



A methodology for wavelength dispersive electron probe microanalysis of unpolished silicate minerals



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ABSTRACT

Evaluation of mineral compositions is a widely used approach in resource exploration strategies where preparation time and cost may prove to be an important factor. In research institutes it is highly beneficial to determine the major element composition of minerals prior to their destructive analysis for trace elements and radiogenic isotopic ratios thus allowing a comprehensive interpretation of mineral petrogenesis. For the analysis of unique and small (submilligram) samples, avoiding sample loss is a key issue in ultimately producing high quality geochemical data. Consequently here we evaluate the precision and accuracy of electron probe microanalysis of unpolished garnet, olivine, orthopyroxene and clinopyroxene grains by comparison of analyses performed on polished thin sections of the same minerals. By utilizing a protocol that focuses on flat mineral surfaces, rejects analyses with low totals (<90%) and major element compositions, magnesium numbers and stoichiometry outside two standard deviation, results had on average a reproducibility of 1.3 times the relative standard deviation of the results of polished thin sections. Major element ratios are indistinguishable from the thin section results. For example, the Mg# for clinopyroxene and olivine is within 0.4% and for garnet within 1–1.5%. Individual analyses of minerals with flat surfaces such as clinopyroxene had a higher rate of success (73%) than minerals with a more variable surface topography such as conchoidally fractured garnet (40%), underlining that a flat topography is the controlling factor in EPMA analyses. These tests establish that accurate and reproducible EPMA analysis can be produced on unpolished minerals that are within error of conventional thin section analyses. The technique is predicted to be of particular use in diamond exploration strategies where knowledge of the geotherm beneath exploration areas is a key parameter. Integrated studies of composition and geochronology of mineral inclusions in diamonds have the potential to significantly improve the understanding of diamond formation processes and the imposed octahedral morphology of the inclusions mean that they have flat crystal faces, ideal for analysis using the proposed methodology.

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1. Introduction

Modern diamond exploration strategies use airborne geophysical techniques to recognize igneous bodies that may represent pyroclastic diatreme deposits (Macnae, 1979). Once potential deposits are recognized on a regional scale, exploration tends to focus on the chemical composition and age of heavy minerals such as garnet, ilmenite and clinopyroxene recovered from drill and soil samples (Coker, 2010). The aim of this strategy is to understand the nature and depth of origin of potential source rocks: i.e., if garnet harzburgite, garnet lherzolite, eclogite etc. are derived from above or below the diamond-graphite phase transition (Averill, 2001; Griffin and Ryan, 1995). The characterization of the rare mineral inclusions found in diamonds using multiple analytical techniques could potentially form an important part of this

strategy by helping to define the past regional geothermal gradient and hence the depth range from which diamonds could be sampled by the host volcanic rocks (Grütter et al., 2004; Gurney et al., 2005). Currently, however, the study of such inclusions is rarely incorporated into the exploration strategy, partly due to their small size (typically <100 μm) and the inability to date the inclusions. Recent advances in analytical techniques now make it possible to determine trace element concentrations and radiogenic isotopic ratios on subnanogram amounts of an element (Koornneef et al., 2014). These developments now allow the possibility to study extremely small samples, for example submilligram melt inclusions (Koornneef et al., 2015) and could be applied to dating individual mineral inclusions derived from diamonds. This offers the exploration industry the opportunity to gain a better understanding of the number and timing of diamond forming events within an exploration area providing better assessment of the potential diamond resources.

Compositional characterization of the inclusions is a pre-requisite prior to destructive trace element or isotopic analysis to determine the

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number of different inclusion populations in the bulk diamond sample. Determining the number of inclusion populations is of particular importance if inclusions are pooled for isotope analysis, as has been the practice in the past (Richardson et al., 1990; Richardson et al., 1984). Wavelength dispersive (WDS) electron probe microanalysis (EPMA) is the usual characterization method of these inclusions in order to obtain high precision pressure temperature estimates (Cookenboo and Grütter, 2010; Gurney et al., 2005). Traditionally EPMA is performed on polished materials such as thin sections or grain mounts, with a carbon coating to avoid charging effects. The dilemma that is now faced is that the analytical precision of the high precision geochemical techniques required to characterize the isotopic and trace element composition of the inclusions will always be limited by sample size; hence it is desirable to avoid any sample loss by polishing for example.

Here we present a methodology for EPMA of unpolished materials. This method is particularly suitable to inclusions from diamonds as they are frequently characterized by flat crystal surfaces due to the tendency of diamond to impose an octahedral symmetry on inclusions (Meyer, 1987).

Previous electron probe microanalysis of unpolished materials in general showed that X-ray emissions are highly scattered leading to lower totals (Kielemoes et al., 2000). The density of the sample, fluorescence and the absorbance of radiation can also affect the WDS analysis on unpolished samples. Further, the beam incidence angle and take-off angle and stability of the beam voltage are part of the calculations for quantitative results. Any rough or tilted surface will cause different beam incidence and take-off angles and influence the WDS analysis (Lifshin and Gauvin, 2001). EPMA analysis of porous aluminous catalysts in non-conductive resin resulted in 15 times larger errors and the significant offsets in the major element composition compared to solid samples were attributed to surface contamination and the assumption that the porous sample had the same atomic formula as the solid sample (Sorbier et al., 2004). Signal loss on these porous materials was attributed to charge trapping effects (Sorbier et al., 2000) and not to the direct effect of porosity and roughness as previously argued by Abo-Namous (1989) and Lakis et al. (1992). For porous materials the analyses were corrected with the peak-to-background method, rather than the normal ZAF correction procedure (Abo-Namous, 1989; Statham and Pawley, 1978). The samples had a very high surface roughness and the total concentration of metals often did not exceed 2 wt%. In contrast, as unpolished minerals have total metal concentrations close to 100% and often relatively flat crystal faces, the traditional ZAF correction procedures are more practical than the peak-to-background method. Although wavelength dispersive microanalysis of unpolished solid materials has been previously reported on stainless steel (Kielemoes et al., 2000), two mineral inclusions (Deines and Harris, 2004) and thin sections (Chinner et al., 1969), no detailed method description has been presented and the available data shows only normalized totals for mineral inclusions and 25.6–33.1% totals for stainless steel. Bjärnberg and Schmitz (2013) assessed the quality of energy dispersive (EDS) analysis of unpolished spinel grains by comparison to WDS measurements of polished spinel grains and concluded that it was possible to obtain reliable compositional data, presumably due to spinel having well-defined crystal faces. By comparing the analysis of polished and unpolished samples the uncertainty in the relative trueness of the analysis when utilizing the ZAF correction procedure is common to both analyses and hence cancels out (Pouchou and Pichoir, 1991).

The study presented here investigates the reliability and reproducibility of the more precise WDS technique on unpolished solid silicate minerals with the aim to apply a method to rare 10 to 300 μm mineral inclusions in diamonds, prior to the Rb–Sr and Sm–Nd isotope analysis of the entire grain. In the discussion below, accuracy is used for the trueness of the values and is assessed by comparing it to the analysis of the polished minerals, and precision refers to random errors and includes how well we can repeat the analyses with the same results (reproducibility).

2. Materials and methods

2.1. Materials

Four clinopyroxene (cpx, OR109), four olivine (ol, LE83), and four garnet (grt, LE83) grains from peridotitic xenoliths from the Orapa and Letlhakane diamond mines, Botswana were measured along with the thin sections of these xenoliths. Garnet grains (AT1361) and orthopyroxene, olivine and garnet grains (AT1324) from peridotitic xenoliths from the Venetia diamond mine, South Africa were also analyzed. The number of spot analyses performed on each sample is shown in Table 3. Minerals from mantle xenoliths were chosen as test material as equilibration took place at high temperatures and pressures, leading to a high diffusion rate and consequently minimal major element zonation. Based on this reasoning it is assumed that the unpolished grains and thin sections have an identical major element composition and that they can be compared directly. A second test was performed on euhedral garnet grains from the El Joyazo volcano, Spain, to investigate the effect of sample surface roughness on the results by comparing the success rate and quality of the measurements of euhedral and broken garnets. The flattest surface of the sample was placed perpendicular to the electron beam, so the possibility of a variable take-off angle is minimized. The take-off angle in the standard geometry of the instrument is 40°. The purpose of this study was to validate if unpolished samples can be measured reproducibly and accurately by treating them as polished samples and therefore the take-off angle was not monitored directly.

2.2. Electron probe microanalysis

The minerals were placed on double-sided sticky carbon tape on a glass plate with their flattest faces upwards and carbon coated. Careful sample manipulation is required to ensure that relatively flat sample surfaces are placed perpendicular to the electron beam. Secondary electron imaging was used to select flat surfaces and avoid irregular surfaces (Fig. 1a and b). Each sample consisted of at least 4 grains and each grain was measured at four to five different spots with a beam size of 1 μm with a beam current of 25 nA and an acceleration voltage of 15 kV on the JEOL JXA-8800 M Electron Probe Microanalyzer with 4 spectrometers at the VU University with a set-up according to Table 1. The second test of garnets was performed with a beam size of 1 μm and a beam current of 20 nA and acceleration voltage of 15 kV on the JEOL JXA-8530JF Electron Probe Microanalyzer with 5 spectrometers at the Utrecht University. Peak dwell time was set at 25 s, and each background was set at 12.5 s at the EPMA at the VU University and peak dwell time was set at 30 s (apart from Si, Al, Ca; 20 s) and background at 15 s (Si, Al; 10 s, Ca; 15 s) at the EPMA at Utrecht University. The standards chromite (Cr), corundum (Al), diopside (Si, Ca), fayalite (Fe), ilmenite (Ti), jadeite (Na), NiO (Ni), olivine (Mg), orthoclase (K), and tephroite (Mn) were used. The ZAF correction method was applied to the raw data, with the atomic number (Z) correction of Philibert and Tixier (1968), the absorption (A) correction of Philibert (1963) with the mass absorption coefficients of (Heinrich, 1966) supplied with the PC EPMA JEOL software, and the fluorescence (F) correction of Reed (1965).

3. Results and discussion

3.1. Reproducibility and reliability

Initial analyses on unpolished orthopyroxene, clinopyroxene, garnet, and olivine grains showed that the measurements of clinopyroxenes were extremely consistent with totals generally between 99.1 and 99.7 wt%, while the garnets and olivines more often gave lower totals. Garnet LE83 had 51% of the analyses between 5 and 90 wt%, while garnets AT1361 (9%) and AT1324 (3.5%) had less analyses below 90%. Olivines LE83 and AT1324 had respectively 14% and 37% of

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