de-energizing electrons as they fall (in energy) from the conduction band to holes in the valence band. Of course, all crystals have defects of some kind, which occupy discrete energy levels in the band gap. There are a great many kinds of defects (to be discussed), which fall into the general categories of impurity ions and lattice defects. These defects constitute electron traps that momentarily intercept and hold electrons as they move through the band gap to the valence band, shown schematically in Figure 2.2 by pairs of short horizontal lines in the band gap. These traps are normally unoccupied by electrons.

Consider now what happens when a beam of energetic electrons, such as from a scanning electron microscope (SEM), impinges on a crystal such as quartz or feldspar. The energy of the primary beam is partitioned in various ways. Some of the energy is converted into X-rays, some appears as backscattered electrons of relatively high energy, some as secondary electrons of much smaller energies, and some as Auger-process electrons, also of small energies (Figure 2.3). Much of the energy is absorbed and transferred to generation of phonons, with consequent release of heat. Phonons are tiny packets of vibrational (nonradiative) energy associated with heat (e.g., Wolfe, 1998).

A little of the total energy carried in the beam acts to promote nonlocalized electrons from the valence band to the conduction band, as schematically indicated in Figure 2.2B, leaving holes behind in the valence band. That is, the electrons go from the ground state to an excited state. Even a small amount of the total energy applied to the

978-0-521-85878-6 - Application of Cathodoluminescence Imaging to the Study of Sedimentary Rocks
Sam Boggs and David Krinsley

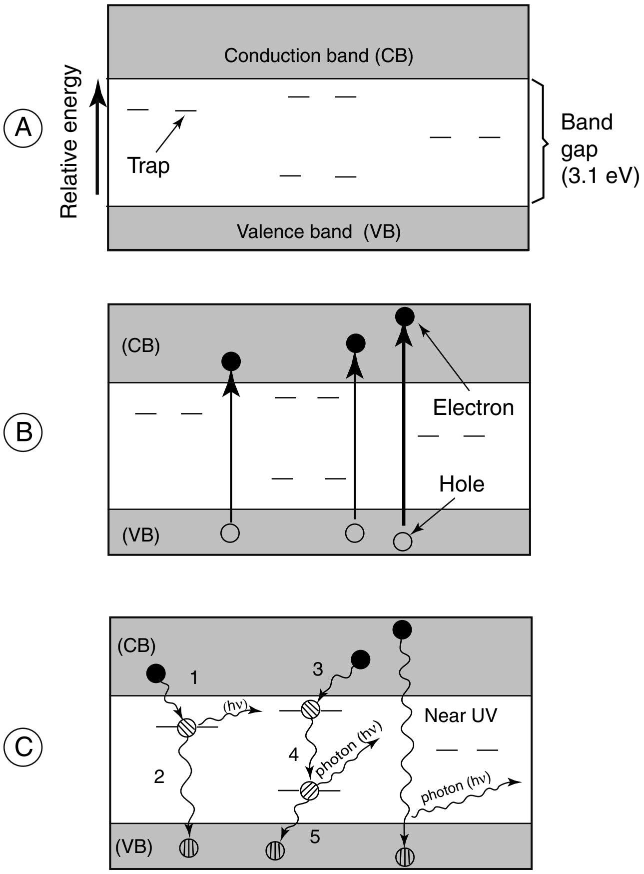

Fig. 2.2. Schematic representation of the processes that cause CL generation in minerals, as illustrated for quartz. (After Boggs *et al.*, 2001, Identification of shocked quartz by scanning cathodoluminescence imaging. *Meteoritics and Planetary Sciences*, **36**, Fig. 2, p. 785. Reproduced by permission.)

valence band may be sufficient to promote many electrons into the conduction band. After a short time, these promoted electrons undergo de-excitation and return to a lower-energy state, moving randomly through the crystal structure until they encounter a trap. (The various kinds of traps are discussed subsequently.) Electrons remain in traps only a very short time before vacating the traps, with concomitant emission of photons, and return to the ground state in the valence band (Figure 2.2C). As indicated in Figure 2.2C, electrons may encounter a single trap or multiple traps at they move through the band gap. The presence of these traps, at discrete energy levels within the band gap, is a precondition for emission of photons