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Correction of secondary X-ray fluorescence near grain boundaries in electron microprobe analysis: Application to thermobarometry of spinel lherzolites

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ABSTRACT

A correction procedure is proposed to account for the effect of secondary X-ray fluorescence near grain boundaries in electron microprobe analysis. The procedure is based on the Monte Carlo simulation method, which is used to calculate the X-ray spectrum emitted by the mineral couple (i.e., the mineral of interest with the neighboring mineral). The contribution of secondary fluorescence from the neighboring mineral, which appears in the simulated spectrum in a natural way, is then subtracted from the measured *k*-ratio and thereafter conventional matrix corrections are applied. The Monte Carlo simulation algorithm used is largely based on the general-purpose simulation package PENELOPE. In order to assess the reliability of this code, simulated "apparent" element profiles are compared with electron microprobe measurements found in the literature, in which the effect of secondary fluorescence was characterized and the reliability of the different assumptions underlying the proposed procedure is discussed.

Finally, the procedure is used to assess data from the olivine-clinopyroxene thermobarometer in a spinel lherzolite xenolith. The application of the secondary fluorescence correction leads to: (1) higher systematic pressure estimations than those obtained from uncorrected data, with lower uncertainties; and (2) a better agreement between the olivine-clinopyroxene temperature estimations and those estimated using the two-pyroxene thermometer. Estimated *P-T* conditions indicate a decompressional path with a slight decrease in temperature from core to crystal rim. However, if the effect of secondary fluorescence is not taken into account, an apparent heating event is observed.

INTRODUCTION

Electron microprobe analysis (EMPA) is a reliable, nondestructive technique for the quantitative analysis of rock-forming minerals (see e.g., Reed 1993). The technique is based on the measurement of characteristic X-ray intensities emitted by the elements that make up the mineral when it is bombarded with a focused electron beam. For each element, the ratio of the X-ray intensity emitted from an unknown to that emitted from a standard of known composition, measured under the same analytical conditions is, to a first approximation, proportional to the ratio of elemental concentrations. A more accurate value of the concentration is obtained by correcting for the differences in electron and photon transport between the unknown mineral and the standard, using the so-called "matrix correction" procedures.

Matrix correction procedures usually assume that the analyzed sample region from which X-rays are emitted has a homogeneous composition. The volume of this region can be estimated by calculating the effective penetration range of incident electrons. For keV electron beams, this range is typically of the order of several micrometers, depending on the material and the analytical conditions. Accordingly, EMPA is adequate for analyzing homogeneous mineral grains that have a diameter larger than several micrometers. However, the range of characteristic X-rays and Bremsstrahlung that are generated by incident electrons, is typically one to two orders-of-magnitude greater, namely several tens or hundreds of micrometers. Consequently, although the electron beam impacts quite a distance from the grain boundary, X-rays may reach a neighboring phase and induce further ionizations (if the photon energy is larger than the binding energy of the considered atomic shell) causing the emission of characteristic X-rays, and this process is usually referred to as secondary fluorescence (SF). As matrix corrections assume chemical homogeneity, the contribution of SF coming from the adjacent mineral will not be taken into account and will lead to an erroneous concentration. Fortunately, this effect is generally small and it can be disregarded. However, in certain situations, SF coming from a neighboring phase should be taken into consideration carefully. One such situation is the analysis for a minor or trace element in a mineral that coexists with another mineral containing the element of interest. In this case, even if we analyze the mineral relatively far from the boundary, SF may affect the results not only qualitatively but also quantitatively. Examples of interest in geology include the analysis for Ti in chromite in contact with ilmenite (Maaskant and Kaper 1991), Ca in olivine close to clinopyroxene (Dalton and Lane 1996), or Ti in garnet close to rutile or ilmenite inclusions (Feenstra and Engi 1998).

The contribution of SF can be minimized by using *L*-lines instead of *K*-lines in the quantitative procedure (Pouchou 1996).

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However, measurement and quantification using *L*-lines is difficult and may lead to larger uncertainties. Besides, for some elements such as Ca, the use of the *L*-line is not a realistic alternative. Several methods have been proposed for correcting SF near phase boundaries (see Dalton and Lane 1996 and references therein). For example, Bastin et al. (1983) developed a numerical method to correct for SF effects in metal couples that can be incorporated into a matrix correction procedure. Myklebust and Newbury (1994) used the Monte Carlo (MC) simulation of electron transport in metal couples to predict SF induced at phase boundaries. These numerical corrections were applied mainly to single-element materials and, moreover, SF induced by the continuum was approximated by very crude methods or even neglected.

In this work, a new correction method is proposed to account for the effect of SF near phase boundaries. The method is based on the simulation of the full X-ray spectrum emitted by the mineral couple, using the MC simulation method. The MC algorithm used is the one developed by Acosta et al. (1998), which is based on a modified version of the general-purpose simulation package PENELOPE (Baró et al. 1995). This code allows the simulation of coupled electron-photon transport in complex material structures consisting of homogeneous regions of arbitrary composition, limited by quadric surfaces. Because both electron and photon transport is considered, the contribution of SF appears in the X-ray spectrum in a natural way and also includes the continuum contribution. In this work, minerals are assumed to be separated by a planar interface; however PENELOPE allows the simulation of other geometries, such as inclined or curved boundaries (Llovet et al. 2000). To assess the reliability of this MC algorithm, simulated element profiles are compared with the EMPA measurements of Dalton and Lane (1996). Those measurements consisted of apparent Ca profiles, which are the result of the effect of SF near grain boundaries, obtained from mineral couples of olivine of increasing Fe content with diopside, and from San Carlos olivine with minerals of increasing Ca content. As an application, we address the problem of analyzing Ca in olivine close to clinopyroxene in spinel lherzolites for purposes of thermobarometry. Indeed, olivine can contain a large amount of Fe and thus emitted Fe*K*α X-rays can be absorbed in coexisting clinopyroxene by Ca atoms, with the result of the emission of secondary Ca*K*α X-rays. This contribution is not negligible, as the Ca content in olivine is typically below 1 wt%. Using conventional EMPA correction procedures, the Ca content in olivine was always found to depend on the distance of the electron beam point of impact from the olivine border: the closer the point, the higher the Ca concentration (Adams and Bishop 1986; Jurewicz and Watson 1988; Kölher and Brey 1990; Dalton and Lane 1996). To avoid such contamination prudently, the latter authors recommended that olivine crystals should be physically separated, mounted on a Ca-free matrix, and analyzed separately. The aim of the present study is to provide an alternative method in an attempt to avoid the physical separation of crystals, which is always tedious and sometimes difficult, e.g., when the phase of interest encloses the contaminant mineral as an inclusion (cf., Feenstra and Engi 1998).

MONTE CARLO SIMULATION OF SECONDARY X-RAY FLUORESCENCE

The penetration and slowing down of a particle (electron or photon) in matter is the result of a sequence of interactions in which the particle is deflected and loses energy. Due to the random nature of these interactions, the Monte Carlo (MC) method is particularly well suited for the numerical simulation of particle trajectories within the material medium. Each trajectory is viewed as a sequence of free flights that end with a scattering event where the particle changes its direction, loses energy, and may generate secondary particles. The trajectory finishes when the particle is stopped in the material or escapes from it. Quantities of interest are obtained by averaging over a great number of simulated trajectories. The usefulness of MC simulation stems from its ability to incorporate realistic physical interation models for the scattering mechanisms, and to keep track of the evolution of all particles (secondary electrons, Auger electrons, characteristic X-rays, Bremsstrahlung photons) generated by primary electrons and their descendents.

In the keV range, the possible interactions of electrons with matter are elastic interactions, inelastic collisions, and Bremsstrahlung emission. Elastic interactions change the direction of the electron. Inelastic interactions are those in which the target is brought to an excited state, i.e., a part of the electron's kinetic energy is taken up by the atomic electrons. Inelastic interactions with relatively large energy transfer normally cause the ionization of the target atom. Excited ions relax to their ground state by migration of the initial vacancy to outer electron shells, which proceeds through emission of primary X-rays or Auger electrons with characteristic energies. Emission of Bremsstrahlung takes place when the electron is decelerated within the electrostatic field of the target atom.

Emitted photons (either as characteristic X-rays or Bremsstrahlung) can further interact with the target via photoelectric absorption, Compton scattering, and Rayleigh scattering. In the case of photoelectric absorption, the photon is absorbed and an atomic electron is ejected from the target atom. The resulting ion relaxes by migration of the vacancy to outer electrons shells, with the emission of (secondary) fluorescent X-rays or Auger electrons.

To calculate the SF contribution, we have simulated X-ray spectra using the MC simulation program of Acosta et al. (1998). This program calls a modified version of the PENELOPE subroutine package (Baró et al. 1995) and provides the X-ray spectrum for a given take-off angle. PENELOPE is a general-purpose simulation package that generates electron-photon showers in homogeneous media of arbitrary composition, for a wide energy range, from about 1 keV up to about 1 GeV. The interaction models implemented in PENELOPE are based on the most reliable information available. They combine results from first-principles calculations (this is the case, for example, for electron elastic scattering or photon Compton scattering), semi-empirical models (in electron inelastic scattering), and information from evaluated databases. The scattering models implemented in the code, together with the simulation algorithm, have been described in detail elsewhere (Baró et al. 1995; Sempau et al. 1997). PENELOPE also includes a package for simulation of complex geometries consisting of homogeneous bodies limited by quadric surfaces. The complete code system (FORTRAN source files and database) is available from the NEA[1] data bank.

VALIDATION OF THE MONTE CARLO SIMULATION ALGORITHM

The reliability of MC simulation largely depends on the accuracy of the underlying scattering model adopted to describe the interactions of electrons and photons with matter. Therefore, it is important to assess the adequacy of a MC code to the particular application of interest.

Recently, it was shown that the MC algorithm of Acosta et al. (1998) correctly reproduces "apparent" *k*-ratio profiles in selected metal couples near phase boundaries (Valovirta et al. 2001). For example, Figure 1 illustrates simulated and measured *k*-ratio profiles for an Fe-Cu couple as a function of the distance from the electron beam to the interface. The Fe *k*-ratio in Cu (right side of Fig. 1) is caused by fluorescence from the continuum and the characteristic Cu X-rays absorbed in the Fe region, whereas the apparent Cu *k*-ratio in Fe results from fluorescence from the Fe continuum in Cu. The agreement between simulation results and measurements is fully satisfactory.

To assess further the accuracy of the MC algorithm used in this work, the EMPA measurements of Dalton and Lane (1996) were simulated. These measurements consist of "apparent" Ca profiles in olivine, as a function of the distance from the point of impact of the electron beam to the boundary, from couples consisting of olivine grains (having an increasing Fe content) with diopside, and couples of San Carlos olivine with minerals with an increasing Ca content. To calculate each theoretical spectrum, we simulated 500 000 primary electron tracks. Relative uncertainties of the simulated Ca profiles range from 8–15%. Figure 2 compares simulated and experimental apparent Ca profiles in olivine ($Fo_{99.5}$, $Fo_{90.7}$, Fo_{50}, and $Fo_{8.4}$) couples with diopside, and in San Carlos olivine ($Fo_{90.7}$) with bytownite and calcite. We can see that SF increases as analyses are taken closer to the boundary. In all the analyzed cases, the experimental data of Dalton and Lane (1996) were found to agree satisfactorily with our MC simulations.

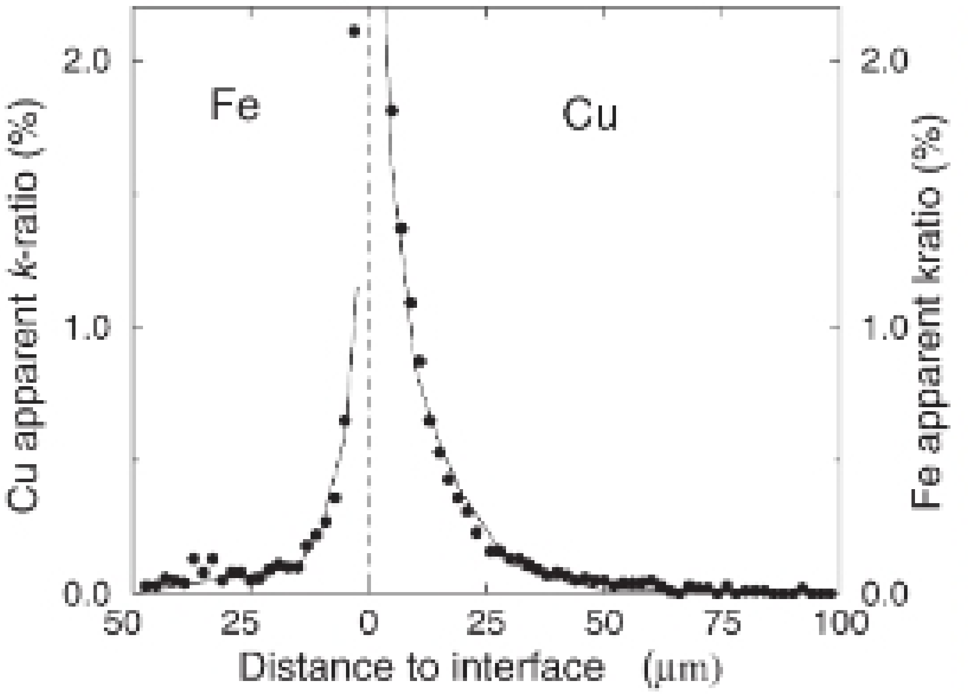

FIGURE 1. Apparent Cu and Fe *k*-ratio profiles from secondary fluorescence for an Fe-Cu couple vs. distance to interface. The Fe *k*-ratio in Cu (right-hand side of the figure) is caused by fluorescence from the continuum and the Cu$K\alpha$ X-rays absorbed in the Fe region, while the apparent Cu *k*-ratio in Fe results from fluorescence from the Fe continuum in Cu. Solid lines represent results of Monte Carlo simulations. Filled circles are measurements from Valovirta et al. (2001).

SECONDARY FLUORESCENCE CORRECTION

The secondary fluorescence correction is performed in several steps. In the first step, we analyze the mineral under consideration and the contaminant mineral with the electron microprobe. The mineral compositions furnish the input data file of the simulation program, which is run in batch mode to obtain X-ray spectra for electron beams impacting along a line perpendicular to the interface, from the interface up to a distance 100 micrometers away. In the simulations, we assume that minerals are separated by a planar interface. We also assume that the element of interest is not present in the mineral under electron bombardement. This approximation is plausible for trace elements as they do not substantially modify the stopping power of the mineral; however, this assumption makes our procedure unsuitable for the correction of other major elements.

To avoid background subtraction of simulated spectra, Bremsstrahlung photons are not counted when escaping from the surface, unless they have interacted in the medium. Therefore, although the generation and transport of Bremsstrahlung photons is simulated, X-ray emission spectra consist only of X-ray peaks, and extracting their intensities is straightforward. When each simulation is complete, we store the *k*-ratio of the element of interest and the distance of the electron beam to the boundary in a separate file. Linear interpolation is then used to calculate the *k*-ratio at the distance actually measured by EMPA, which is estimated from the measured profile along a line crossing the interface. The interpolated *k*-ratio is then subtracted from the measured *k*-ratio and matrix corrections are applied. In the simulations of Ca *k*-ratios in olivine done in this study, the relative statistical uncertainties range typically from 5–20% (2σ level).

APPLICATION TO THERMOBAROMETRY OF SPINEL LHERZOLITES

In an attempt to validate further the SF correction close to phase boundaries, we have analyzed olivine crystals in contact with clinopyroxene to estimate the *P-T* path of an ultramafic xenolith entrained by the mafic alkaline pyroclasts of the Canet d'Adri volcano (Girona, Catalonia, NE Spain). The uncertainty and deviation of corrected and uncorrected results are compared and the effect on the geological history is assessed.

Catalan mafic alkaline volcanism is Neogene-Quaternary in age and is characterized by the extrusion of basanites, leucite basanites, and alkali basalts, with minor trachytes (Tournon 1968; Araña et al. 1983; López Ruiz and Rodriguez Badiola 1985; Cebriá et al. 2000). This volcanism has been related to middle-late Alpine extensional fractures (Araña et al. 1983; Marti et al. 1992), as is the case in the central-western Euro-

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