



Electron probe microanalysis and microscopy: Principles and applications in characterization of mineral inclusions in chromite from diamond deposit



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ABSTRACT

Electron probe microanalysis and microscopy is a widely used modern analytical technique primarily for quantifying chemical compositions of solid materials and for mapping or imaging elemental distributions or surface morphology of samples at micrometer or nanometer-scale. This technique uses an electromagnetic lens-focused electron beam, generated from an electron gun, to bombard a sample. When the electron beam interacts with the sample, signals such as secondary electron, backscattered electron and characteristic X-ray are generated from the interaction volume. These signals are then examined by detectors to acquire chemical and imaging information of the sample. A unique part of an electron probe is that it is equipped with multiple WDS spectrometers of X-ray and each spectrometer with multiple diffracting crystals in order to analyze multiple elements simultaneously. An electron probe is capable of analyzing almost all elements (from Be to U) with a spatial resolution at or below micrometer scale and a detection limit down to a few ppm.

Mineral inclusions in chromite from the Wafangdian kimberlite, Liaoning Province, China were used to demonstrate the applications of electron probe microanalysis and microscopy technique in characterizing minerals associated with ore deposits, specifically, in this paper, minerals associated with diamond deposit. Chemical analysis and SE and BSE imaging show that mineral inclusions in chromite include anhydrous silicates, hydrous silicates, carbonates, and sulfides, occurring as discrete or single mineral inclusions or composite multiple mineral inclusions. The chromite–olivine pair poses a serious problem in analysis of Cr in olivine using electron probe. Secondary fluorescence of Cr in chromite by Fe in olivine drastically increases the apparent Cr₂O₃ content of an olivine inclusion in a chromite. From the chemical compositions obtained using electron probe, formation temperatures and pressures of chromite and its mineral inclusions calculated using applicable geothermobarometers are from 46 kbar and 980 °C to 53 kbar and 1130 °C, which are within the stability field of diamond, thus Cr-rich chromite is a useful indication mineral for exploration of kimberlite and diamond deposit. A composite inclusion in chromite composed of silicate and carbonate minerals has a bulk composition of 33.2 wt.% SiO₂, 2.5 wt.% Al₂O₃, 22.0 wt.% MgO, 7.5 wt.% CaO, 2.5 wt.% BaO, 0.8 wt.% K₂O, 25.5 wt.% CO₂, and 0.8 wt.% H₂O, similar to the chemical composition of the Wafangdian kimberlite, suggesting that it is trapped kimberlitic magma.

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1. Introduction

Electron probe microanalyzer (EPMA), also known as electron microprobe analyzer (EMPA), is a specialized SEM with multiple wavelength dispersive spectrometers (WDS). Because of uses of secondary electron (SE) and backscattered electron (BSE) detectors and field emission gun (FEG), an EPMA can also be used to acquire images of the

sample analyzed at magnifications up to 100,000×. This analytical technique is capable of determining concentrations of elements from Be to U on the micron scale. The term “electron microscope” was first used by Knoll and Ruska (1932), who made the concept of an electron lens a reality. There are two types of electron microscope, i.e., scanning electron microscope (SEM) and transmission electron microscope (TEM). Both SEM and TEM use electrons and electro-magnet lenses to examine small objects. However, SEM usually detects signals emitted from the surface of a sample, while TEM detects signals that pass through the sample, thus requiring the sample to be thin. Other differences between SEM and TEM include 1) accelerating voltages are commonly up to 30 kV in SEM, much lower than 200 kV, a common accelerating voltage for TEM; and 2) SEM uses a focused electron beam to scan across the

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sample surface line by line while TEM uses a parallel static beam. But most modern TEMs have scanning transmission electron microscopy mode (STEM), which also uses a focused electron beam.

In this article, we first review the principles and instrumentation of EPMA technique that is used primarily for X-ray quantitative analysis of chemical compositions and qualitative mapping of elemental distributions in solid materials (Castaing, 1951; Goldstein et al., 2003, 2011; McGee and Keil, 2001; Potts, 1987; Reed, 1993, 1995, 2005; Smith, 1976). We then discuss the applications of EPMA in characterization of mineral inclusions in chromite associated with the diamond deposits in the Wafangdian kimberlite, Liaoning Province, China (No. 50 and No. 42 diatremes). As an important indicator mineral for exploration of kimberlite and diamond deposits (e.g., Dong, 1994; Huang et al., 1992; Mitchell, 1986), chromite could contain abundant mineral inclusions that are small in size ranging from a few microns to hundreds of microns (Zhao, 1998). The high Cr content of chromite is considered to be an indication of high pressure although in general pressure of chromite formation can only be constrained by certain mineral assemblages. Studies on mineral assemblages inside chromite grains from kimberlite help understand origins of kimberlite, diamond and chromite. Previous studies on mineral inclusions in chromite include samples from layered mafic–ultramafic rocks (McDonald, 1965), ophiolites (Matsukage and Arai, 1998; Peng et al., 1995), Alpine-type ultramafic rocks (Peng, 1987), Alaskan-type complexes (Talkington and Lipin, 1985), as well as kimberlites and lamproites (Logvinova and Sobolev, 1991, 1995; Rovsha, 1962). Logvinova and Sobolev (1991, 1995) reported olivine, clinopyroxene, orthopyroxene, garnet, phlogopite and sulfide inclusions in chromite (>0.5 mm) from Siberian kimberlites and Western Australian lamproites.

2. Principle and instrumentation of EPMA

2.1. Principles of EPMA

The first electron microprobe was developed by Raimond Castaing (1951) when he was a doctoral student at the University of Paris. A topical symposium was held by the Microbeam Analysis Society in 1999 to honor Dr. Castaing (see special issue on EPMA published by Microscopy and Microanalysis in 2001, Volume 7, Number 2). An electron microprobe allows elemental concentrations on the micron scale in materials to be quantified routinely at levels as low as 100 ppm or 0.01 wt.%. Quantification of elemental compositions is achieved by comparing the intensity of a characteristic X-ray from an unknown sample with that from a known standard. Using long count times, high beam currents and multipoint background correction, a detection limit of 10 ppm or lower is achievable for some specific analysis, such as the measurement of Ti in quartz (Donovan et al., 2011; Wark and Watson, 2006). EPMA analysis is generally considered to be non-destructive, although the electron beam can damage beam-sensitive materials, such as feldspars, apatite, and glasses, and cause migration of components in alkali- or volatile-bearing phases.

2.1.1. X-ray generation and interaction volume

Characteristic X-rays are generated by a focused electron beam that bombards and interacts with solid materials. Mosley (1913) discovered that the wavelength of the characteristic X-ray from an element is inversely related to its atomic number Z . The range of electrons and X-rays generated by an electron beam within a sample is called interaction or excitation volume, which depends on the energy of the electron beam and average atomic number of the sample. The shape and size of the interaction volume represent the source from which analytical signals originate.

As beam electrons travel through the sample, collision processes between the beam electrons and atoms in the sample are either elastic or inelastic, depending on whether or not energy change is involved. During inelastic collisions, the beam electrons lose part of their energy.

If the lost energy is high enough to overcome the critical ionization energy of an element, it will be able to remove an inner-shell electron from the atom, which leaves an inner-shell vacancy. The excited atom is not stable and a higher-shell electron will fall into the vacancy, resulting in release of a characteristic X-ray photon or an Auger electron.

2.1.2. Wavelength dispersion and focusing of characteristic X-ray

X-ray generated in the interaction volume is detected using WDS spectrometers, a key component that makes an EPMA different from other SEM although some modern SEMs may be equipped with a WDS detector. A WDS detector includes a few diffracting crystals and a gas-flow or sealed proportional counter. The X-ray source in the sample, the surface of a diffracting crystal and the gas proportional counter define an imaginary circle of constant diameter, which is called the Rowland's circle (Fig. 1). Diffracting crystals are used to disperse wavelengths of characteristic X-rays and focus a specific X-ray wavelength onto a gas-flow or sealed proportional counters for measurement. Since only a small portion of the X-ray photons from the sample reach a diffracting crystal, the intensity of the X-ray detected by WDS is generally lower than that detected by an energy dispersive spectrometer (EDS) for a given beam current.

2.1.3. Standards and matrix correction

Well characterized and accepted standards are critical for quantitative EPMA. In quantitative EPMA, the concentration of a given element in an unknown sample is obtained by comparing the intensity of a characteristic X-ray of that element with that from a standard with known chemical composition. The intensities of an X-ray line in both sample and standard must also be corrected for matrix effects, deadtime, background and instrumental drift, overlapping, etc. in order to obtain accurate results. According to the Castaing approximation, the intensity I of a characteristic X-ray is proportional to the mass concentration C of the element measured (Reed, 2005). The measured X-ray intensity of an element in EPMA is affected by the concentrations of all the other elements present in the sample. These matrix effects include mainly influence of atomic number (Z), X-ray absorption (A), and secondary

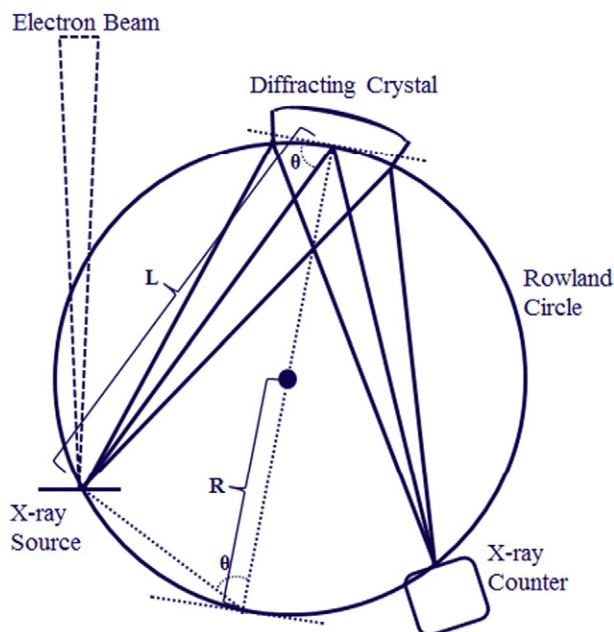


Fig. 1. An imaginary Rowland circle composed of the X-ray source in the sample, the diffracting crystal and the gas proportional counter. R – radius of the Rowland circle, L – detection position which is the distance between the X-ray source and the diffracting crystal, θ – angle of diffraction at which the diffracted characteristic X-rays are in phase and the intensity is constructively enhanced. Since $L = 2R \sin \theta$, combining this equation with Bragg's law, $n\lambda = 2d \sin \theta$, yields $L = n\lambda R / d$.

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