

# Cathodoluminescence in Quaternary carbonate deposits



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## ABSTRACT

The cathodoluminescent oscillatory and sectoral growth zones common in crystals formed in ancient limestone successions in a variety of putative environments appear to be rare or absent from Recent and Pleistocene marine carbonate sequences. The factors controlling cathodoluminescence and reasons for this disparity are examined. The cathodoluminescent zones in the cements of ancient rocks have been interpreted as responses to variations in the redox potential of formative pore waters during crystal growth; although similar cathodoluminescent behaviour is recorded from some deposits, including travertines and Quaternary speleothems, formed in what are thought to have been strongly oxidizing environments. The apparent absence of cathodoluminescence in the most Recent and Pleistocene marine deposits, that presumably reflect deposition and diagenesis in environments that are also characteristically oxidized, therefore seems anomalous. The controlling influences on cathodoluminescence are reviewed, together with evidence relating to observations of Pleistocene marine deposits and likely conditions of formation but, where it is present, the mechanism(s) for its development remain elusive.

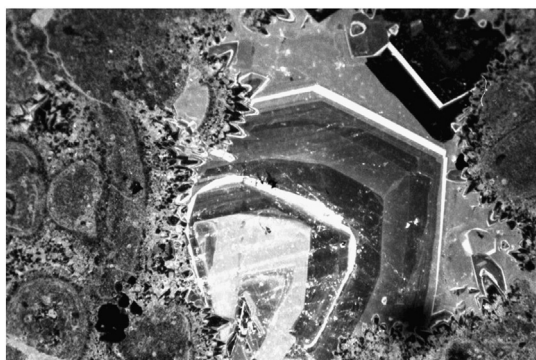
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## 1. Introduction

The pioneering work on cathodoluminescence (CL) by Sippel (1965, 1968) and Sippel and Glover (1965) opened the door to a new dimension in the petrography of carbonate diagenesis. Work begun in a tentative way by Evamy (1963) and by Dickson (1965) and others, using staining techniques, expanded rapidly as it was realised that optical cathodoluminescence (Fig. 1) was commonly able to provide far more detailed records of the growth and burial histories of carbonate cements. It has recently been used, for example, to underpin detailed chronologies of cave deposits in particular (Sierralta et al., 2010; Fernandez-Cortes et al., 2011). It is, however, important to differentiate the growth zones formed by chemical changes during the growth of individual crystals identified by staining or cathodoluminescence and successive generations of crystal growth characterized by new nucleation events. Increasingly elaborate sequences were revealed in the seminal work of Meyers (1974, 1978, 1991) on the Mississippian limestones of New Mexico, by Frank et al. (1982) on the Upper Cambrian Taum Sauk Limestone of southeastern Missouri, and by others, demonstrating both lateral and chronological correlation. Later work went on to show that the sequences identified might be used to map basal flow paths in the Newman Limestone of Kentucky (Niemann and Read, 1988), in the Burlington–Keokuk Formation of Illinois and Missouri (Kaufman et al., 1988), in Ordovician carbonates of Virginia (Grover and Read, 1983) and in Siluro–Devonian carbonates of the Central Appalachians (Dorobek, 1987). There was no doubt that the growth zones defined reflected variations in the characteristics of the natal fluids. However, it remained a moot point whether these were the result of large-scale compositional variations or merely reflected fluctuations in the fluid

supply. These works and others suggested the continuity of zonal patterns over areas ranging from 6000 km<sup>2</sup> in the Newman Limestone in Kentucky (Niemann and Read, 1988) to 100,000 km<sup>2</sup> in the Burlington–Keokuk Formation in Illinois and Missouri (Kaufman et al., 1988). Essentially similar cathodoluminescence patterns were apparently repeated throughout the Phanerozoic and were present in rocks of widely differing ages (Bruckschen and Richter, 1994); and on evidence of this kind, it was argued (e.g. Braithwaite, 1993) that patterns of growth were widely distributed and capable of description in terms of a cement sequence stratigraphy.

Compelling though these results seemed to be at the time, there was clear evidence that this was not the whole story. Grover and Read (1983), in a study of Ordovician carbonates in Virginia, were able to demonstrate down-dip transitions resulting from regional changes in cement sequences. Different parts of the basin had experienced different geochemical events. Work by Goldstein (1988) on Pennsylvanian limestones in New Mexico identified 15 separate cement lenses interpreted to be the products of separate freshwater bodies generated during periods of subaerial exposure. A similar relationship was demonstrated by Berry (1984) and Walkden (1987) in Carboniferous (Mississippian) Limestones in the English Lake District and Derbyshire. Cathodoluminescent zones in these were apparently traceable laterally over considerable distances but were commonly vertically restricted, and, like Goldstein (1988), were interpreted as having been exposed to subaerial influence. The critical point in these studies was that although zones apparently had lateral continuity, they were probably diachronous. Savard et al. (1995) described cathodoluminescence in limestones of Permian to Carboniferous age in the Sverdrup Basin in Arctic Canada. These were deposited in diagenetic environments



**Fig. 1.** Typical cathodoluminescence of Carboniferous limestone from Ireland. Note new nucleation of successive cement generations with sharply defined compositional boundaries within those generations. Varying tones reflect compositional changes in successive growth phases (oscillatory zoning).

ranging from fully marine to meteoric (including pedogenic!). Bruckschen et al. (1992) also reported cements in complex Jurassic sequences interpreted as reflecting meteoric diagenesis. These results are of particular significance in relation to the discussion of Quaternary deposits here. However, it had also been shown that there were examples of different sequences of cements in adjacent pores of the same rock (Searle, 1988; Kaufman et al., 1990; Machel and Burton, 1991; Bruckschen et al., 1992). In addition to growth stratigraphies Meyers (1978), Dorobek (1987), Thierault and Hutcheon (1987), and Jones and Kahle (1989) had noted that cements not only grew but also dissolved. Because aquifers vary widely in their saturation (or undersaturation), crystals may be corroded, and individual zones may be selectively dissolved, with parts of sequences entirely removed, generating omissions when sequence accumulation is renewed (Braithwaite and Heath, 1989).

The repetition of similar cathodoluminescence patterns in cement sequences of a variety of ages led Bruckschen and Richter (1994) to propose, in the face of known inter-pore variation (Searle, 1988; Kaufman et al., 1990; Machel and Burton, 1991), a universal sequence of growth stages. A generation of calcite with patchy brown-orange cathodoluminescence was interpreted as the result of recrystallization of Mg-calcite. This, however, would be difficult to prove because although there have been observations of variations in Mg compositions in crystals in which other features suggest recrystallization, there is commonly no textural evidence and recrystallization does not always result in cathodoluminescence. The second generation, of blue-luminescing cement, was interpreted (Habermann et al., 1998) as expressing structural imperfections. These have been attributed to formation under oxidizing conditions resulting either from penetration by meteoric waters or shallow burial beneath a marine phreatic zone (Richter et al., 1992). This cement generation is normally separated from the next by a thin, light orange zone interpreted as the result of a reversion to reducing conditions (but see Savard et al., 1995, below). The last generation, with mid- to dark-orange cathodoluminescence, commonly shows sectoral zoning. Similar patterns, described by Lee and Harwood (1989) and by Wallace et al. (1991), have been attributed to decreasing Eh-potentials accompanying cementation during basin subsidence. In some areas, this sequence is overlain by a series of thin bright orange zones in which stable isotope compositions reflect uplift into a near-surface, meteoric (and presumably oxidizing) environment (Bruckschen et al., 1995). Sectoral growth zones have sometimes been regarded as typical of cements formed under deeper burial conditions (Bruckschen et al., 1992), and attributed to preferential sequestration of activator elements on particular crystal faces during growth (Reeder and Paquette, 1989; Götze et al., 2013). However, the reasons why this should be more common at depth have not been explained and, as experiments by Reeder and Paquette (1989) showed, similar features can also form at room temperature.

Thus, the problem is that whereas cathodoluminescent features seem to have formed in the past in a wide range of environments with chemistry ranging from reducing to oxidizing, such features are absent from marine Quaternary deposits. This may perhaps be attributed to the persistent oxidative state (see below) of the latter, but such features are developed in many ancient limestones regarded as forming in similar environments. So how can their absence in younger rocks be explained?

## 2. Factors affecting cathodoluminescence

Almost from the outset, the factors controlling cathodoluminescence have been contested, and discussions are to be found in Marshall (1988), Machel and Burton (1991), Reeder (1991), Pagel et al. (2000), Richter et al. (2003), Richter et al. (2004), Barker and Kopp (1991), and others. The consensus is that the presence and proportions of manganese and iron are critical and the principal factor controlling their incorporation into carbonate mineral structures is the redox conditions of crystal growth (Barnaby and Rimstidt, 1989), with most examples reflecting reducing conditions. The principal agent in excitation is thought to be  $Mn^{2+}$  and trivalent REE-ions (Pr, Eu, Dy, Tb etc.; Marshall, 1988; Machel and Burton, 1991; Pagel et al., 2000). These typically substitute for calcium in the lattice structure (Meyers, 1974; Glover, 1977; Pierson, 1981; Frank et al., 1982), although other elements may serve as either excitors or sensitizers (Gies, 1975; Machel, 1985). Richter et al. (2003) described a number of examples of rare-earth elements including  $Dy^{3+}$  and  $Sm^{3+}$  functioning as activators, and Fernandez-Cortes et al. (2011) recorded  $Sm^{3+}$ ,  $Dy^{3+}$ , and  $Ce^{3+}$  from luminescent stalactites in caves in west-central Spain, derived from a variety of minerals in the host rocks. However, Hemming et al. (1989), using spectrophotometric analysis, found no evidence that rare earths could act in this way. Richter et al. (2003) noted that in dolomite,  $Mn^{2+}$  may occupy either  $Ca^{2+}$  or  $Mg^{2+}$  sites, resulting, respectively, in red or yellow cathodoluminescence. The green cathodoluminescence of aragonite is also Mn-activated (Götze and Richter, 2009). The amount of Mn necessary to generate cathodoluminescence appears to depend in part on the presence of other activators and quenchers, the most important of the latter being  $Fe^{2+}$  (Gies, 1975; Frank et al., 1982; Hemming et al., 1989).

Typical figures quoted for the minimum proportion of Mn required to promote cathodoluminescence have varied from as little as 15 (ten Have and Heijnen, 1985) or 20 ppm (Savard et al., 1995) to around 300 ppm (Frank et al., 1982) with values as high as 1000 ppm quoted for calcite (Füchtbauer and Richter, 1988). Richter et al. (2003) argued that there is effectively no lower limit for Mn activation, while Hemming et al. (1989) indicated that calcites with more than about 100 ppm Mn will luminesce even if moderate amounts of a quencher are present, and calcites that contain no detectable Fe (quencher) may nevertheless show moderate cathodoluminescence with only 150–650 ppm Mn and with greater concentrations (>700 ppm) are brightly luminescent. Habermann et al. (1998) recorded activation in calcite by  $Mn^{2+}$  in the range of 700 ppb. Gillhaus et al. (2001) indicated that in dolomite, concentrations of less than 1 ppm of Mn are technically detectable as there is a linear correlation between spectroscopic peak areas, increasing to Mn concentrations of 1000–1500 ppm. However, it is important to note that these very low levels of activation have only been detected by specialized CL systems such as the hot-cathode apparatus developed in Bochum (Neuser, 1995). Savard et al. (1995) indicated that cathodoluminescence in calcite is at least partly quenched when the Fe content rises above ~1400 ppm, irrespective of the proportion of Mn present. Below this level, bright cathodoluminescence is possible with Mn in the range of 20–225 ppm. These authors went on to suggest that the cathodoluminescence behaviour of calcites cannot be predicted at low concentrations of Mn and Fe. In this range, (20–225 ppm) luminescent, dull and non-luminescent calcites can co-exist, leading to the conclusion that their behaviour is not directly related to

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