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## **Element Depletion Due to Missing Boundary Fluorescence in Electron Probe Microanalysis: The Case of Ni in Olivine**

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#### Abstract

Secondary fluorescence (SF) is known to be a potential source of error in electron probe microanalysis (EPMA) when analyzing for a trace or minor element near a phase boundary. This often overlooked effect leads to a concentration enhancement whenever the neighboring phase contains a high concentration of the analyzed element. Here we show that SF may also lead to a concentration decrease, which can be mistakenly interpreted as a depletion. To examine this issue, we compare Ni profiles measured on well-characterized, homogeneous olivine [(Mg,Fe)<sub>2</sub>SiO<sub>4</sub>] grains embedded in basaltic glass, with semi-analytical calculations and numerical simulations of SF across phase boundaries. We find that the Ni content consistently decreases with decreasing distance to the interface or grain radius, deviating from the expected concentration by  $\sim 2-5\%$  at  $10 \,\mu$ m from the interface. This decrease is explained by the lower bremsstrahlung fluorescence emitted from the sample as compared to that emitted from the standard. The analytical error due to boundary fluorescence affecting other elements of petrologic importance in olivine is discussed.

Key words: electron probe microanalysis, nickel, olivine, secondary fluorescence, trace analysis

#### Introduction

The use of electron probe microanalysis (EPMA) for the analysis of trace and minor elements in rock-forming minerals has increased over the years owing to the improved stability of electron-beam columns operated at high-beam currents and of the development of new crystal analyzers with larger areas (Llovet et al., 2021). Although trace and minor elements have been measured by EPMA from the early days of the technique (e.g., Smith & Stenstrom, 1965), the mentioned advances have made it possible to routinely achieve detection limits of a few parts per million at relatively acceptable precisions and micrometer spatial resolution. This makes the technique attractive to decipher petrological questions that require trace and minor element data from minerals such as olivine [(Mg,Fe)<sub>2</sub> SiO<sub>4</sub>] (Sobolev et al., 2005, 2007; Batanova et al., 2015, Gavrilenko et al., 2016a, 2016b; Gómez-Ulla et al., 2017; Su et al., 2019; Goltz et al., 2020; Wang et al., 2021; Jiang et al., 2022; Zhang et al., 2023). However, the accuracy of EPMA analysis worsens at low concentration levels as sources of systematic uncertainty are magnified (Robinson et al., 1998; Jercinovic & Williams, 2005). The accuracy of measured concentrations can be assessed by using suitable reference samples (Batanova et al., 2019; Jiang et al., 2022) or by comparing with the results of other measurement methods (Batanova et al., 2015). However, some systematic uncertainties may require a more detailed examination for a proper evaluation of data quality (Wieser et al., 2023).

One such systematic uncertainty is the effect of secondary fluorescence (SF) from adjacent phases (Reed & Long, 1963). Although the electron range is typically of the order of a few  $\mu$ m, characteristic and bremsstrahlung X-rays emitted

from interactions of primary electrons can reach distances much larger than the electron range and can produce SF through photoabsorption in a sample region far away from the electron point of impact. This may lead to an overestimation of measured concentrations, as matrix corrections assume that the sample is chemically homogeneous, especially when analyzing for a minor or trace element in a phase coexisting with another phase that contains a high abundance of the element of interest. Secondary fluorescence can therefore compromise the interpretation of concentration gradients close to grain boundaries with large concentration contrasts or the analysis of fine-grained, run products typically obtained in experimental petrology.

The effect of SF across phase boundaries has been known for decades. One of the first studies pointing out this effect was by Agrell et al. (1963), who were interested in determining the Ni contents of kamacite adjacent to taenite (both kamacite and taenite are Fe-Ni solid solutions present in iron meteorites). Since then, the potential analytical errors due to SF in the analysis of rock-forming minerals have been widely discussed in the literature (Reed & Long, 1963; Feenstra & Engi, 1998; Llovet & Galán, 2003; Fournelle et al., 2005; Jercinovic et al., 2008; Wade & Wood, 2012; Jennings et al., 2019; Llovet et al., 2020; Gavrilenko et al., 2023). Yet, the incorporation of SF corrections into matrix correction procedures has remained elusive, mainly because it not only depends on the compositions at both sides of the boundary and on the distance to the boundary but also on the boundary geometry, which is usually poorly known.

In contrast with other systematic uncertainties, those introduced by SF can be quantified and corrected. Experimentally,

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the contribution from SF can be estimated by preparing coldpressed couples of the two involved materials, after they have been ground and polished in order to obtain a sharp interface, and measuring line profiles across the boundary (Dils et al., 1963; Reed & Long, 1963; Duke & Brett, 1965; Bastin et al., 1983; Dalton & Lane, 1996; Borisova et al., 2018). The apparent concentration due to SF can also be calculated theoretically (Maurice et al., 1966; Hénoc et al., 1969; Bastin et al., 1983; Llovet et al., 2012). The simplest approach to calculating SF is to assume that the sample consists of two semi-infinite half-spaces separated by a plane boundary perpendicular to the sample surface (undiffused couple), and solve the equations that give the X-ray fluorescence intensity as a function of the distance to the interface. These kinds of calculations can be currently performed using the computer code FANAL (Llovet et al., 2012). Note that even for an undiffused couple geometry, solving these equations requires numerical integration.

The experimental or theoretical SF data obtained for undiffused couples can be used to correct for SF effects on large crystals, but its application to fine-grain minerals is limited (D'Souza et al., 2020). Measurements of SF on wellcharacterized mineral grains are rare (Gavrilenko et al., 2023). In this case, SF can be calculated by using the Monte Carlo simulation method (Llovet & Salvat, 2017; Ritchie, 2017), which allows the simulation of more realistic sample geometries such as inclusions (Llovet et al., 2020) or lamellae structures (Gopon et al., 2022). The main drawback of the Monte Carlo method is that it requires long computing times, and therefore it is not suitable for online correction; however, it provides a convenient basis to check the quality of EPMA data (Llovet et al., 2000) and/or to obtain parameterizations better suited for practical purposes (Gavrilenko et al., 2023).

It has been suggested that errors due to SF may also arise from calibrating in a large standard compared to analyzing small sample micro-volumes (Fournelle et al., 2005; Llovet et al., 2020), but as yet, this possibility has not been explored. The aim of this study is to assess quantitatively this potential source of analytical error. To this end, we rely on the experimental data reported by Gavrilenko et al. (2023). These authors made systematic EPMA measurements on a large number of olivine grains of different compositions embedded in basaltic glass. We focus on Ni, mainly because it is an element of key petrogenetic interest (Koshlyakova et al., 2022), with concentrations in the range  $\sim 0.3-0.4$  wt% NiO in the considered olivine samples, and is not expected to be enhanced by SF owing to the much lower Ni abundance in the adjacent glass. Nickel concentration profiles measured by Gavrilenko et al. (2023), as well as additional measurements performed on smaller crystals, are compared to detailed semi-analytical SF calculations using FANAL and numerical simulations using the Monte Carlo simulation program PENEPMA (Llovet & Salvat, 2017). Comparison of calculated and measured concentration profiles for Al, Ti, and Ca are used as means to assess the reliability of calculations.

#### **Materials and Methods**

## Sample Preparation and EPMA Measurements

This study relies mainly on the EPMA data reported in our previous study (Gavrilenko et al., 2023). The details of the EPMA measurements, which follow the procedures described

 Table 1. Olivine Compositions that Were Used for Secondary

 Fluorescence Calculations (in wt.%).

Oxide (wt%)	MongOl Sh11-2 <sup>a</sup>	XEN <sup>b</sup>
Na <sub>2</sub> O	0.0174(13)	_
$Al_2O_3$	0.046(3)	0.009(2)
CoO	0.0188(5)	-
ZnO	0.0070(2)	-
$P_2O_5$	0.0152(17)	-
CaO	0.096(5)	0.036(2)
TiO <sub>2</sub>	0.0067(4)	0.0016(8)
NiO	0.359(4)	0.387(6)
MnO	0.1445(19)	0.131(2)
$Cr_2O_3$	0.0182(4)	0.0055(17)
MgO	48.79(9)	49.6(5)
FeO	10.17(2)	9.07(14)
SiO <sub>2</sub>	40.7(3)	40.9(3)
Total	100.39	100.14

Uncertainties  $(2\sigma)$  in the least significant figure(s) are given in parentheses, thus 0.0174(13) should be read as  $0.0174 \pm 0.0013$ . <sup>a</sup>From Batanova et al. (2019).

<sup>b</sup>From Gavrilenko et al. (2023).

by Sobolev et al. (2007) and Batanova et al. (2015), are reported in Gavrilenko et al. (2023). The samples consisted of fragments of MongOl Sh11-2 olivine (Batanova et al., 2019) embedded in 08-430 glass (A.V. Sobolev's collection) (samples SF10 and SF22), MongOl Sh11-2 olivine embedded in BCR-2 glass (Basalt Columbia River reference material, see, e.g., Raczek et al., 2001; Jochum et al., 2016) (sample SF9), XEN olivine (Batanova et al., 2015) embedded in 08-430 glass (sample SF12) and XEN olivine embedded in BCR-2 glass (sample SF11). A detailed description of the sample preparation process is given in Gavrilenko et al. (2023). Briefly, crushed pieces of the considered olivine along with basalt powder were mixed with weak polyvinyl alcohol-water glue, suspended on Pt loops, heated at 1230-1250°C for 3-30 min, and guenched. The run products were mounted in epoxy resin and polished for EPMA analysis. The olivine and glass compositions of the selected samples are tabulated in Tables 1 and 2.

Additional olivine fragments were analyzed for Al, Ti, Ca, and Ni on one of the samples (SF-22) using a IEOL IXA-8230 electron microprobe at the University of Barcelona. Analyses were conducted in WDS mode using the same analytical conditions as those used by Gavrilenko et al. (2023), namely an accelerating voltage of 20 kV, a beam current of 500 nA and a 1-µm focused spot size. Standards were natural and synthetic minerals and oxides. Counting times were 200 s peak and 100 s background. Aluminum was simultaneously measured on two spectrometers. The ZAF correction procedure implemented in the JEOL software was applied to convert measured X-ray intensity ratios into concentration, with Si, Mg, Mn, and Fe nominal concentrations being adopted in the reduction process. To assess potential defocusing effects affecting X-rays emitted away from the spectrometer focal, beam scan X-ray maps were collected on homogeneous standards of Al, Ti, Ca, and Ni (see Supplementary Material).

#### **Calculation Methods**

#### Semi-analytical Calculations with FANAL

FANAL is a computer code for the fast calculation of the k-ratio emitted from a sample consisting of two materials, A

Table 2. Glass Compositions that Were Used for Secondary Fluorescence Calculations (in wt.%).

Oxide (wt%)	08-430	BCR-2
Na <sub>2</sub> O	1.79(11)	3.0(3)
K <sub>2</sub> O	0.05(2)	1.6(3)
Al <sub>2</sub> O <sub>3</sub>	15.0(5)	12.1(12)
$P_2O_5$	0.06(3)	0.31(5)
CaO	12.8(5)	6.3(7)
TiO <sub>2</sub>	0.87(5)	2.2(3)
NiO	0.02(4)	0.01(4)
Cr <sub>2</sub> O <sub>3</sub>	0.07(2)	0.01(2)
MnO	0.18(5)	0.22(5)
MgO	10.2(9)	7(3)
FeO	9.9(6)	13.0(14)
SiO <sub>2</sub>	47.9(6)	52.4(18)
Total	98.74	98.05

Uncertainties  $(2\sigma)$  in the least significant figure(s) are given in parentheses, thus 1.79(11) should be read as 1.79  $\pm$  011.

and B, separated by a plane interface perpendicular to the surface (Llovet et al., 2012). Primary characteristic photons of energy  $E_1$  as well as bremsstrahlung (continuum) photons from material A may induce emission of fluorescent photons of energy  $E_2$  from both materials A and B. A simplifying assumption is made that the detected SF X-rays travel only through the material where they are produced, which means that the detector is located over the fluorescing phase. FANAL reports the k-ratio for a given active element and X-ray line, distance of the electron beam to the interface, incident electron energy, and take-off angle.

The k-ratio for a characteristic line of element  $Z_a$  composing the A–B couple, identified by the photon energy  $E_2$ , is given by

$$k = \frac{I_{\rm A}^{\rm det}(E_2) + J_{\rm AB}^{\rm det}(d; E_2)}{I_{\rm S}^{\rm det}(E_2) + J_{\rm S}^{\rm det}(E_2)},\tag{1}$$

where  $I_A^{det}(E_2)$  is the primary fluorescence intensity (photons originated by electron impact) of the measured line on material A and  $J_{AB}^{det}(d; E_2)$  is the SF intensity (photons originated by the interaction of primary characteristic X-rays and bremsstrahlung) of the measured line on the A–B couple when the electron beam impacts on material A at a distance *d* from the interface.  $I_S^{det}(E_2)$  and  $J_S^{det}(E_2)$  are the primary and SF intensities, respectively, of the same line measured on a bulk standard S.

For a bulk sample of material A,  $J_{AB}^{det}(d; E_2)$  reduces to  $J_A^{det}(E_2)$ , and then k in equation (1) is the conventional k-ratio (Reed, 1993). In the case of measurements on a couple A–B such that the active element  $Z_a$  is present only in material B,  $I_A^{det}(E_2) = 0$  and k can be interpreted as the apparent k-ratio of element  $Z_a$  in material A due to fluorescence from material B.

Below we summarize the semi-analytical expressions implemented in the computer code FANAL to calculate the k-ratio [equation (1)]. A detailed deduction of these expressions is given elsewhere (Llovet et al., 2012).

The primary fluorescence  $I_A^{det}(E_2)$  [equation (1)] is given by

$$I_{\rm A}^{\rm det}(E_2) = I_{\rm A}(E_0, E_2) \\ \times \left( \frac{\alpha(\rho/a\gamma)}{\mu_{\rm A}(E_2) \sec\theta_{\rm d} + \rho/a\gamma} + \frac{(1-\alpha)(\rho/a\gamma)^2}{\left[\mu_{\rm A}(E_2) \sec\theta_{\rm d} + \rho/a\gamma\right]^2} \right),$$
(2)

where

$$I_{A}(E_{0}, E_{2}) = a_{1}(E_{0} - E_{i}^{\text{ion}}) + a_{2}(E_{0} - E_{i}^{\text{ion}})^{2} + a_{3}(E_{0} - E_{i}^{\text{ion}})^{3}$$
(3)

is the intensity of primary characteristic X-rays, with  $E_i^{\text{ion}}$  and  $E_0$  being the ionization energy of the active atomic subshell and the incident electron energy, respectively, and  $a_i$  are fitting parameters that depend on the X-ray line energy  $E_2$ .  $(\pi/2 - \theta_d)$ is the take-off angle, and  $\mu_A(E)$  is the attenuation coefficient of photons of energy E in material A. The parameters  $\gamma$  and  $\alpha$  are given by

$$\gamma = (E_0/\text{keV})^{1.65} - (E_i^{\text{ion}}/\text{keV})^{1.65}, \qquad (4)$$

$$\alpha = 0.18 - \frac{2}{\gamma} + 0.008(E_i^{\text{ion}}/\text{keV}) + 0.005\sqrt{Z_{\text{av}}}, \qquad (5)$$

where  $Z_{av}$  is the average atomic number of the material (mass fraction average). Equation (2) is also used to obtain the primary fluorescence on the standard S,  $I_{S}^{det}(E_2)$  (by replacing A by S).

The SF intensity  $J_{AB}^{det}(d; E_2)$  [equation (1)] is given by

$$J_{AB}^{det}(d; E_2) = J_{ch}^{L}(E_2) + J_{ch}^{R}(E_2) + J_{br}^{L}(E_2) + J_{br}^{R}(E_2),$$
(6)

where

$$J_{\rm ch}^{\rm L,R}(E_2) = \sum_j J^{\rm L,R}(E_j, E_2) \quad (E_j > E_2)$$
(7)

and

$$J_{\rm br}^{\rm L,R}(E_2) = J_{E_2}^{E_0} J^{\rm L,R}(E_1, E_2) \frac{dI_{\rm br,A}(E_0)}{dE_1} dE_1$$
(8)

are the contributions from primary characteristic photons and bremsstrahlung quanta, respectively. The terms  $J^{L}(E_1, E_2)$  and  $J^{R}(E_1, E_2)$  are given by

$$J^{L}(E_{1}, E_{2}) = I_{A}(E_{0}, E_{1})F_{A}(E_{1}, E_{2})2\pi \frac{\cos\theta_{d}}{\mu_{A}(E_{2})}$$

$$\times \ln\left(1 + \frac{\mu_{A}(E_{2}) \sec\theta_{d}}{\mu_{A}(E_{1})}\right) - I_{A}(E_{0}, E_{1})F_{A}(E_{1}, E_{2})$$

$$\times \int_{\pi/2}^{\pi} d\theta \frac{\sin\theta}{\mu_{A}(E_{1}) - \mu_{A}(E_{2})\cos\theta \sec\theta_{d}}$$

$$\times G\left(d \frac{\mu_{A}(E_{1}) - \mu_{A}(E_{2})\cos\theta \sec\theta_{d}}{\sin\theta}\right)$$

and

$$J^{R}(E_{1}, E_{2}) = I_{A}(E_{0}, E_{1})F_{B}(E_{1}, E_{2})$$

$$\times \int_{0}^{\pi/2} d\theta \frac{\sin \theta}{\mu_{B}(E_{1}) + \mu_{B}(E_{2})\cos\theta \sec\theta_{d}}$$

$$\times G\left(d\frac{\mu_{A}(E_{1}) + \mu_{B}(E_{2})\cos\theta \sec\theta_{d}}{\sin\theta}\right), \quad (10)$$

respectively, where  $\mu_{\rm B}(E)$  is the attenuation coefficient of photons of energy E in material B,

$$G(x) = \int_0^\pi \exp\left(-\frac{x}{\sin\phi}\right) d\phi \tag{11}$$

and

In equation (12),  $P_{j,2}$  is the probability that the vacancy in the *j*-th shell migrates to an outer subshell by emission of a photon of energy  $E_2$ , and  $V_A$  is the number of vacancies produced per unit path length of a primary photon of energy  $E_1$  penetrating material A and generating characteristic X-rays of energy  $E_2$ , from transitions that fill a vacancy in the shell *j* of element  $Z_b$  (Llovet et al., 2012). Equation (12) is also used to calculate  $F_B$  (by replacing A by B). The intensity of bremsstrahlung photons needed in equation (8) is expressed as

$$\frac{dI_{br,A}(E_0, E_1)}{dE_1} = Z_{av} \frac{(E_0 - E_1)}{E_1} \times \left[ (b_0 + d_0 E_0) + (b_1 + d_1 E_0) \left(\frac{E_1}{E_0}\right) + (b_2 + d_2 E_0) \left(\frac{E_1}{E_0}\right)^2 \right], \quad (13)$$

where  $b_i$  and  $d_i$  are fitting parameters. All the physical quantities involved in equations (2)–(13) are extracted from the PENELOPE database (Salvat, 2019), with the exception of parameters  $a_i$  [equation (3)] and  $b_i$  and  $d_i$  [equation (13)], which are determined by least-square fittings to precalculated Monte Carlo simulations for the specific materials A, B, and S. Once the abovementioned parameters have been precalculated, FANAL reports the *k*-ratios in a few seconds.

*K*-ratios were calculated using FANAL for beams impacting on olivine for the olivine–glass couples listed in Tables 1 and 2, and for electron beam distances to the boundary from 1 to  $500 \,\mu$ m.

#### Monte Carlo Simulation with PENEPMA

PENEPMA is a computer code that performs Monte Carlo simulation of EPMA measurements (Llovet & Salvat, 2017). The method of Monte Carlo consists of the numerical generation of electron trajectories in the sample; quantities of interest are obtained as the average of contributions from a large number of trajectories. Each trajectory is viewed as a sequence of free flights where the electron changes its direction, loses energy, and may generate secondary radiations (electrons and photons). The term Monte Carlo arises from the use of random numbers to select a particular value of the angle and energy loss (or any other variable) at each interaction event. Due to the statistical nature of the method, simulation results are affected by statistical uncertainties, which can essentially be reduced by increasing the simulation time.

PENEPMA uses the Monte Carlo simulation subroutine package PENELOPE (Salvat, 2019), which covers the energy range 50 eV–1 GeV and can simulate targets consisting of homogeneous bodies limited by quadric surfaces. Electron trajectories are simulated by using a mixed simulation algorithm, which combines detailed and condensed simulation methods. Photon trajectories are simulated in detail. Simulations can be further optimized by forcing the interaction mechanisms using several variance-reduction techniques. To set up a simulation, the user must specify the parameters that characterize their EPMA experiment (e.g., electron beam energy, sample composition and geometry, electron beam point of impact, detector aperture and take-off angle, simulation time or precision, etc.), as well as the simulation and forcing parameters.

For a target formed by two materials A and B (e.g., a hemisphere A embedded in a matrix B or a couple A–B), PENEPMA provides the intensity (in absolute units) and statistical uncertainty (at  $3\sigma$  level) of all emitted X-ray lines, splitted in different contributions, namely the primary fluorescence intensity,  $I_{AB}^{det}(E_2)$ , the SF originated by primary characteristic X-rays,  $J_{AB,ch}^{det}(E_2)$ , and the SF intensity originated by bremsstrahlung,  $J_{AB, br}^{det}(E_2)$ . Noting that

$$J_{AB}^{det}(E_2) = J_{AB,ch}^{det}(E_2) + J_{AB,br}^{det}(E_2)$$
(14)

and that  $I_{AB}^{det}(E_2) = I_A^{det}(E_2)$  for a beam impacting on material A far away from material B, the information yielded by PENEPMA can be readily used to calculate the *k*-ratio [equation (1)]. Simulations of SF near the interface of two materials are demanding and it is highly recommended to benefit from the application of variance-reduction techniques.

Simulations with PENEPMA were performed for olivine hemispheres with radii from 4 to 100  $\mu$ m embedded in basaltic glass. Different olivine/glass compositions were simulated (Tables 1 and 2). Simulations were performed for 20-keV electron beams impacting both on the center of the hemispheres as well as along traverses from rim to rim. Simulations were also performed for pure, bulk specimens of the considered fluorescing elements. The simulation and forcing parameters used in this work are the same as those reported in Llovet et al. (2020). Annular detectors that cover an angular aperture of 10° around a direction of 40° relative to the sample surface were used to increase the simulation efficiency. We note that the use of an annular detector is justified whenever there is axial symmetry about the electron beam axis (e.g., in simulations performed on the center of a hemisphere).

The Fortran source files of PENEPMA and FANAL are available from their authors upon request. To simplify their execution and visualization of results, the software suite CALCZAF (Donovan et al., 2020) implements a Windows graphical user interface for PENEPMA and FANAL.

#### Converting k-Ratios into Concentrations

In EPMA, the concentration *c* of a given element is obtained from  $k = c \times ZAF$ , where ZAF is the matrix correction factor (Reed, 1993). To allow comparison of calculated *k*-ratios with measured concentrations, the ZAF factors were obtained as ZAF =  $k_{\infty}/c$  where  $k_{\infty}$  is the *k*-ratio calculated by FANAL or PENEPMA for a bulk sample of the considered material. The differences between the ZAF factors obtained in this way with those obtained using a conventional ZAF model [e.g., the Armstrong/Love-Scott phi-rho-z model, which is the default model implemented in CALCZAF (Donovan et al., 2020)] were found to be ~3% for Ca, ~2% for Ti, ~1% for Ni, and ~6% for Al.

#### **Results and Discussion**

When comparing WDS measurements with FANAL calculations and PENEPMA simulations, the following should be borne in mind. Both FANAL and PENEPMA assume that all X-rays emerging in the direction of the spectrometer are recorded, regardless of the position from where they are emitted. However, SF X-rays originating at larger distances from the electron beam may actually not be detected by a WDS spectrometer because of their displacement relative to the focal point of the spectrometer (Kronz et al., 2012; Buse et al., 2018). To assess the error made in neglecting defocusing effects, X-ray maps scanned on homogeneous materials containing the elements of interest were obtained, and the maximum intensity drop for each element was extracted (see Supplementary Material). The maximum intensity drop, suitably normalized to 1, was used to estimate the uncertainty band arising for not accounting for spectrometer defocusing in the calculations (see below).

On the other hand, because of the much higher range of primary X-rays, absorption of fluorescent X-rays within the sample may be sensitive to the relative position of the X-ray spectrometer (Fournelle et al., 2005; Llovet & Salvat, 2017). As discussed earlier, FANAL assumes that the detected SF X-rays travel only through the glass phase. To assess the error made in assuming this detector configuration, simulations with PENEPMA were performed for an undiffused MongOI Sh11-2 olivine/BCR-2 glass couple using two semi-annular detectors, one of them facing towards the olivine side of the couple and a second facing towards the glass side of the couple. The differences between the resulting profiles, which are mainly caused by the different absorption of SF X-rays in olivine and in glass, were less than ~0.5% for Ca and Ti and therefore they were disregarded.

#### Comparison of Experimental Profiles with Calculations

Figures 1–4 compare measured and calculated Al, Ca, Ti, and Ni concentrations (in wt% oxide) as a function of distance to the interface, for a series of core-to-rim traverses in olivine grains that ranged from 200 to 300  $\mu$ m in diameter. The grain diameter was obtained by fitting a circle to the grain boundary. The location of the step traverses is depicted in Figures 1e–4e. The plotted uncertainty bars represent the relative standard deviations (counting statistical uncertainties) of the EPMA analyses at 2 $\sigma$  level, which were typically ~2.8% for Al, ~0.8% for Ca, ~7.7% for TiO<sub>2</sub>, and 0.6% for Ni. Because the penetration range of 20 keV electrons in olivine is ~2.5  $\mu$ m, analyses collected at less than 5  $\mu$ m from the interface were disregarded in order to avoid characteristic X-rays arising from direct electron impact in the glass.

Measured Ti and Ca concentrations progressively increase in a line profile towards the adjacent phase (glass), thus they can be mistaken for diffusion profiles. The nominal Ti and Ca concentrations (represented by red dashed lines) are recovered at ~80–100  $\mu$ m from the interface; above this distance, the effect of SF can be safely neglected. The concentration increase depends not only on the distance to the boundary but also on the composition of olivine and glass, being larger when the abundance of the analyzed element is higher in the glass. For instance, at  $10 \,\mu m$  from the boundary, the Ca content in MongOl Sh11-2 olivine adjacent to BCR-2 glass (6.34 wt% CaO) is ~20% higher than its nominal value, while the increase amounts to ~28% in MongOl Sh11-2 olivine adjacent to 08-430 glass (12.75 wt% CaO). In the case of Ti, the concentration enhancement is ~180% at 10  $\mu$ m from the interface in MongOl Sh11-2 olivine adjacent to BCR-2 glass  $(2.15 \text{ wt}\% \text{ TiO}_2)$ , reducing to ~58% when the adjacent glass is 08-340 (0.87 wt% TiO<sub>2</sub>). For Al, the enhancement due to SF is almost negligible at a distance farther than  $\sim 20 \,\mu m$  from the interface, increasing rapidly very close to the boundary. Nevertheless, at 10 µm from the interface, the measured/calculated Al<sub>2</sub>O<sub>3</sub> content in MongOl Sh11-2 olivine adjacent to both BCR-2 and 08-430 glasses is only ~2% higher than its nominal value.

The uncertainty band for not including defocusing effects in the calculations is plotted for Al, Ca, and Ti in Figure 1 (see Supplementary Material). For Ca and Ti, the uncertainty band is less than 1% at all distances (see insets in Figs. 1b and 1c). For Al, the uncertainty is very small and is hardly visible on the plot. Because the Ni content in glass is very low (i.e., one order of magnitude lower than in olivine), no Ni enhancement due to SF from the adjacent phase is expected and thus spectrometer defocusing will only affect the continuum fluorescence intensity (Ni fluorescence by Zn Ka X-rays can also be neglected due to the very low Zn content in olivine). However, as defocusing will affect similarly the continuum X-ray intensities emitted from sample and standard, the Ni concentration will remain unaffected by defocusing effects. The uncertainty bands corresponding to the cases shown in Figures 2-5 are similar to those shown in Figure 1 and they have not been included in the figures for the sake of simplicity.

In general, measured Ca, Al, and Ti concentrations are in good agreement with calculated concentrations, within the experimental uncertainties. In some cases, however, discrepancies between calculations and measurements are observed. For example, the measured CaO profile for the MongOl Sh11-2/08-430 olivine-glass pair (Fig. 2b) lies systematically above the calculated concentrations, but because the dispersion of the experimental data largely exceeds that predicted by the statistical uncertainties, this discrepancy can be reasonably ascribed to some measurement issue, most probably to some surface uncleanliness. We note here error bars in Figure 2b are smaller than the size of the symbols. In the case of the XEN olivine/08-430 glass pair (Fig. 4), measured profiles show a bump at  $\sim$ 35  $\mu$ m from the interface, which appears to be wider for Al. The origin of this bump is unknown, but it very likely arises from some sample issue (e.g., hole) not exposed at the sample surface.

The behavior of Ni is completely different. For the four olivine–glass pairs considered, the experimental Ni profiles progressively decrease as we approach the boundary (Figs. 1d–4d), reaching values that are ~2% lower than the nominal concentrations at 10  $\mu$ m from the interface. Measured and calculated concentrations are in accord with the nominal concentrations at distances larger than ~100  $\mu$ m from the interface. It should be pointed out that the Ni contents measured in these glasses range from 0.01 to 0.02 wt% NiO. This concentration range is one order of magnitude smaller than that of the olivine grains (0.359–0.387 wt% NiO), thus no SF contribution from the glass phase is expected.

The observed Ni decrease is confirmed unambiguously by the calculations. The good agreement between measured and calculated Ni profiles, along with the progressive decrease towards the interface, allows ruling out other possible sources of systematic uncertainty as responsible for the Ni drop. Namely background subtraction errors, interferences from other elements, beam damage, carbon contamination, or holes in the spectral background, which become important for trace element analysis (Robinson et al., 1998; Jercinovic et al., 2008). It also rules out the possibility that the studied olivine grains are not homogeneous. The observed Ni profiles are consistent with those corresponding to homogeneous olivine grains where SF due to bremsstrahlung (continuum) emission contributes more substantially to the standard emission because the longrange fluorescing volume reduces significantly near a boundary.

Consequently, SF will not only worsen the accuracy of measured concentrations but it will also affect the precision



**Fig. 1.** Comparison of measured and calculated Al (a), Ca (b), Ti (c), and Ni (d) concentrations along a transect from the BCR-2 glass boundary into a MongOI Sh11-2 olivine grain. Dashed horizontal lines represent nominal element concentrations. Symbols are EPMA measurements (sample SF9; Ol4) from Gavrilenko et al. (2023). Solid lines are calculations done with FANAL. The inset in (b) and (c) is a zoom for distances above 20  $\mu$ m. Error bars represent two-standard-deviation statistical uncertainties of the EPMA measurements. (e) BSE image showing the olivine grain and location of the traverse. MongOI Sh11-2 is abbreviated as MongOI.

of the analyses when obtained from repeat measurements. For example, the relative precision from counting statistics ( $2\sigma$ ) for the individual analyses shown in Figures 1d–4d ranged from ~0.5 to 0.6% for Ni (note that error bars added to the measurements only represent the precision component of the error budget). However, the relative standard deviation ( $2\sigma$ ) from replicated analyses amounts to ~1.5–2.8%. Thus, whenever the Ni profiles are corrected for SF effects, the accuracy and precision of the analyses will both improve.

It should be noted that although the contribution from the bremsstrahlung fluorescence to the total X-ray intensity can be quite significant (for instance, it amounts up to 6.7% in the case of bulk MongOl Sh11-2 olivine, according to the FANAL calculations), it is usually disregarded in the ZAF correction. The reason is that the contributions from sample and standard are assumed to be similar and thus they cancel out when forming the *k*-ratio. Indeed, the JEOL software reported a value of F = 1.000 for Ni, where *F* represents the fluorescence correction factor in the ZAF model.

Concentration profiles for Al, Ca, Ti, and Ni, measured along a line crossing a small XEN olivine grain of  $14.5 \,\mu\text{m}$  in radius embedded in BCR-2 glass are compared with calculated



Fig. 2. Comparison of measured and calculated Al (a), Ca (b), Ti (c), and Ni (d) concentrations across a MongOl Sh11-2 olivine grain adjacent to 08-430 glass. Dashed horizontal lines represent nominal concentrations of the considered elements. Symbols are EPMA measurements (sample SF10; Ol4) from Gavrilenko et al. (2023). Solid lines are calculations done with FANAL. Error bars represent two-standard-deviation statistical uncertainties of the EPMA measurements. BSE image showing the olivine grain and location of the traverse (e). MongOl Sh11-2 is abbreviated as MongOl.

concentrations in Figure 5. The location of the traverse is plotted in Figure 5e. Because of the small grain size, concentration profiles cannot be accurately calculated with FANAL and therefore they were simulated using PENEPMA, assuming a hemisphere geometry for the olivine grain. The statistical uncertainties of simulation results were less than 0.5% for Ca, Ti, and Ni, and ~5% for Al. Error bars in the simulation results indicate two-standard-deviation statistical uncertainties. We note here that, despite the lack of axial symmetry about the electron beam axis in these simulations, the differences between the concentrations obtained using an annular detector from those using

detectors placed at various azimuthal angles were less than 0.6%.

Measured and calculated concentrations at the grain center overestimate the nominal concentration values by ~52% (Ca), ~94% (Ti), and ~16% (Al). This overestimation is much larger than that observed at the same distance for the larger XEN olivine crystal adjacent to BCR-2 glass (Fig. 3), which amounts to ~29% (Ca), ~86% (Ti), and ~5% (Al). This is because SF emitted from beneath a small grain is more likely to be detected than from a much larger grain, as the emission is closer to the surface for the former. In the case of Ni, measured



Fig. 3. Comparison of measured and calculated AI (a), Ca (b), Ti (c), and Ni (d) concentrations across a XEN olivine grain adjacent to BCR-2 glass. Dashed horizontal lines represent nominal concentrations of the considered elements. Symbols are EPMA measurements (sample SF11; OI3) from Gavrilenko et al. (2023). Solid lines are calculations done with FANAL. Error bars represent two-standard-deviation statistical uncertainties of the EPMA measurements. (e) BSE image showing the olivine grain and location of the traverse.

concentrations lie systematically below the expected value, with differences that are also larger ( $\sim 5\%$  at the grain center) than those observed for the larger XEN olivine grain adjacent to the BCR-2 glass of Figure 3d ( $\sim 2\%$  at the same distance). Thus, the Ni drop will be underestimated by a factor of 2 if we assume an undiffused couple geometry in order to correct it.

For the small XEN olivine grain of Figure 5, measured and calculated Al, Ca, and Ti concentrations agree satisfactorily with each other; for Ni, measured values are slightly higher than the values predicted by PENEPMA. The reason for this

small discrepancy is unknown. The Ca, Ti, and Al concentrations slightly increase when analyses are performed near the glass boundary. This increase is not likely due to the electron interaction volume crossing the interface as the primary fluorescence intensities (e.g., those arising only from electron impact) reported by PENEPMA agree with each other within 0.1% for all the displayed points. A slight decrease in the Ni contents is observed near the boundary, also not due to the electron interaction volume crossing the boundary.

Concentration profiles for Al, Ca, Ti, and Ni measured and calculated at the center of MongOl Sh11-2 olivine grains





Fig. 4. Comparison of measured and calculated AI (a), Ca (b), Ti (c), and Ni (d) concentrations across a XEN olivine grain adjacent to 08-430 glass. Dashed horizontal lines represent nominal concentrations of the considered elements. Symbols are EPMA measurements (sample SF12; Ol4) from Gavrilenko et al. (2023). Solid lines are calculations done with FANAL. Error bars represent two-standard-deviation statistical uncertainties of the EPMA measurements. (e) BSE image showing the olivine grain and location of the traverse.

embedded in 08-430 glass, as a function of grain radius, are displayed in Figure 6. The grains display polygonal outlines with round shapes and are relatively small  $(10-20 \,\mu\text{m}$  in radius). Because of this, concentrations were simulated with PENEPMA. The concentration profiles were also calculated using the analytical formulae developed by Gavrilenko et al. (2023). The number of data points is smaller than in previous comparisons because of the limited number of small olivine grains in the sample.

An enhancement in the Ca, Al, and Ti concentrations, with respect to the corresponding nominal values, is observed with decreasing grain size. This increase amounts up to ~84% for Ca, ~250% for Ti, and ~6% for Al, for grains of 10  $\mu$ m radius, and is a factor ~2.4 (Ca), ~3.75 (Ti), and ~1.5 (Al) larger than that observed for the larger, equivalent MongOl Sh11-2 olivine grain embedded in 08-430 of Figure 2. The drop in Ni concentration, with respect to its nominal value, ranges from ~2.7% for 60- $\mu$ m radius grains to ~5% for 10- $\mu$ m radius grains. The calculations predict that for grains 200  $\mu$ m in radius, calculated Ni concentrations correspond to the Ni nominal value. The agreement between measured and simulated Ca, Ti, Al, and Ni abundances can be considered to be



**Fig. 5.** Comparison of measured and simulated AI (**a**), Ca (**b**), Ti (**c**), and Ni (**d**) concentrations across a small XEN olivine grain (14.5 μm in radius) embedded in BCR-2 glass. Dashed horizontal lines represent nominal concentrations of the considered elements. Symbols are EPMA measurements (sample SF11; OI1) from Gavrilenko et al. (2023). Crosses joined by solid lines are simulations done with PENEPMA. Error bars represent two-standard-deviation statistical uncertainties of the EPMA measurements and simulation results. (**e**) BSE image showing the olivine grain and location of the traverse.

satisfactory, with differences being attributed mostly to the approximation, in the calculations, that grains are hemispheres (Figs. 6e–6h). The predictions of the analytical formulae developed by Gavrilenko et al. (2023) agree satisfactorily with the PENEPMA simulations. It is worth recalling that these analytical formulae are only valid for analyses performed at the center of the olivine grains; moreover, for Al, the validity of the analytical expressions is limited to olivine hemispheres with radii less than  $40 \,\mu$ m. The uncertainty band for assuming that grains are hemispheres can be assessed by simulating other

geometries such as truncated spheres or ellipsoids with different degrees of burying (Llovet et al., 2020); such analysis goes beyond the purpose of this paper.

## *Effect of Beam Energy, Olivine Composition, and Adjacent Phase on Boundary Fluorescence*

It is of interest to examine the effect of the incident electron energy on the magnitude of the boundary fluorescence effect. Figure 7a compares the Ni concentration in olivine as a



Fig. 6. Comparison of measured, simulated, and calculated AI (a), Ca (b), Ti (c), and Ni (d) concentrations measured at the center of MongOI Sh11-2 olivine grains embedded in 08-430 glass, as a function of the grain radius (sample SF22). Dashed horizontal lines represent nominal element concentrations. Symbols represent EPMA measurements. Crosses joined with solid lines are simulations done with PENEPMA. Error bars represent two-standard-deviation statistical uncertainties of both EPMA data and simulation results. Solid lines are results obtained from the analytical expressions developed by Gavrilenko et al. (2023). (e–h) BSE images showing selected olivine grains. Red crosses and red circles represent beam locations and modeled hemispheres, respectively. MongOI Sh11-2 is abbreviated as MongOI.



Fig. 7. Calculated Ni (a) and Ca (b) concentration for a MongOI Sh11-2 olivine/08-430 glass couple for different incident electron energies, as a function of distance to the interface. The calculations were done using FANAL, assuming an undiffused couple geometry. MongOI Sh11-2 is abbreviated as MongOI.

function of distance to the interface for a MongOl Sh11-2 olivine/08-430 glass couple with a straight boundary and different incident electron energies. The departure from the nominal Ni concentration decreases much faster for the lower incident electron energies. This shows that, counterintuitively, the SF contribution from bremsstrahlung emission to the standard emission decreases with increasing incident electron energy. We note that for those elements for which a concentration enhancement due to SF is observed, i.e., those elements having larger abundances in the adjacent phase relatively to the analyzed phase, the deviation of their concentrations with respect to the nominal values increases with increasing accelerating voltages. As an example, Figure 7b shows Ca profiles for the same MongOl Sh11-2 olivine/08-430 glass couple at different incident electron energies, where the highest departure from the theoretical Ca concentration is obtained for the highest beam energies. Thus, it can be concluded that the apparent element depletion due to SF near a phase boundary can be minimized by using high accelerating voltages.

To investigate the influence of SF on other elements of petrological interest in olivine, *k*-ratios emitted from MongOl Sh11-2 olivine adjacent to 08-430 glass were calculated using FANAL for different fluorescing elements and an incident electron beam of 20 keV. The calculated *k*-ratios were converted into concentrations using the same procedure detailed above.

Figure 8a shows the percentage deviation between the calculated concentrations for Na, Cr, Mn, Fe, Co, and Zn and the corresponding nominal values. The percentage deviation  $\Delta$  was obtained as

$$\Delta = \frac{c - c_{\rm t}}{c_{\rm t}} \times 100,\tag{15}$$

where *c* is the concentration obtained with FANAL and *c*<sub>t</sub> is its nominal value. The percentage deviation is positive for Cr, almost null for Mn, and negative for Fe, Co, and Zn. In the case of Na,  $\Delta$  is almost zero above 10  $\mu$ m, increasing abruptly for distances less than 10  $\mu$ m, a behavior similar to that observed for Al.

Whether the percentage deviation is negative (apparent concentration depletion) or positive (apparent concentration enhancement) for a given element depends on its relative abundance between olivine and glass: those elements whose abundances are higher in glass (Na and Cr) show an apparent concentration enhancement, while those elements whose abundances are lower in glass (Fe, Co, Zn) show an apparent depletion. Furthermore, those elements whose concentrations are similar at both sides of the interface (e.g., Mn) remain unaffected by SF effects, showing no significant deviation with respect to their nominal values. For Si, Mg, and P, the deviation is less than 0.1 % and has not been included in Figure 8a for the sake of clarity. The largest percentage deviation corresponds to Zn (~3.5% decrease at 10  $\mu$ m from the interface).

To disentangle the effect of SF from the relative abundance of the considered element at both sides of the interface, k-ratios for MongOl Sh11-2 olivine adjacent to epoxy were calculated using FANAL for a 20-keV electron beam. The percentage deviation of the Al, Ti, Mn, Fe, Ni, and Zn concentrations, with respect to their nominal values, are displayed in Figure 8b. Because epoxy does not contain any of the considered fluorescing elements, the observed deviation is negative for all of them, ranging from ~1% for Ti at  $10 \,\mu\text{m}$  from the interface to  $\sim 3.5\%$  for Zn at the same distance. The apparent depletion due to SF increases for increasing atomic number of the fluorescing element and is most significant for transition metals. For elements with atomic number less than that of Ti, the observed depletion is small and can be considered to be within the analytical error of EPMA. Here it should be noted that even for a major element such as Fe, a concentration drop of  $\sim 1.5\%$  relative is observed at 10  $\mu$ m from the interface, thus worsening the accuracy (or lateral resolution) of the technique. Because the concentration drop depends on the distance to the boundary, which is generally not reported, it may be difficult to pinpoint systematic errors in published data.

As discussed earlier, the apparent depletion due to boundary fluorescence in small grains is approximately twice that corresponding to an undiffused couple with straight boundaries, for the same distance of the electron beam to the boundary. In the example shown in Figure 8b, it will therefore range from ~2% for Ti to ~7% for Zn for olivine grains of 10  $\mu$ m in radius. Consequently, it may not be recommended to use small mineral grains (less than 100  $\mu$ m in radius) as primary calibration standards, especially for first-row transition metals.

The effect of olivine composition on the apparent Ni depletion due to boundary fluorescence is illustrated in Figure 8c, where FANAL calculations have been done for



Fig. 8. Percentage deviation of calculated concentrations from nominal values, as a function of distance to interface for the indicated elements in MongOl Sh11-2 olivine adjacent to 08-430 glass (a) MongOl Sh11-2 olivine adjacent to epoxy (b) and three hypothetical olivines with varying Fo content adjacent to 08-430 glass (c). Calculations were done using FANAL, assuming an undiffused couple geometry. MongOl Sh11-2 is abbreviated as MongOl. See text for details.

three hypothetical olivines having the same Ni content (6.00 wt% NiO) but varying forsterite (Fo) content  $[Fo = Mg/(Fe + Mg) \times 100 (in mol)]$ , in contact with 08-430 glass (Table 2). The olivine compositions are as follows: 52.51 wt% MgO, 41.49 wt% SiO<sub>2</sub>, 6.00 wt% NiO (Fo100Ni6), 44.75 wt% MgO, 9.51 wt% FeO, 39.75 wt% SiO<sub>2</sub>, 6.00 wt% NiO (Fo90Ni6), and 28.11 wt% MgO, 30.01 wt% FeO, 39.90 wt% SiO<sub>2</sub>, 6.00 wt% NiO (Fo62Ni6). The apparent Ni decrease depends inversely on Fo number, i.e., the higher the FeO contents, the less significant the Ni decrease.

Although the contribution from SF can, in general, be minimized by using L-lines instead of K-lines (Pouchou, 1996), quantification of transition metal compounds using L-lines poses numerous difficulties, which may lead to much larger uncertainties (Llovet et al., 2016). On the other hand, a widely used solution to deal with SF consists of extracting the mineral of interest and analyzing it separately, after it has been mixed with epoxy and polished (see, e.g., Hermann et al., 2005). While this procedure satisfactorily overcomes any excitation from an adjacent phase, it will not prevent the concentration drop shown in Figure 8b. Correction of this effect is expected to improve the accuracy of quantities derived from EPMA analyses of experimental run products (e.g., partition coefficients) or of diffusion profiles near phase boundaries.

#### Conclusions

We have shown that Ni concentration profiles measured by EPMA in olivine grains embedded in or adjacent to basaltic glass progressively deviate from their nominal values with decreasing distance to the glass boundary. Computer simulations that account for SF effects for olivine-glass couples and olivine hemispheres embedded in glass precisely match the experimental data, and provide evidence that the observed deviations arise from SF effects. Namely, near the olivineglass boundary, the continuum fluorescence intensity emitted by the sample is lower than that emitted by the standard, resulting in the observed concentration depletion, which is more significant for transition metals. Our results and conclusions are applicable to a broad range of EPMA applications requiring high-accuracy data near phase boundaries and/or from small grains and provide further evidence that computer programs such as FANAL or PENEPMA are valuable tools for a proper evaluation of the quality of EPMA data.

### Supplementary Material

To view supplementary material for this article, please visit https://doi.org/10.1093/micmic/ozad100.

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## **Conflict of Interest**

The authors declare that they have no competing interest.

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