Diagenetic history of sedimentary carbonates: Constraints from combined cathodoluminescence and trace element analyses by micro-PIXE

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Abstract
Trace element data for a succession of cements can contribute to the reconstruction of the diagenetic history of sediments. In the case of carbonate cements, cathodoluminescence (CL) microscopy has been successfully utilized for qualitative description of different cementation environments. In order to interpret correctly CL colour, trace element data other than Mn and Fe are often required. Due to frequent microscale zonation of trace elements in natural calcites and due to their low threshold concentration for CL activation, microsampling techniques with high spatial resolution and low detection limits are required. In this case study, trace element concentrations have been correlated with the CL behaviour of carbonate cements using the Bochum proton microprobe (PIXE) and a hot cathode luminescence device. The CL patterns, including the fine zonation, correlate well with the trace element distribution.

1. Introduction
Sediments, during their diagenetic history, pass through a variety of environments (e.g. marine, meteoric, deep burial) having different pore water chemistry. Their chemical attributes are commonly encoded in contemporaneous mineralization, the so-called cements. Since this cementation process spans considerable time intervals (up to \(10^9\) y), the cement minerals contain, under favourable conditions, complete records of post-depositional history of sediments. In addition, if contemporaneous markers can be detected, the zonation scheme can be utilized as an “internal clock” that enables dating of diagenetic events. This, in turn, permits reconstruction of complex histories in post-depositional life of a sediment.

For carbonate cements, the most favourable marker is the chemical zonation within the minerals. This zonation can be visualized by different techniques, such as staining (e.g. for Fe-zonation [1]), cathodoluminescence (Fe and Mn distribution [2]) or by more sophisticated physical methods such as micro-PIXE [3].

The knowledge of relation between hydrocarbon generation and the degree of cementation may be of decisive significance for determination of hydrocarbon migration pathways and for delineation of potential reservoirs. The research on zoned cements is therefore not solely of scientific interest, but it may have an economic importance, particularly in petroleum geology.

The objective of this paper is twofold. In the first part we discuss quantitative relations between cathodoluminescence (CL) intensity and iron and manganese concentrations in natural calcites. The second section presents case studies that utilize combined cathodoluminescence and PIXE trace element technique in the research of diagenetic/cementation history of rocks.
2. Methods

For CL observations, polished, 30 μm thin sections of carbonate rock samples were coated with a thin gold film to avoid charge build-ups. The utilized CL device operates with a hot cathode [4], resulting in a very low threshold for CL activation [5]. The setup was: beam energy 14 keV, beam current 0.5 mA, spot diameter 2 mm.

Trace element data were measured with the Bochum proton microprobe (PIXE), using a 3 MeV beam. The spatial resolution of the PIXE beam is in the range of a few microns and the detection limits for iron and manganese are in the range of 10 ppm, below the minimum threshold concentration for CL activation (20 ppm Mn in iron free calcites [5]). In addition to spot measurements, PIXE linescans were performed and element maps were produced.

The evaluation of absolute concentrations from the measured spectra was performed using the GUPIX software package [6, 7]. The instrumental constant \( H \), comprising the remaining unknown parameters (i.e. the detector solid angle and the calibration of the charge integrator) was derived from the analysis of samples that are routinely utilized as standard material in X-ray fluorescence analyses of geological samples. These are fused discs consisting of a 10% mixture of NBS standard powder in Spectromelt® (66% dilithiumtetraborate, 34% lithiumtetraborate) as flux. For our purpose, we consider this procedure superior to the analysis of pure elemental standards [6, 8–10] or pure standard powder that is fused without flux [7, 11, 12]. The justification for this statement is based on the following: (1) these samples are easily available to a great number of geochemical laboratories, (2) the chemical composition of the Spectromelt® is well constrained, (3) Spectromelt® consists of light elements and therefore does not contribute to the PIXE spectrum, and (4) \( H \) can be derived from a multitude of trace elements covering a great range of the periodic system.

Repeated measurements of the standard reference material AGV-1 (Andesite) and comparison with recommended values [13] yield an internal precision and an external accuracy of ~ 10% for a number of elements (K, Ca, Ti, Mn, Fe; see Fig. 1). Deviations in the case of Sr and Zn are believed to have been caused by their inhomogeneous distribution within the sample. The latter two were therefore not considered in the \( H \) determination.

As a test of the calibration technique, the quantitative analyses of standard reference material NIST 610 ("the ultimate challenge to Micro-PIXE" [7]) yielded a good agreement with the recommended values for a number of elements (Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr). Most of these elements are of importance to calcite geochemistry.

3. CL characteristics relative to Fe and Mn concentration

Although there is a general consensus in literature that the yellow–orange–red luminescence of natural calcite is activated by \( \text{Mn}^{2+} \) substituting for the calcium ion in the lattice, and that \( \text{Fe}^{3+} \) ions are the main CL quenching parameters, controversy still exists as to quantitative relationships between CL characteristics and concentrations of these elements [14]. One of the reasons for this discrepancy is a microscale CL zoning, common in
natural calcites, that requires analytical techniques with a high spatial resolution. In addition, utilization of different luminescence devices (e.g. hot vs. cold cathode) results in further controversy.

Our results for the combined CL and PIXE trace element investigations are summarized in Fig. 2. The CL fields delineated by the heavy lines are derived from a literature compilation by Machel and Burton [15] and represent what these authors believed to have been the best approximations of trace element concentrations for differently luminescing calcites. Note that Machel and Burton differentiated only three types of luminescence, in contrast to five types in our study. These two additional CL types are moderate or medium luminescence and intrinsic CL. The latter is a dark blue luminescence that is activated by lattice defects in nearly pure calcite and not by the presence of specific ions. It can be detected only by highly sensitive hot cathode CL devices. With conventional techniques these calcites generally appear to be nonluminescent. This is one of the reasons for the wide Mn and Fe concentration ranges of nonluminescing calcites in Machel and Burton’s diagram. Overall, many of our bright and nonluminescing samples plot into the corresponding fields in the Machel and Burton diagram. On the other hand, their field for dull luminescing calcites can contain any of our CL types. A great deal of this discrepancy may result from personalized visual description of the CL impressions, as demonstrated by the comparison of the visually estimated CL intensities and photometer measurements by Hemming et al. [16]. The measured intensities of visually classified CL-types were clearly overlapping and in the range of 25–35% of maximum intensity the entire range of visual impressions, from dull to bright, were possible [16].

On the basis of our data, the following concentration fields for differently luminescing calcites can be defined in the iron–manganese space (Fig. 2): (i) Intrinsic CL that occurs at low iron and manganese concentrations, mostly below 200 ppm. (ii) Bright luminescence at Mn concentrations between 1000 and 10,000 ppm and Fe contents between 10 and 10,000 ppm. (iii) Nonluminescence at iron concentrations between 1 and 10 wt% and at manganese levels between 500 and 10,000 ppm. (iv) Intermediate CL.

Despite a wide scatter of data, the field of intermediate CL can be subdivided further. For Fe/Mn ratios < 10, this field contains brightly and medium luminescing samples, whereas at ratios exceeding 10 only medium, dull, and nonluminescence can be observed.

Our data clearly support the earlier assertions [16, 17] that CL of natural calcites depends on both, the iron/manganese ratio as well as the absolute concentrations of these elements. Furthermore, our results indicate that for Fe/Mn ratios < 10 the response to manganese activation overwhelms the impact of iron quenching. This is supported by the observation that medium CL turns to bright one with increasing absolute concentrations of both elements at constant ratios. In contrast, for Fe/Mn ratios > 10 iron quenching appears to be the dominant influence.

4. Applications of combined PIXE and CL studies to diagenetic research

As Fe and Mn change their valence at different Eh, resulting in a “redox fractionation” of these elements, carbonates precipitated under successively reducing conditions should display a succession from intrinsic via yellow bright to dull orange luminescence colours [18]. Furthermore, waters from different environments are characterized by typical trace element (e.g. Sr, Mg, Fe, Mn [19]) concentrations. This enables reconstruction of precipitation from CL and trace element data.

4.1. Triassic limestones from Hydra (Greece)

The studied Triassic limestones from Hydra (Greece), contains three cement generations that can be detected by CL. The generation 1 is characterized by a blotchy distribution of brightly luminescing domains, indicating...
Fig. 4. PIXE element map of calcitic fissure cements from the Perachora peninsula (Greece). A dark green luminescing cement zone is characterized by low Fe and Mn contents and by increased Sr and Y concentrations. As Sr is an unlikely activator element of CL, this luminescence colour is related to yttrium activation. On the basis of yttrium and strontium contents, these cements are interpreted as hydrothermal mineralisations.
a primary high Mg calcitic composition and thus a marine origin of this generation [20, 21]. The subsequent generation 2 displays a homogeneously intrinsic CL that is terminated by a brightly luminescing zone. The final generation 3 shows a transition from a moderate to a dull orange CL. This is exactly the pattern that would be postulated for a cement sequence that was precipitated from increasingly reducing pore waters in the course of basin subsidence [18]. While the generation 1 represents a synsedimentary marine cementation, the generation 2 was precipitated from oxidizing meteoric or modified marine shallow burial brines, and the final generation 3 can be interpreted as a deep burial cement. Consequently, the iron concentration should be highest in the final, dark luminescing part of the generation 3, while manganese should significantly increase in the bright luminescing zone of the generation 2. The intrinsically luminescing part of the generation 2 should, however, yield only very low iron and manganese contents.

These assumptions are supported by a PIXE linescan that transects the generations 2 and 3 (Fig. 3). Furthermore, the progressively decreasing Sr content in the course of cementation may indicate a marine memory effect for the early cements [19].

4.2. Triassic limestones from northern Germany

The cement sequence of a Triassic limestone from northern Germany is characterized by a first generation of either blotchy luminescing cements or by red luminescing microdolomite inclusions. Both CL features hint at a primary high Mg calcitic composition and, therefore, at a marine origin of this cement generation. The next generation is an orange luminescing calcite that can be subdivided into a zoned subgeneration 3.1 and a younger, homogeneously luminescing, subgeneration 3.2.

The generation 2 is missing in this sequence. The cementation ends with a mainly intrinsically luminescing generation 4 that is characterized by very thin, brightly yellow subzones. In a few samples an intensely zoned, dull to moderate luminescing, subgeneration 3.3 can be detected that is intercalated between generations 3.2 and 4.

On the basis of CL investigations, the succession from generation 1 to 3.3 reflects decreasing Eh values, while the generation 4 cement mirrors oxidizing conditions at the time of its precipitation. The sequence reflects a complete basin evolutionary cycle, from marine sedimentation via burial diagenesis to telogenetic meteoric diagenesis, the latter following basin inversion [20].

The above interpretation is supported by PIXE trace element data, as the cements display successively decreasing Sr concentrations, coupled with contemporaneous increase in Mn and Fe contents, up to generation 3.3. Enhanced Mn concentrations (up to 1800 ppm) were also detected in the bright zones of the generation 4. These final cements are characterized also by significant zinc contents, a common feature of meteoric calcites. The subsequent decrease in Sr concentrations may indicate the evolution from a closed rock buffered system to an open system with high water/rock ratio.

4.3. Fissure cement in Triassic/Jurassic limestones from Perachora (Greece)

Fissure cements in Triassic/Jurassic limestones from Greece can display narrow ( < 30 μm) cement zones with dark, bottle green luminescence color. This CL feature is a rarity that has not yet been reported for natural calcites. In a PIXE element map (Fig. 4), this green zone is characterized by low Fe and Mn contents and by increased Sr and Y concentrations. Since strontium, as a major group element, is unlikely to be an activator of CL and since green CL due to lattice defects caused by its incorporation is unknown, we believe that this luminescence color is activated by yttrium. On the basis of the high yttrium and strontium contents, these cements can be interpreted as hydrothermal mineralisations.

It must be noted that the green CL zone and the increased yttrium contents do not correlate perfectly. Some of the Y enrichment goes along with significantly increased Mn concentrations causing a yellow CL that masks the Y-induced CL in this part of the crystal. The above example clearly highlights the need for high-resolution trace element analyses in order to correctly interpret the cementation history of a rock.

5. Conclusions

- Microscale zoning of natural calcites and the low threshold values for CL activation require a microanalytical technique with low detection limits and a high spatial resolution for the study of trace element/CL interrelationships. The proton microprobe is a tool well suited for this purpose.
- Our PIXE analyses indicate that the CL of natural calcites depends on both the absolute iron and manganese concentrations and the iron/manganese ratio. For Fe/Mn ratios < 10 the sensitivity to manganese activation exceeds iron quenching, while for ratios ≥ 10 iron quenching dominates if the concentrations increase at a constant ratio.
- The frequently observed moderate CL of calcites coincides with a wide scatter in iron and manganese concentrations, with a considerable overlap into the fields of bright and dull luminescing calcites.
- Combined CL and PIXE studies yield useful information as to the diagenetic history of sedimentary carbonates. Even the fine-scale CL zonation patterns in cements can be studied for their trace element signature.
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References