CHATODOLUMINESCENCE MICROSCOPIC ANALYSIS TO INTERPRET THE REDOX CONDITION DURING THE FORMATION OF CARBONATE VEIN

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Abstract

Cathodoluminescence (CL) is generated by an electron gun coupled to an optical microscope. There are two types of chatodoluminescence, i.e., cold CL and hot CL. In the cold cathode microscopic equipment, the electrons are generated by an electric discharge between two electrodes under a low gas pressure, whereas in the hot CL microscope, the electrons are generated by heating a filament (2000–3000°C). In this paper we utilize cold CL combine with electron microprobe analysis (EMPA). The CL microscopy of carbonate shows at least three carbonate generations, i.e., rhodochrosite with dull or no luminescence, Mg-rich calcite with dark red luminescence, manganese-bearing calcite with up to 0.04 wt.% Mn with bright orange luminescence, and pure calcite and Mn-rich calcite (> 0.15 wt.% Mn) with dull or no luminescence. The result also suggests that the luminescence pattern of calcite is controlled by the amount of Mn^{2+}. *Sectoral zoning and chevron-shape growth zoning exist in some coarse-grained calcite aggregates. The sectorial zoning of calcite as reflected by dull to bright CL color indicated that slightly to more reducing environment during calcite deposition.*

Keywords: *Chatodoluminescence, rhodochrosite, calcite, sectorial zoning*

1 Introduction

Carbonates are the dominant gangue minerals (up to 60%) in most of epithermal deposits (Warmada, 2003). They consist of calcite and minor rhodochrosite, kutnahorite, dolomite, ankerite, and siderite. The formation of calcite in hydrothermal systems is controlled by f_{CO_2}, pH, temperature, and aqueous calcium ion activity (Fournier, 1985; Simmons and Christenson, 1994). For most present-day geothermal systems f_{CO_2} appears to be the limiting factor, and the presence or absence of calcite in a hydrothermal mineral assemblage directly reflects the carbon dioxide abundance of the coexisting fluid (Giggenbach, 1981, 1988).

A cathodoluminescence (CL) phenomenon, i.e., emission of light under electron bombardment, is known for a long time and now is widely used in nearly all black-and-white, color cathode-ray tubes (Petrov, 1996). There are two types of chatodo-luminescence, i.e., cold CL and hot CL. In the cold cathode microscopic equipment, the electrons are generated by an electric discharge between two electrodes under a low gas pressure, whereas in the hot CL microscope, the electrons are generated by heating a filament (2000–3000°C). In this paper we utilize cold CL combine with electron microprobe analysis (EMPA).

Cathodoluminescence microscopy is a petrographic tool widely used in studies of diagenesis. It is particularly suitable for documenting

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details of crystal growth in calcite and dolomite cements and for understanding pore evolution in carbonate sequences (Savard, *et al.*, 1995). In hydrothermal mineral deposits CL microscope is widely used to help determining petrogenetic type of fluid inclusions (Kerkhof and Hein, 2001).

The intensities of CL in calcites are usually grouped into three categories: nonluminescent (dead, distinguished, or black), dull (brown and very dull), and luminescent (bright yellow, orange, and moderate). Within a single crystal, numerous CL zones can alternate and form features that may not be discernible by conventional light microscope or staining. CL features of calcites have generally been attributed to variations in Mn concentrations as the main activator, and to Fe as the main quencher (for a review, see Pierson, 1981; Reeder and Paquette, 1989; Savard, *et al.*, 1995). The CL features are also caused by subtitution of Ca^{2+} by trace elements (Barnaby and Rimstidt, 1989).

Mn and Fe contents of calcite reflect water (hydrothermal water) chemistry prevailing during carbonate precipitation. Various studies (Grover and Read, 1983; Dorobek, 1987) have suggested that the increaseing Fe and Mn contents in the commonly observed sequence of CL zonation from nonluminescent to brightly luminescent to dully luminescent reflects a progressive decrease in Eh. The intensity and color of luminescence are also dependent on the relative proportions of Mn and Fe.

In this paper, we would like to presents cathodoluminescence petrography combined with EMPA of data of carbonate samples from the Pongkor gold-silver deposit.

2 Samples and methods

Eight samples were collected from Pongkor epithermal gold-silver deposit during mine visits in mid-1999 and 2001 and analyzed with cathodoluminescence (CL). The Technosym instrument was used for CL studies of double polished thin sections. The CL analyses were carried out in the Institute of Geology and Palaeontology, Technical University of Clausthal. The thin sections of carbonate samples were bombarded with electrons with an energy of 15 kV accelerating potential and 245 μA beam current.

The micro-chemical analysis of carbonate minerals was performed with a Cameca SX-100 electron microprobe at the Institute of Mineralogy and Mineral Resources, Technical University of Clausthal. The two operating conditions were applied: 15 kV accelerating potential and 15 nA beam current for major elements, while 20 kV and 100 nA were used for minor elements; with 5-10 μm beam diameter.

3 Results and discussion

3.1 Carbonate mineralogy

Carbonate is the most common hydrothermal mineral (up to 60 %) in the Pongkor gold-silver deposit. The principal occurrences of carbonate in this area are: (1) replacement of rock-forming minerals (especially Ca-feldspar) and volcanic glass; and (2) vein infill as a main component of the carbonate-quartz stage and the manganese carbonate-quartz stage. A hydraulic breccia connected to carbonate-quartz stockworks is commonly developed in the footwall and hanging wall of the veins.

The vein-carbonate material is dominantly composed of fine to coarse crystalline calcite with locally banded rhodochrosite. Three calcite generations are found in the veins. Fine to medium-sized white calcite is formed in the early stage of mineralization, mostly along the footwall and hanging wall of the veins. A second generation of white, brown or honey-colored calcite is more massive and coarsely crystalline. The latest calcite generation, which is mostly coated by iron oxides, filled the fractures of existing veins.

Rhodochrosite ($MnCO_3$) is mostly altered to manganese oxides and was observed only locally as pink-banded lenses (up to 1 cm thick) in the deeper levels of the Ciguha and Kubang Cicau veins. It is associated with calcite, quartz and banded adularia. Manganoan or manganese-rich calcite, with up to 15 wt.% Mn is common in Pongkor. The abundant manganese oxide pockets are probably the result of weathering of these minerals. Dolomite

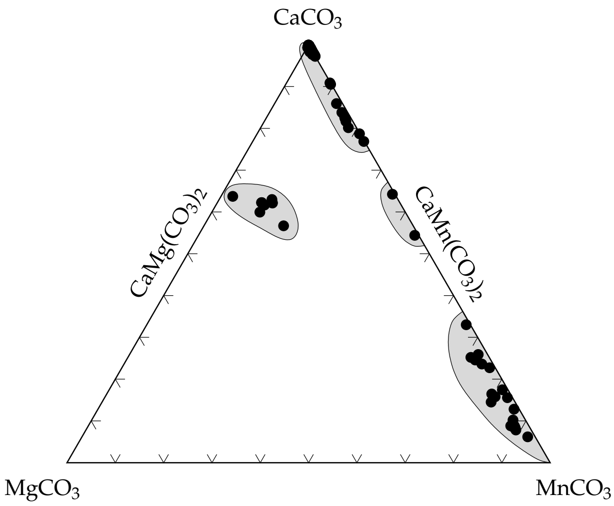

Figure 1: Ternary diagram of carbonate composition from the Pongkor gold-silver deposit, which shows the solid-solution of $CaCO_3$–$MnCO_3$ with the presence of pseudokutnahorite

($CaMg(CO_3)_2$) and kutnahorite ($CaMn(CO_3)_2$) are rare and were found only by microprobe analysis (Fig. 1).

3.2 Cathodoluminescence of carbonate

Ca, Mn, Mg, and Sr were analyzed in the electron microprobe in order to document compositional change between sector of calcite zone (Figure 2). Fe content of calcite was not analyzed in this research.

Cathodoluminescence microscopy of carbonate shows at least three carbonate generations, i.e. rhodochrosite with dull or no luminescence, Mgrich calcite with dark red luminescence, manganese-bearing calcite with up to 0.04 wt.% Mn with bright orange luminescence and pure calcite and Mn-rich calcite (>0.15 wt.% Mn) show dull or no luminescence. Figures 2 and 3 suggest that the luminescence pattern of calcite is controlled by the amount of Mn^{2+}. Luminescence intensities varied from dull to nonluminescent (i.e., below the detection limit for the CL device used. If manganese (Mn^{2+}) is the activator of luminescence, a minimum amount of Mn2+ is required in order to produce a detactable luminescence. Pierson (1981) suggested that this minimum amount was close to 1000 ppm Mn^{2+} (0.1 wt.%). In the light of the analytical data presented in this study, it appears that the actual lower limit of luminescence is well around 1000 ppm Mn^{2+} (Figure 3). Mn^{2+} is generally regarded as the principal activator and Fe^{2+} acts as the main CL quencher in calcite (Spötl, 1991).

Bright calcite is precipitated from meteoric fluids that were slightly reducing condition, allowing manganese and lesser amount of iron to be in reduced (2+) valence states and to substitute for calcium in calcite. Dull calcite is precipitated from more reducing fluids than bright calcite or nonluminescent, as suggested by high iron or manganese contents. These results are also confirmed by Dorobek (1987). Sectoral zoning and chevron-shape growth zoning (Reeder and Paquette, 1989) exist in some coarse-grained calcite aggregates. The sectorial zoning of calcite as reflected by dull to bright CL color indicated that slightly to more reducing environment during calcite deposition.

As manganese occurs in natural environments in the valence states +2, +3, and +4 (Wolfram and Krupp, 1996) and the higher oxidation states have a strong tendency to hydrolyse and precipitate, transport of Mn in aqueous solutions is generally favored by reducing conditions, and the Mn^{2+} ion, and its complexes, constitute the principal transport species. This confirms that the present of significant amount of Mn and Fe as well as trace elements in calcite can effect the cathodoluminescence patterns of calcite. Measuring the calcite luminescence can be used to estimate/interpret the redox conditions during calcite deposition.

4 Conclusions

The CL study of hydrothermal carbonate anable to classify the three carbonate generations, i.e. rhodochrosite with dull or no luminescence, Mgrich calcite with dark red luminescence, manganese-bearing (manganoan) calcite with up to 0.04 wt.% Mn with bright orange luminescence and pure calcite and Mn-rich calcite (>0.15 wt.% Mn) show dull or no luminescence. Sectoral zoning and chevron-shape growth zoning exist in some coarse-grained calcite aggregates. The sectorial zoning of calcite as reflected

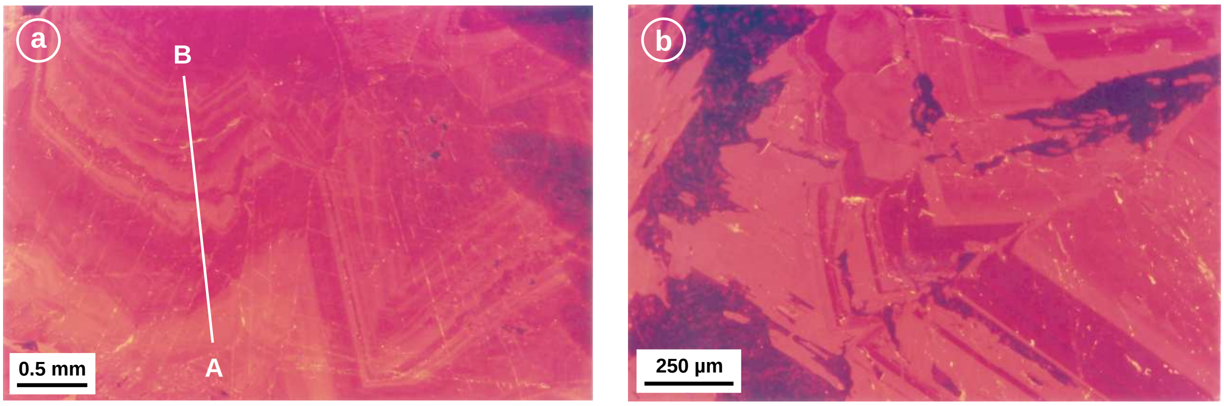

Figure 2: Cold cathodoluminescence image of calcite, section A–B refers to Figure 3

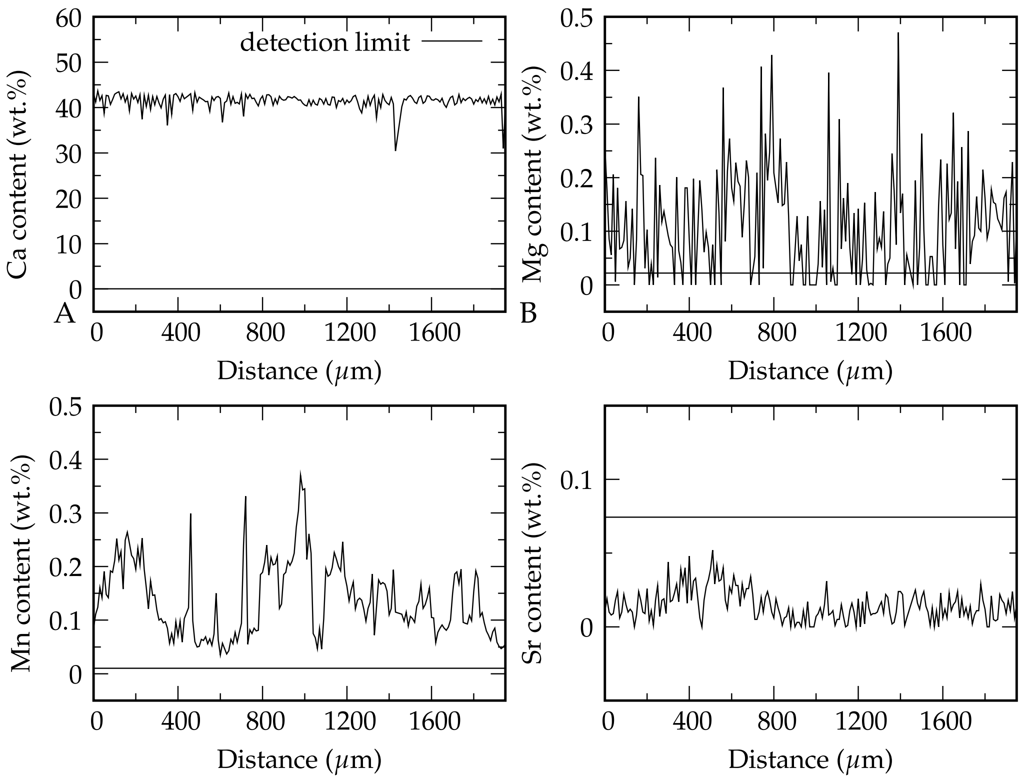

Figure 3: Microprobe analyses of sectorally zoned calcite of a selected carbonate sample

by dull to bright CL color indicated that slightly to more reducing environment during calcite deposition.

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