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Accurate electron probe microanalysis of key petrogenetic minor and trace elements in Cr-spinel

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ABSTRACT

The trace element composition of Cr-spinel is paramount for interpreting the petrogenesis of a large group of mafic to ultramafic rocks. Although laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has proven to be very useful for the determination of trace element abundances of Cr-spinel, the characterization of Cr-spinel grains that are inhomogeneous over micrometer length scales requires the use of techniques that provide a better spatial resolution than LA-ICP-MS. In this work, we develop a protocol for the determination of trace and minor elements in Cr-spinel by electron probe microanalysis (EPMA) using the software provided by the manufacturer. The optimized analytical conditions (25 kV accelerating voltage, 900 nA beam current, 60–480 s peak counting times, aggregate spectrometer data) allowed us to achieve detection limits (3σ) in the range 4–26 ppm with relative analytical precisions (2σ) in the range 1–3 % for all analyzed elements (Ti, V, Mn, Co, Ni, and Zn), except for Sc and Ga, for which the precision was much lower (36-46 %). The developed methodology was applied to the analysis of Cr-spinel grains from the Mayarí-Baracoa Ophiolitic Belt (eastern Cuba), in correspondence with previous LA-ICP-MS analyses, which were used to assess the reliability of the EPMA results. The root mean square percentage deviation (RMS) between the EPMA and LA-ICP-MS data was in the range 4.7–22.5 % for Ti, V, Mn, Co, Ni, and Zn, while for Ga the RMS value was 32.5 %. For Sc, the RMS value was much higher (171 %), despite the low detection limit achieved (4 ppm) for this element. Our results indicate that the trace element composition of primary Cr-spinel obtained by EPMA can be readily used, except for Sc, to constrain petrogenetic information on chromitites in a reliable way.

1. Introduction

The chemical composition of Cr-spinel is extensively used as an important petrogenetic indicator in a wide suite of ultramafic to mafic rocks (e.g. Irvine, 1967; Dick and Bullen, 1984; Arai, 1992; Barnes and Roeder, 2001). Cr-spinel major and trace elements composition has also been widely employed to characterize parental magmas and primary magmatic processes of ophiolitic sequences (e.g. Arai, 1997; Melcher et al., 1997; Proenza et al., 1999; Rollinson, 2008; Marchesi et al., 2016; Chen et al., 2019; Pujol-Solà et al., 2021), large magmatic stratiform complexes (e.g. Irvine, 1975; Teigler and Eales, 1993; Schulte et al., 2012; Junge et al., 2014), and Ural-Alaskan-type intrusions (e.g. Garuti et al., 2003; Krause et al., 2007). Additionally, it has also been used as a discriminant tool for magma chemistry in volcanic rocks (e.g. Arai,

1992; Kamenetsky et al., 2001) and in provenance studies of sedimentary basins (e.g. Harstad et al., 2021; Wang et al., 2024). In the case of ophiolites, which represent fragments of ancient oceanic lithosphere that have been tectonically emplaced on land (e.g. Nicolas, 1989; Dilek and Furnes, 2011, 2014; Condie and Stern, 2023), Cr-spinel is widely present in the upper mantle section of the ophiolitic sequence, either constituting chromitites or as an accessory mineral within mantle peridotites. Contrary to most of the silicates present in the mantle rocks (e.g. olivine, orthopyroxene, and clinopyroxene), Cr-spinel resists most of the post-magmatic mineral transformations that take place after the formation of the oceanic lithosphere, such as metamorphism (e.g. Suita and Streider, 1996; Barnes, 2000; Proenza et al., 2008; Colás et al., 2018), serpentinization (e.g., Bach et al., 2004; Lissenberg et al., 2024), hydrothermal circulation of metal-rich fluids (e.g. Nimis et al., 2008;

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Fig. 1. Examples in which LA-ICP-MS proves inadequate to measure the trace element composition of Cr-spinel. (a) Backscattered electron (BSE) image of a Cr-spinel with patchy zoning and an altered rim, from a massive chromitite of the Calzadilla ophiolite (SW Spain), (b) reflected light (RL) microscope picture of a Cr-spinel grain from a massive chromitite in the Neoproterozoic western ophiolitic belt of Pampean Ranges of Córdoba (Argentina), containing a large amount of silicate inclusions, (c) RL photomicrograph of a vermicular Cr-spinel in a serpentinite from the Havana-Matanzas ophiolite (Cuba), (d) RL microscope picture of a Cr-spinel grain with an alteration rim and surrounded by sulfides, from the UM-VMS of the Havana-Matanzas ophiolite (Cuba), (e-f) BSE image of a weathered Cr-spinel crosscut by numerous dissolution cracks from the Moa-Bay lateritic district (Cuba). Abbreviations: Chl: Chlorite; Cpy: Chalcopyrite; Cr-Spi: Cr-spinel; Hem: Hematite; Po: Pyrrhotite; Srp: Serpentine. The typical laser spot size of LA-ICP-MS analyses is shown for comparison in each image.

Patten et al., 2022; Domínguez-Carretero et al., 2022) or laterization under supergene conditions (Traore et al., 2008; Wells et al., 2022). Consequently, Cr-spinel is of upmost importance at deciphering the nature of ancient upper mantle, magma composition, fluid/melt-rock interactions, and large-scale geodynamic processes (e.g., Arai, 1992; Arai, 1997; Ohara et al., 2002; Rollinson, 2008; Pagé and Barnes, 2009; González-Jiménez et al., 2011; Uysal et al., 2018; Chen et al., 2019).

For the first time, Pagé and Barnes (2009) used laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to measure the trace elements composition of Cr-spinel to understand the origin of ophiolitic chromitites in the Thetford Mines Ophiolite (Canada). Since then, trace elements, in combination with major element composition of Cr-spinel, have been used to discriminate the parental magma compositions and tectonic setting of ophiolitic chromitites. This allowed constraining the formation of chromitites, and in extension, of the entire ophiolitic sequence, in two major geodynamic scenarios: i) subductionrelated, characterized by their formation in suprasubduction zones, either during subduction initiation, with chromitites in equilibrium with fore-arc basalts (FAB) and boninitic melts (e.g. Zhou et al., 2014; Uysal et al., 2018; Chen et al., 2019; Pujol-Solà et al., 2021), or during more advanced stages of the subduction process in the back-arc (e.g. Gervilla et al., 2005; González-Jiménez et al., 2011; Hernández-González et al., 2020); and ii) subduction-unrelated, characteristic of mid-ocean ridges (MOR) and mantle plumes magmatism (e.g. Leblanc and Nicolas, 1989; Wojtulek et al., 2019; Farré-de-Pablo et al., 2020).

Despite LA-ICP-MS being a very useful technique for obtaining the trace element composition of Cr-spinel, there are times in which this technique proves inadequate at measuring certain Cr-spinel grains. Indeed, conventional LA-ICP-MS analysis involves a laser spot size of \sim 40–80 µm in diameter, which sometimes is too large for the different, minute and complex textures that can occur in a Cr-spinel grain (Fig. 1). For example, in massive chromitites, Cr-spinel may present patchy zoning (Fig. 1a), alteration, exsolutions and/or contain a large amount

of silicate inclusions (Fig. 1b) that hinder measurement with LA-ICP-MS (Proenza et al., 2008; Gervilla et al., 2012; Merinero et al., 2014; Ramírez-Cárdenas et al., 2023). Additionally, Cr-spinel from serpentinized peridotites often have vermicular textures which are too thin to be measured with a laser beam of \sim 40 µm (Fig. 1c). Another example is the partially altered, small Cr-spinel grains from ultramafic-hosted volcanogenic massive sulfide deposits (UM-VMS) where sulfides have replaced all the silicates from the original peridotite and Cr-spinel are the only remnants that can be used to constrain the origin of that peridotite (Fig. 1d; Nimis et al., 2008; Domínguez-Carretero et al., 2022). In this case, LA-ICP-MS may mix the signal of Cr-spinel with the ones from the surrounding sulfides. Finally, Cr-spinel is also present in lateritic profiles, but it is usually physically and chemically weathered by a series of dissolution cracks that difficult the measurement of its trace element composition with LA-ICP-MS (Fig. 1e-f; Traore et al., 2008; Wells et al., 2022). Reducing the laser beam diameter is possible but leads to larger analytical errors and worsens the detection limits, since less material reaches the ICP-MS. Thus, it may be convenient to look for an alternative technique that combines high-spatial resolution and lower detection limits for an accurate characterization of inhomogeneous Cr-spinel grains.

Electron probe microanalysis (EPMA) is an in-situ, non-destructive analytical technique with a micron-scale spatial resolution (Llovet et al., 2021). Although conventional EPMA analyses are limited by their higher detection limits (hundreds of ppm), trace element analyses by EPMA have been reported from the early days of the technique (see e.g., Smith and Stenstrom, 1965). In recent years, the number of studies focusing on trace analyses of minerals by EPMA has increased significantly (Merlet and Bodinier, 1990; Nakano et al., 1991; Robinson et al., 1998; Fialin et al., 1999; Jercinovic and Williams, 2005; Donovan et al., 2011; van der Zwan et al., 2012; Kronz et al., 2012; Donovan et al., 2016; Batanova et al., 2015; Cui et al., 2019; Jia et al., 2022; Jiang et al., 2022; Zhang et al., 2022, 2023a, 2023b; Hammerli and Boroughs, 2023; Li et al., 2023; He et al., 2024; Zhang et al., 2024; Johnson et al., 2024). This is in part due to a combination of technical and software developments (Llovet et al., 2021), which have allowed to routinely achieve detection limits lower than hundred parts per million at relatively acceptable precision. Yet, the accuracy of trace and minor element analyses by EPMA may largely differ from that achieved for major elements, mainly because systematic uncertainties that can be disregarded for major elements are magnified at low concentration levels. These include background subtraction errors, interferences (overlaps) from other elements, sample modification during analysis (beam damage), and secondary fluorescence from adjacent phases. Moreover, operating the EPMA at a high-accelerating voltage may increase the matrix correction factors, especially that of X-ray absorption. The accuracy of trace element EPMA data can be assessed either by analyzing a reference standard which is homogeneous at trace level (e.g. Jiang et al., 2022; He et al., 2024) or by comparing with the results of other microanalysis methods such as µ-PIXE (Gervilla et al., 2004) or LA-ICP-MS (Batanova et al., 2015). Trace element analyses by EPMA have been reported for a range of minerals, namely olivine (Batanova et al., 2015; Korolyuk and Pokhilenko, 2014; Jiang et al., 2022), quartz (Donovan et al., 2011; Kronz et al., 2012), garnet (Pyle et al., 2005), sulfides (Robinson et al., 1998), monazite (Jercinovic and Williams, 2005; Jercinovic et al., 2008), rutile (Cui et al., 2019; He et al., 2024), glass (Fialin et al., 1999; Zhang et al., 2022) or gold (Gauert et al., 2015). However, only a few studies have focused on Cr-spinel (Jia et al., 2022).

In this study, we present our approaches for measuring minor and trace elements of Cr-spinel by EPMA. We focus on the elements: Sc, V, Ti, Mn, Co, Ni, Zn, and Ga, which are used as petrogenetic indicators. The operating conditions (accelerating voltage, beam current, counting times) are optimized with a view to improve both the analytical precision and detection limit of the analyses, both parameters being further improved by using multiple spectrometers to analyze the same element. To the latter end, the individual spectrometer data are aggregated by using the inverse-variance weighting average method (Knoll, 1999; Lyons, 1986). Care is exercised to minimize systematic uncertainties which may worsen the accuracy of results, namely background settings and interferences (overlaps) from other elements (Robinson et al., 1998; Fialin et al., 1999; Reed, 2000; Jercinovic and Williams, 2005). Our methodology is applied to selected Cr-spinel grains from chromitites of the Mayarí-Baracoa Ophiolitic Belt (eastern Cuba), in correspondence with previous LA-ICP-MS analyses (Domínguez-Carretero et al., 2025); a total of 59 paired EPMA vs. LA-ICP-MS analyses were obtained, which have been utilized to assess the accuracy of the developed protocol. Finally, in this paper, we discuss the potential of EPMA to effectively measure minor and trace elements in Cr-spinel from ophiolitic chromitites, taking advantage of its higher spatial resolution compared to the LA-ICP-MS, and we show how the trace element composition of primary Cr-spinel obtained by EPMA can be used to constrain petrogenetic information on chromitites in a reliable way.

2. Materials and methods

2.1. Sample description

Four chromitite samples from the Mayarí-Baracoa Ophiolitic Belt (eastern Cuba) were selected for this study (Proenza et al., 1999; Gervilla et al., 2005; Domínguez-Carretero et al., 2025). All samples have massive textures, composed mostly (>90 vol%) of unaltered, subhedral Cr-spinel grains ranging from ~ 100 µm to ~ 3 mm in size (Domínguez-Carretero et al., 2025). The four samples are classified depending on the Cr# [Cr/(Cr + Al)] of their Cr-spinel, into high-Al (Cr# < 0.6) and high-Cr (Cr# > 0.6) chromitites. High-Al samples belong to the Los Naranjos and Amores deposits, located within the Moa-Baracoa mining district in the eastern sector of the Mayarí-Baracoa Ophiolitic Belt. On the contrary, high-Cr chromitites were collected from the Estrella de Mayarí and Negro Viejo deposits, situated within the Mayarí and Sagua de Tánamo

mining districts respectively, located in the western and central sectors of the Mayarí-Baracoa Ophiolitic Belt.

Polished thin-sections of the selected samples were previously analyzed by LA-ICP-MS (Domínguez-Carretero et al., 2025). After the LA-ICP-MS analyses, the selected thin sections were cleaned with a view to remove any rest of the ablated material around the laser spots and were carbon coated for EPMA analysis.

2.2. Electron probe microanalysis: instrument specifications

EPMA analyses were conducted on a JEOL JXA-8230 electron microprobe equipped with four wavelength-dispersive spectrometers at the Centres Científics i Tecnològics of the Universitat de Barcelona (CCiTUB). The JEOL microprobe software was used for quantitative analyses. Data was collected during different sessions in order to optimize the analytical conditions (beam current, background settings, counting times) to improve both the analytical precision of analyses and detection limits. Analyses were conducted using a 25 kV accelerating voltage with a focused spot size.

Major elements were measured in a first pass using a low beam current with a view to minimize deadtime and pulse-shift problems, and trace and minor elements were measured in a second pass using higher beam currents. Specifically, Fe, Cr, Mg and Al were first measured with 10 nA beam current, 10 s peak and 5 s on each background, and, in a second pass, Sc, V, Ti, Mn, Co, Zn, Ga were measured with various beam currents (20-900 nA), background offsets and counting times. No significant beam shift position was observed when changing the beam current, as observed on a willemite sample. Elements Ni, Mn, Co, Zn and Ga were each measured on two spectrometers simultaneously using LiFH and LiFL crystals, Sc was measured on four spectrometers using 2 different PETJ crystals, one PETH crystal and one PETL crystal, and Ti and V were both measured on 2 spectrometers using two different PETJ crystals. For every analysis point, the two sets of data (major elements and minor/trace elements) were added using JEOL software to produce one single result. The standards used were natural rhodonite (Mn), natural Fe₂O₃ (Fe), synthetic rutile (Ti), synthetic NiO (Ni), synthetic sphalerite (Zn), synthetic GaAs (Ga), and synthetic periclase (Mg) (all of them from P&H Developments, UK), and natural kyanite (Al) and and natural Cr-spinel (Cr) (both from C.M. Taylor, USA). Pure metals were used for Co and V (both from Microanalysis Consultants Ltd., UK). The latter materials were either carbon coated (V) or repolished down to 0.05 µm with alumina suspension (Co) to minimize surface oxidation. The XPP matrix correction method was used to convert X-ray intensity data into concentration (Pouchou and Pichoir, 1991).

The EPMA analyses were performed at a distance of $\sim 10 \ \mu m$ from of the LA-ICP-MS spots, which were still visible after the cleaning procedure. A total of 59 paired EPMA vs. LA-ICP-MS measurements were obtained. To compare the data from the two instruments, the EPMA data collected as oxide weight per cent were converted to elemental weight ppm. The relative precision (at 2σ level) of major elements (Mg, Al, Cr, Fe), as estimated from counting statistics, were in the range $\sim 0.8-2.1 \ \%$ (see Appendix 1). The detection limits (at $3\sigma\sigma$ level) for these elements were $\sim 260-430$ ppm.

3. Results and discussion

3.1. Combining data from multiple spectrometers

The use of multiple spectrometers for the analysis of the same element allows to improve the analytical precision and detection limit without increasing the counting time. This is very useful e.g., for the analysis of beam sensitive materials, for which large irradiation times may result in sample damage. At the same time, it minimizes instrumental drift without the need of applying cyclical data collection strategies (Robinson et al., 1998; Merlet and Bodinier, 1990).

The so-called "aggregate intensity counting" method has been used

Table 1

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Element	Number of spectrometers	Parameter	Aggregate counting	Weighted average	Difference from aggregate counting (%)	JEOL software	Difference from aggregate counting (%)
Sc	4	k-ratio (%)	0.00085	0.00079	-6.39	0.0010	17.85
		Relative precision(%)	32.95	32.69	-0.80		
		Detection limit (ppm)	3.94	3.79	-3.72		
Λ	2	k-ratio (%)	0.11999	0.11826	-1.44	0.1217	1.43
		Relative precision(%)	1.36	1.36	-1.26		
		Detection limit (ppm)	18.91	18.86	-0.29		
Ti	2	k-ratio (%)	0.34644	0.34645	0.00	0.3460	-0.01
		Relative precision(%)	0.84	0.84	-0.02		
		Detection limit (ppm)	14.50	14.47	-0.22		
Mn	2	k-ratio (%)	0.53848	0.53500	-0.65	0.5401	0.30
		Relative precision(%)	1.35	1.35	-0.13		
		Detection limit (ppm)	20.76	20.47	-1.37		
Co	2	k-ratio (%)	0.03204	0.03164	-1.25	0.0322	0.50
		Relative precision(%)	2.81	2.80	-0.60		
		Detection limit (ppm)	11.46	11.24	-1.85		
Ni	2	k-ratio (%)	0.13690	0.13688	-0.01	0.1369	0.00
		Relative precision(%)	1.49	1.48	-0.62		
		Detection limit (ppm)	17.46	17.16	-1.72		
Zn	2	k-ratio (%)	0.06422	0.06357	-1.00	0.0643	0.13
		Relative precision(%)	2.87	2.83	-2.43		
		Detection limit (ppm)	16.13	15.67	-2.86		
Ga	2	k-ratio (%)	0.00653	0.01	2.17	0.0069	5.65
		Relative precision(%)	23.75	22.24	-6.36		
		Detection limit (ppm)	10.54	10.10	-4.16		
The k-ratios n	eported by JEOL software are	e also listed.					

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to aggregate data from different spectrometers (Donovan et al., 2011, 2016; Audétat et al., 2014, 2023; Kronz et al., 2012; Acosta et al., 2020, Nelson et al., 2021; Zhang et al., 2023a, 2023b; He et al., 2024). The method consists in adding the counts measured on different spectrometers as if they had been measured on a single spectrometer (see Appendix 2). By doing so, the Poisson character of the counting values is preserved, and this makes it possible to apply the conventional formulas to calculate the k-ratio, analytical precision and detection limit (see Appendix 1). However, the JEOL microprobe software (PC-EPMA version 1.19.1.2) does not implement this method. Instead, it calculates the combined k-ratio by using some sort of count averaging (McSwiggen, 2024, personal communication) but neither the aggregated precisions nor the detection limits are reported, leaving it to the user to decide which of the individual estimates they prefer.

There are several methods to combine measurements with different uncertainties (e.g. Birch and Singh, 2014). The simplest approach is to use the inverse-variance weighted average method (Knoll, 1999; Lyons, 1986). By using this technique, each measurement is weighted in inverse proportion to its variance, thus the method gives more weight to those measurements with small uncertainty, and less weight to the measurements for which the uncertainty is large. If variances are equal, the weighted average is equivalent to conventional average. Let k_i and σ_i be the *k*-ratio and statistical uncertainty (precision) of spectrometer *i*. The weighted average k-ratio k_W is given by Knoll (1999):

$$k_{\rm W} = \frac{\sum\limits_{i}^{k} k_i w_i}{\sum\limits_{i}^{i} w_i} \tag{1}$$

where $w_i = 1/\sigma_i^2$, and the uncertainty on k_W is obtained as

$$\sigma_{K_{\rm W}} = \sqrt{\frac{1}{\sum\limits_{i} 1 / \sigma_i^2}} \tag{2}$$

It is worth mentioning that σ_{K_W} takes no account of whether or not the individual measurements are consistent with each other, although statistical tests have been suggested to assess the consistency of the individual measurements (Pomme and Spasova, 2008).

Since the detection limit can also be regarded as an uncertainty (see Appendix 1), the aggregated detection limit DL_W can also be, in principle, determined by applying Eq. (2) (e.g. Specht et al., 2017; Vivier et al., 2012; Specht et al., 2017; Mostafaei et al., 2015). Thus

$$DL_{\rm W} = \sqrt{\frac{1}{\sum_{i} 1 / \left(DL_{i} \right)^{2}}} \tag{3}$$

where DL_i is the detection limit corresponding to spectrometer *i*. However, we note here that a formal proof of Eq. (3) remains to be found.

The accuracy of the weighted average method for the calculation of the k-ratio, analytical precision and detection limit was verified, for selected analyses of the Cr-spinel samples, by comparison with the results from the aggregate counting method. The latter method was applied off-line, with information extracted from JEOL internal data files. As an example, Table 1 compares the k-ratios, analytical precisions and detection limits obtained by using the two methods in one representative analysis. Table 1 also includes the k-ratios reported by JEOL software. In general, the k-ratios calculated by weighting average differ from those calculated by aggregate counting by less than about \sim 2 %, while differences in the analytical precisions estimated by the two methods are less than \sim 6 %. In the case of detection limits, those obtained by weighting average (considering the detection limit as an uncertainty, see above) differ from those calculated by aggregate counting by less than \sim 5 %. On the other hand, the k-ratios reported by JEOL software agree well with the values calculated by aggregate counting, with differences generally less than 1.5 %, except in the case of Sc and

Table 2

Composition of Cr-spinel standard from the Taylor multi-element standard mount (C.M.Taylor), labelled as "chromite #5 Australia".

Element	wt%	Oxide	wt%
0	10.41		
Al	12.65	Al_2O_3	23.91
Ti	0.07	TiO ₂	0.12
V	0.12	V_2O_5	0.207
Cr	31.23	Cr_2O_3	45.65
Mn	0.10	MnO	0.13
Fe	9.89	FeO	12.72
Ni	0.13	NiO	0.171
Sum	100.1	Sum	100.2

Ga, where the observed differences are much larger. We believe that, for these elements, the differences may be in part due to rounding errors, owing to the fact that k-ratios (%) are reported with only 4 decimal places. Overall, the results reported in Table 1 provide evidence that the weighting average method is sufficiently accurate for the purpose of obtaining detection limits and analytical precisions for the elements and analytical configuration of the present study. Thus, our strategy is to combine k-ratios (concentrations) reported by JEOL software with analytical precisions and detection limits obtained by weighting average. A more detailed investigation on the suitability of the latter

method for multi-spectrometer EPMA analysis for other materials and analytical configurations is beyond the scope of the present study.

To illustrate the effect of using multiple spectrometers on the analytical precision and detection limits, measurements were performed on a Cr-spinel standard (Table 2). As an illustration, Fig. 2 compares the individual precisions (Fig. 2a) and detection limits (Fig. 2b) for Ti obtained for each spectrometer, as well as the combined values resulting from aggregating the data of the four spectrometers by weighting average. The improvement in both the analytical precision and detection limit is noteworthy. The combination of the four spectrometers outperforms each individual spectrometer, including the one equipped with the larger crystal (PETH). A relative precision of ~ 1.2 % and a detection limit of ~ 5.2 ppm at 900 nA is achieved by using the four spectrometers, for a counting time of 60 s on peak and 30 s on each background.

3.2. Analytical precision and detection limits

Trace element analysis seeks to maximize the peak intensity and the peak-to-background ratio. Both quantities generally increase with increasing accelerating voltage (Reed, 2000), although there are cases where strongly absorbed elements in certain matrices may not see benefit with this, as X-ray generation is driven deeper in the sample. Thus, the accelerating voltage was set to 25 kV in all sessions.



Fig. 2. Comparison of individual spectrometer (a) analytical precisions (2σ) and (b) detection limits (3σ) , with the combined values obtained by aggregating the results of all the spectrometers, as a function of beam current.



Fig. 3. (a) Analytical precisions (2 σ) for Ti, V, Ni and Mn and (b) detection limits (3 σ) for Sc, V, Ti, Mn, Co, Ni, Zn Ga, obtained on a Cr-spinel reference standard as a function of beam energy, in the conditions indicated.

To assess the effect of beam current on the analytical precision and detection limit, analyses were performed on the Cr-spinel standard (Table 2) at increasing beam currents (20, 100, 500, and 900 nA), with count times of 60 s on peak and 30 s on each background for all the considered elements. The analytical precision and detection limits were evaluated by weighting average of the individual spectrometer values of these magnitudes (see Appendix 1). Fig. 3a shows the dependence of the relative precision (at 2σ level) for Mn, Ti, V and Ni on beam current. All these elements were measured on 2 spectrometers (Mn and Ni with LiFH and LiFL crystals, and Ti and V with two different PETJ crystals). The relative precision in the determination of these elements improves by a factor of \sim 5–7 when the beam current increases from 20 nA to 900 nA. The dependence of the detection limit (at 3σ level) for Ti, V, Sc, Ga, Ni, Co, Zn, and Mn, on beam current is depicted in Fig. 3b. We note here that even if the standard does not contain any Sc, Ga or Zn, it is possible to estimate their detection limit since the latter is determined by the precision in the background measurement within the peak region of interest. All the elements were measured on two spectrometers (Ti and V with two PETJ crystals, and Ni, Co, Zn, Ga and Mn with LiFH and LiFL crystals) except for Sc, which was measured on four spectrometers (with two PETJ crystals, one PETH crystal and one PETL crystal). The peak position reproducibility after crystal change was better than 0.3 %. The detection limit shows a \sim 6–7-fold decrease when the beam current goes from 20 nA to 900 nA.

In view of the obtained results and considering that Cr-spinel is a beam-resistant mineral, the beam current was set to 900 nA for the trace and minor elements. Counting times and analyzing crystals were optimized as follows: Ti and V (2 PETJ, 150 s on peak each), Ni and Mn (LiFH and LiFL, 30 s on peak each), Co and Zn (LiFH and LiFL, 60 s on peak each), Ga (LiFH and LiFL, 120 s on peak each), Sc (2 PETJ, PETL, PETH, 120 s on peak each). Background counting times on either side of the peaks were set to half of the respective peak counting times. With this analytical configuration, the total time for each analyzed point amounted to ~15 min. The analytical parameters and spectrometer configuration are summarized in Table 3.

The range of measured concentrations, precision and detection limits are listed in Table 4. We note that, for Sc, we have not excluded those values that are below the detection limits quoted in Table 4. Although these values would not be regarded as significant statistically, they are considered here analytically meaningful.

The average relative precision (at 2σ level) achieved was ~46 % for Sc, 2 % for Ti, 1 % for V, 1.7 % for Mn, 2.7 % for Co, 1.3 % for Ni, 3 % for Zn, and 36.5 % for Ga. The detection limits (at 3σ level) were ~ 4 ppm for Sc, 20 ppm for Ti, 20 ppm for V, 26 ppm for Mn, 10 ppm for Co, 15 ppm for Ni, 14 ppm for Zn, and 10 ppm for Ga.

3.3. Background offsets and interferences

In EPMA, the spectral background is generally estimated by linear interpolation of two measurements performed on each side of the peak (Reed, 1993). If $N_{\rm bL}$ is the number of counts measured at a distance $d_{\rm L}$ on the left side of a peak and $N_{\rm bR}$ is the number of counts at a distance $d_{\rm R}$ on the right side of the peak, the background $N_{\rm b}$ is calculated as

$$N_{\rm b} = \frac{N_{\rm bL}d_{\rm R} + N_{\rm bR}d_{\rm L}}{d_{\rm B} + d_{\rm L}} \tag{4}$$

Errors due to background nonlinearity, which can be disregarded for major elements, can become important for trace elements (Fialin et al., 1999; Reed, 2000; Allaz et al., 2019). Fig. 4 shows representative detailed wavelength scans around the peaks of the elements of interest. To minimize errors due to possible background nonlinearity, background offsets (displayed in the figures) were carefully chosen closer to the peak for all elements (Sc, V, Ti, Ni, Zn, Co, and Ga), except for Mn, for which a large offset was set on the left side of the peak in an attempt to minimize the interfering tail of the Cr K β (Fig. 4d) line. An external correction was further applied to Mn, which was directly derived from

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Element	Calibration standard	Beam current (nA)	X-ray line	Number of spectrometers	Crystal(s)	Total count time	Background offset low (mm)	Background offset high (mm)
Fe	Fe_2O_3	10	Fe Kα	4	LiFH	20	4	3
Cr	Cr-spinel	10	Cr Kα	4	LiFH	20	6	3
Al	Kyanite	10	Al K α	1	TAP	20	5	3.5
Mg	Periclase	10	Mg Ka	2	TAP	20	5	3
Sc	Sc	006	Sc Ka	1,2,3,4	PETJ, PETJ, PETL, PETH	096	1	1
Ti	Rutile	006	Ti Ka	1,2	PETJ,PETJ	600	1.5	1.5
v	Λ	006	V Κα	1,2	PETJ,PETJ	600	1	1
Mn	Rhodonite	006	Mn Ka	3,4	LiFL,LiFH	120	4.2	1.8
Co	Co	006	Co Ka	3,4	LiFL,LiFH	240	0.5	0.8
Ni	NiO	006	Ni Ka	3,4	LiFL,LiFH	120	1	1.4
Zn	ZnS	006	Zn Kα	3,4	LiFL,LiFH	240	1	1.4
Ga	GaAs	006	Ga Kα	3,4	LiFL,LiFH	480	0.5	0.5

Summary of EPMA minor and trace element analyses of Cr-spinel samples.

Element	Number of analyses	Concentration range (ppm)	Average concentration (ppm)	Precision range (RSD(%))	Average precision (RSD (%))	Detection limit range (ppm)	Detection limit average (ppm)	RMS (%)	R(%)
Sc	57	3.3–26.7	6.7	8.9–98	46.2	4.2–4.3	4.2	171	133
Ti	59	490-3044	1449	0.4-2.1	2	16.2-18.3	17.4	14.2	9
v	59	367-1269	838	1.1-3.6	1	19.1-20.1	20	11.1	-8.5
Mn	59	1059–1485	1319	1.4-2.1	1.7	26.0-28.0	26.6	7.4	-2.4
Со	59	208-347	261	2.4-3.6	2.7	9.8-10.5	10.2	4.7	2.7
Ni	59	385-1699	1191	0.1-2.4	1.3	15.1-16.2	15.6	10.9	-7.4
Zn	59	279-508	455	2.6-4.9	3	13.7-14.6	13.9	22.5	$^{-21}$
Ga	59	12–56	36	18.7–91.6	36.5	10.1 - 10.8	10.3	32.5	-18.5

measurements on a Cr-spinel standard (Table 2) as follows:

 $[MnO] = [MnO]_{\rm m} - 0.00112 \times [Cr_2O_3]_{\rm m}$, where [MnO] and $[MnO]_{\rm m}$ are the corrected and measured MnO concentrations in weight %, respectively, and $[Cr_2O_3]_{\rm m}$ is the measured Cr_2O_3 concentration in weight %. We note that this correction may only be valid for a narrow range of Cr-spinel compositions that are close to the Cr-spinel standard. No overlap correction was applied to V, owing to the low TiO₂ contents of the samples. It must be noted that the wavelengths scans showed no "holes" in the background near the peaks of interest (Self et al., 1990; Kato and Suzuki, 2014).

3.4. Spatial resolution and secondary fluorescence across phase boundaries

Although EPMA is an analytical technique with a typical micron spatial resolution, the latter may worsen under the conditions used for trace analysis (25 kV accelerating voltage and 900 nA beam current). This is because the spatial resolution is mainly governed by the interaction volume of incident electrons inside the specimen, which depends on beam energy and material. A practical estimation of the radius of the interaction volume (assuming that it is a hemisphere) is provided by the Bethe range, which is defined as the average path length that electrons travel before slowing down to rest (Reimer, 1998). We note here that the Bethe range slightly overestimates the maximum penetration range of electrons (straight-distance measured from the sample surface that electrons travel before slowing down to rest) since the latter follow zigzag trajectories. We have calculated the Bethe range for the Taylor Crspinel standard using the program TABLES included in the PENELOPE distribution (Salvat, 2019), assuming $\rho = 4.79$ g/cm³. The Bethe range increases from 1.47 µm at 15 keV to 3.57 µm at 25 keV. Assuming a negligible beam size, the analytical resolution (maximum width of the interaction volume) of the Cr-spinel analyses is estimated to be $\sim 7~\mu m$ with a focused beam. This resolution is sufficient to characterize heterogeneous Cr-spinel grains at trace level.

On the other hand, it is well known that characteristic and continuum X-rays emitted from interactions of primary electrons in the analyzed phase can reach distances one-to-two orders of magnitude larger than the electron range and thus produce secondary fluorescence in an adjacent phase far away from the analyzed grain (Reed and Long, 1963). As a result, fictitious analytical results can be obtained for an element present in low concentration in the analyzed phase, whenever a second nearby phase contains a high abundance of this element. The potential analytical errors due to secondary fluorescence in the analysis of minerals have been widely discussed in the literature (see e.g., Reed and Long, 1963; Dalton and Lane, 1996; Llovet and Galán, 2003; Jercinovic et al., 2008; Wade and Wood, 2012; Borisova et al., 2018; Llovet et al., 2020, 2023; Gavrilenko et al., 2023).

In our samples, there is a potential risk for an overestimation of Ti in Cr-spinel from nearby rutile by secondary fluorescence of Cr K α X-rays, owing to the occurrence of such mineral in some of the studied samples. We note that a significant enhancement could be found even on a relatively large scale, due to the long range of secondary fluorescence

effects. To estimate the scale of this effect, the program FANAL was used (Llovet et al., 2012). This program assumes the simplest geometry (an ideal non-diffusion couple), i.e., the sample is assumed to consist of two semi-infinite media separated by a plane boundary perpendicular to the sample surface. FANAL has been implemented in the software suite CALCZAF/Standard (Donovan et al., 2020) and it is freely available. Fig. 5 shows the apparent Ti concentration from a Ti-free Cr-spinel/ rutile couple, as a function of distance of the electron beam to the rutile phase. The results indicate that a statistically significant apparent concentration of 20 ppm Ti is obtained when analyzing the Ti-free Cr-spinel phase at a distance of 120 µm from the boundary with rutile. Considering that the Ti concentration of the analyzed samples is in the range 490-3044 ppm (see Table 4), the error due to secondary fluorescence would be in the range 0.6–4 % if analyses were performed at 120 μm from the interface. In the case of the Cr-spinel grain with the lower Ti contents (490 ppm Ti), analyses should be performed at a minimum distance of ${\sim}200\,\mu\text{m}$ from the rutile phase for the Ti enhancement due to secondary fluorescence to be less than 1 %. For the grain with the higher Ti contents (3044 ppm Ti), such distance is \sim 100 µm. In the samples of the present study, no rutile phases were found at such distances from the analyzed Cr-spinel grains, thus, secondary fluorescence effects are negligible.

3.5. Comparison with LA-ICP-MS data

Most studies reporting trace and minor analyses by EPMA focus on the precision and detection limits of the results. In this sense, trace analysis by EPMA is often referred to as high-precision EPMA or HP-EPMA (Batanova et al., 2015). However, as discussed below, the accuracy of trace element concentrations may largely differ from that of major elements, mainly because systematic uncertainties that can be disregarded for major elements are magnified at low concentration levels.

The reliability of the developed protocol was assessed by point-bypoint comparison of EPMA analyses performed on selected Cr-spinel grains in correspondence with previous LA-ICP-MS analyses. The LA-ICP-MS data were obtained using a Resolution M-50 Excimer laser coupled to a ThermoICap Qc ICP-MS, with a 44 µm laser spot. For more details see Domínguez-Carretero et al. (2025). Although matrix corrections and quantification are much better established for EPMA than for LA-ICP-MS, in our analysis below we will regard the LA-ICP-MS data as the "true" compositions.

Fig. 6 shows Sc, V, Ti, Mn, Co, Ni, Zn, and Ga concentrations determined in 59 Cr-spinel grains by EPMA and LA-ICP-MS plotted against each other. The one-to-one line (plot of equal values) is provided for comparison. The data scatter about the one-to-one line indicates the degree of agreement between the two techniques (a perfect match between the EPMA and LA-ICP-MS data would fall exactly along a one-to-one line). For a qualitative comparison, the shaded areas present the boundaries at ± 10 %. Error bars are estimates of the 2-standard-deviation precisions of measured concentrations. In the case of the EPMA data, the precisions were calculated following the formulas given in



Fig. 4. Representative wavelength spectra around the peaks of interest obtained in one of the Cr-spinel grains, acquired in the conditions indicated in each panel. The positions where the background was measured are also indicated.



Fig. 5. Apparent Ti concentration (in ppm) due to secondary fluorescence for a Cr-spinel/rutile couple predicted by the program FANAL (Llovet et al., 2012), as a function of distance of the analysis point to the Cr-spinel/rutile interface. The horizontal line represents the detection limit of Ti in Cr-spinel achieved in the present study. See text for details.

Appendix 1, while for the LA-ICP-MS data, the precisions were estimated from replicate analyses on a Cr-spinel standard (see Domínguez-Carretero et al., 2025). Most of the pairs for Ni (Fig. 6f), Co (Fig. 6e), and Mn (Fig. 6d) are distributed along the one-to-one line within around ± 10 %, while the data for Ti (Fig. 6c) and V (Fig. 6b) exhibit a somewhat larger degree of scatter (~20 %) around the one-to-one line. An increased deviation of data scatters from the one-to-one straight line is seen for Zn (\pm 35 %) (Fig. 6g). EPMA and LA-ICP-MS concentrations agree with each other within approximately ± 30 % discrepancy for Ga (Fig. 6h), while Sc (Fig. 6a) exhibits the larger degree of scatter around the one-toone line. For the latter element, the data show significant deviations above the 1:1 line. Such deviations are somewhat expected owing to the closeness of the detection limit (4 ppm) to the average measured Sc abundances (6.6 ppm).

A more quantitative evaluation of the degree of agreement between the EPMA and LA-ICP-MS concentrations can be obtained by calculating the root-mean-square percentage deviation, *RMS*, and the mean percentage deviation, *R*, of the EPMA concentrations from the LA-ICP-MS concentrations. The *RMS* and *R* values provide measures of the degree of agreement between the two sets of data and are defined as follows:

$$RMS = \sqrt{\frac{1}{n} \sum_{i} (\Delta_i)^2}$$
(5)

$$R = \frac{1}{n} \sum_{i} (\Delta_i) \tag{6}$$

where n is the number of data points, and

$$\Delta_i = \frac{c_i^{\text{EPMA}} - c_i^{\text{LA-ICP-MS}}}{c_i^{\text{LA-ICP-MS}} \times 100} \tag{7}$$

 c_i^{EPMA} and $c_i^{\text{LA-ICP-MS}}$ are the paired EPMA and LA-ICP-MS concentrations. *RMS* and *R* values were calculated for each paired measurement and are tabulated in Table 4. The *RMS* values range from 4.7 % to 11.1 % for V, Mn, Co and Ni, while the *R* values range from -8.5 % to 2 %, indicating a similar degree of agreement between the EPMA and LA-ICP-MS data for these elements. The *RMS* and *R* values for Ti are slightly larger than those obtained for V, Mn, Co, and Ni (14.2 % and 9 %, respectively). For Zn, the *RMS* and *R* values are 22.5 % and - 21 %, respectively, while those for Ga, are 32.5 % and - 18.5 %, respectively. For Sc, the *RMS* and *R* values are much larger, with values of 163.9 % and 107 %, respectively.

The degree of agreement between the EPMA and LA-ICP-MS data can be considered as satisfactory for V, Mn, Co, Ni, and Ti. For these elements the results plotted close to the 1:1 line, demonstrating that both methods yielded consistent results for different Cr-spinel grains. Deviations between the methods could in part be due to chemical zoning of

the grains at trace level on a µm scale. We recall that EPMA covers a spot of \sim 7 µm in diameter (see above), while that covered by LA-ICP-MS is about 40 µm in diameter. For Ga, the degree of agreement obtained between the two methods is also considered to be satisfactory, given the precision that can be achieved by EPMA for this element (36.5 %, see Table 4). For Zn, a large group of EPMA analyses underestimate the Zn concentrations given by LA-ICP-MS, suggesting a systematic error (Fig. 6g). The observed discrepancies were consistently obtained using different Zn standards (willemite, pure Zn, red brass), background offsets and matrix correction methods (ZAF, XPP, Armstrong). To further check the Zn result, we analyzed an olivine reference standard (Batanova et al., 2019), which contains 70 ppm ZnO, and obtained a value of 91 \pm 18 ppm ZnO (in this case Zn was measured under the same analytical conditions as those used for the Cr-spinel analyses, and nominal concentrations for the remaining olivine elements were adopted in the data reduction process). Thus, the origin of the observed differences for Zn is not well understood. The results for Sc suggest that our methodology might not be suitable for the determination of Sc in Crspinel, owing to its extremely low concentration (6.6 ppm), despite the low detection limit (4 ppm) and reasonable analytical precision (46 %) achieved (see Table 4).

3.6. Adequacy of EPMA Cr-spinel trace element composition to establish the petrogenesis of ophiolitic chromitites

The chemistry of unaltered Cr-spinel cores from chromitites have been widely used to constrain the petrogenesis of chromitites. Chromitites are usually classified according to the Cr# of their Cr-spinel. Most authors (e.g. Leblanc and Nicolas, 1992; Arai and Abe, 1994; Zhou and Robinson, 1994; Melcher et al., 1997; Proenza et al., 1999; Arai and Miura, 2016; Zhu and Zhu, 2020) catalogue chromitites either as high-Cr (Cr# > 0.60) or high-Al (Cr# < 0.60). The trace element composition of Cr-spinel from high-Cr chromitites normalized to accessory Crspinel in mid-ocean ridge basalts (MORB; Pagé and Barnes, 2009) shows depletion in V, Ga, Ti, and Ni (Fig. 7a and c). This depletion, characteristic from other high-Cr chromitites (Pagé and Barnes, 2009; Zhou et al., 2014; Chen et al., 2019), is well-marked by both techniques, and the median trace element value of Cr-spinel obtained by EPMA mimics perfectly the median value acquired by LA-ICP-MS (Fig. 7e). On the contrary, the normalized trace element composition of Cr-spinel from high-Al chromitites is characterized by flat patterns (Fig. 7b and d) resembling the composition of accessory Cr-spinel in MORB (Pagé and Barnes, 2009). Both EPMA and LA-ICP-MS show similar median trace element results of high-Al chromitites, being Sc the only element with remarkable differences between techniques (Fig. 7f). These discrepancies in Sc are most likely due to the large differences that occur after normalizing very low concentrations (average measured contents for EPMA and LA-ICP-MS of 5 and 3 ppm, respectively).

Using the trace element composition of Cr-spinel from MORB and boninitic lavas, Pagé and Barnes (2009) empirically measured the partition coefficients for several trace elements in Cr-spinel. These partition coefficients have been later used to estimate the trace element composition of magmas in equilibrium with high-Al or high-Cr chromitites (Zhou et al., 2014; Chen et al., 2019). Following this methodology, we have calculated the trace element composition of the magmas in equilibrium with the studied high-Al and high-Cr chromitites using both EPMA and LA-ICP-MS measurements. Irrespective of equilibrium with high-Cr or high-Al Cr-spinel, the estimated calculated melts are very similar in composition, specifically in elements such as Ni, Zn, Co, and Mn (Fig. 8). Additionally, Ga, an element which is way more abundant in high-Al chromitites (Fig. 7), has similar concentrations in high-Al and high-Cr associated magmas (Fig. 8; Zhou et al., 2014). Conversely, Ti and V show remarkable differences in the different calculated melts, being those more depleted in the parental magmas of the high-Cr chromitites compared to those of the high-Al chromitites (Fig. 8). These data allow to determine the nature of the melts in



Fig. 6. Comparison of (a) Sc, (b) V, (c) Ti, (d), Mn (e), Co (f), Ni (g), Zn (h), and Ga (I) abundances obtained by EPMA and LA-ICP–MS analyses. Error bars indicate precisions (two-standard-deviation limits). Element abundances and precisions, as well as detection limits, are listed in Table S1. The blue lines represent the one-to-one line (plot of equal values). The shaded areas mark the ±10 % boundaries. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. (a-d) Spider diagrams showing the composition of minor and trace elements of Cr-spinel unaltered cores of chromitites obtained by EPMA and LA-ICP-MS, and (e-f) the comparison of their median values. Data are normalized to the composition of accessory Cr-spinel in MORB reported by Pagé and Barnes (2009).



Fig. 8. Calculated trace element composition of the melts in equilibrium with the studied chromitites using EPMA and LA-ICP-MS data, and comparison to the trace element composition of boninites and FABs from Bonin Island (Li et al., 2019). Data are normalized to the composition of MORB in Gale et al. (2013).

equilibrium with the two types of chromitites. In the case of the high-Cr chromitites parental magmas, the calculated MORB-normalized trace element patterns mimic the ones from boninites (Li et al., 2019), which are melts typical of fluid-mediated melting of the suprasubduction zone mantle wedge in advanced stages of subduction-initiation (Shervais et al., 2021). As for high-Al chromitites parental magmas, these have low Ti/V ratios (median value of 23 and 19 for EPMA and LA-ICP-MS, respectively; Shervais et al., 2019), and have MORB-normalized patterns that resemble, except for Ni, the pattern described by FAB (Fig. 8; Li et al., 2019), which are melts produced by the decompression and subsequent partial melting of the ascending asthenospheric mantle during the earliest stages of the subduction-initiation process (e.g. Reagan et al., 2010, 2019; Shervais et al., 2019).

4. Conclusions

We have developed a protocol for the analysis of trace and minor elements in Cr-spinel by EPMA, aimed at characterizing Cr-spinel grains that are inhomogeneous over micrometer length scales. We have assessed the accuracy of the developed protocol by comparing EPMA analyses of Cr-spinel from chromitites of the Mayarí-Baracoa Ophiolitic Belt (eastern Cuba), with the results of previous LA-ICP-MS analyses, and found that the degree of agreement between the two techniques is generally consistent, although differences exist in some elements. Despite this, our study shows that the composition of trace and minor elements obtained by EPMA can be readily used to decipher the nature of melts in equilibrium with ophiolitic chromitites, and therefore help constraining the geodynamic scenario in which they formed.

CRediT authorship contribution statement

Diego Domínguez-Carretero: Writing – original draft, Investigation, Data curation, Conceptualization. Xavier Llovet: Writing – original draft, Methodology, Data curation, Conceptualization. Núria Pujol-Solà: Writing – review & editing. Cristina Villanova-de-Benavent: Writing – review & editing, Funding acquisition. Joaquín A. Proenza: Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data is found in Supplementary Table 1.

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Appendix 1. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2024.122579.

Appendix 1. Calculation of the analytical precision and detection limit in EPMA

In this section, we review the calculation of the analytical precision (statistical uncertainty) and detection limit in EPMA. The concentration *c* of a given element in the sample is obtained from $k = c \times ZAF$, where *k* is the so-called *k*-ratio and ZAF are the matrix correction factors (Scott et al., 1995). The *k*-ratio is defined as

$$k = \frac{I}{I^{\text{std}}} = \frac{I_p - I_b}{I_p^{\text{std}} - I_b^{\text{std}}}$$
(1.1)

where *I* is the net count rate, and $I_p = N_p/t_p$ and $I_b = N_b/t_b$ are the peak and background count rates, respectively. N_p is the number of peak counts, N_b is the number of background counts and t_p and t_b are the peak and background counting times, respectively. The superscript "std" means that the corresponding quantity is evaluated on a reference standard. For simplicity we will assume that $t_p = t_p^{\text{std}}$ and $t_p = t_p^{\text{std}}$.

The precision in the evaluated concentration *c* is assumed to be that of the k-ratio *k*. In EPMA, the precision can be estimated either from replicate analyses or from a single measurement. This is because the detection of X-rays follows the Poisson statistics, thus the standard deviation of N_p is given by $\sigma_{N_p} = \sqrt{N_p}$. Likewise, $\sigma_{N_b} = \sqrt{N_b}$. It follows that the standard deviation of I_p is $\sigma_{I_p} = \sqrt{N_p}/t_p$ and that of I_b is $\sigma_{I_b} = \sqrt{N_b}/t_b$. By using error propagation rules, the standard deviation of the net count rate $I = I_p - I_b$ can be obtained by adding in quadrature the individual standard deviations,

$$\sigma_{I} = \sqrt{\left(\sigma_{I_{p}}\right)^{2} + \left(\sigma_{I_{b}}\right)^{2}} = \sqrt{\frac{N_{p}}{t_{p}^{2}} + \frac{N_{b}}{t_{b}^{2}}} = \sqrt{\frac{I_{p}}{t_{p}} + \frac{I_{b}}{t_{b}}}$$
(1.2)

To obtain the standard deviation of *k*, we must first obtain the relative standard deviation of *k* by adding in quadrature the relative standard deviations of the count rates for sample and standard, which are given by $\epsilon_I = \sigma_I / I$ and $\epsilon_{Istad} = \sigma_I / I^{std}$, respectively. Since

$$\epsilon_k = \sqrt{(\epsilon_I)^2 + (\epsilon_{I^{\rm std}})^2} \tag{1.3}$$

and taking into account that $\sigma_k = \epsilon_k k$, we obtain:

$$\sigma_{k} = \sqrt{\left(\frac{I_{p}}{t_{p}} + \frac{I_{b}}{t_{b}}\right) / \left(I_{p} - I_{b}\right)^{2} + \left(\frac{I_{p}^{\text{std}}}{t_{p}} + \frac{I_{b}^{\text{std}}}{t_{b}}\right) / \left(I_{p}^{\text{std}} - I_{b}^{\text{std}}\right)^{2} \times \left(\frac{I_{p} - I_{b}}{I_{p}^{\text{std}} - I_{b}^{\text{std}}}\right)$$
(1.4)

The detection limit is the lowest concentration that can be detected with certain statistical significance. At 99 % confidence level, the detection limit is defined as the concentration for which $N > 3\sigma_N$, where N are the net counts $N = N_p - N_b$. The standard deviation of N is

$$\sigma_N = \sqrt{\left(\sigma_{N_p}\right)^2 + \left(\sigma_{N_b}\right)^2} = \sqrt{N_p + N_b} \tag{1.5}$$

but when the concentration approaches the detection limit, we can assume that $N_{\rm p} \sim N_{\rm b}$, thus

$$\sigma_N = \sqrt{2 N_b} = \sqrt{\frac{2 I_b}{t_b}} \tag{1.6}$$

Converting counts into concentration, the detection limit DL can be written as:

$$DL = 3 \frac{C^{\text{std}}}{I^{\text{std}}} \text{ ZAF} \sqrt{\frac{2I_{\text{b}}}{t_{\text{b}}}}$$
(1.7)

where C^{std} is the concentration of the element of interest in the standard. From Eq. (1.7) it follows that the detection limit can be lowered by decreasing I_{b} and I^{std} . Eqs. (1.4) and (1.7) are implemented in JEOL software, except for the factor (ϵ_{Fstd}) in Eq. (1.3), which is ignored (the JEOL software implicitly assumes that the error in the measurement of the standard is negligible).

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(2.6)

Appendix 2. The aggregate intensity counting method

The aggregate counting method (Donovan et al., 2011) consists of adding the individual peak and background counts from all the spectrometers as if they had been measured by a single spectrometer, and the counting time is set as the sum of the individual counting times. We note that it is the number of counts, and not the X-ray intensities (counts per second), the quantity that needs to be added in order to preserve the Poisson character of the counting values. Although a rigorous proof of the aggregate intensity counting method remains to be found, it appears to fulfill the so-called combining principle, which states that any "combining technique should give the same answer as if all the data had been regarded as a single experiment" (Lyons, 1986).

If $N_{p,i}$ is the number of counts in the peak measured by spectrometer *i* during time $t_{p,i}$, and $N_{b,i}$ is the number of counts in the background measured by the same spectrometer during time $t_{b,i}$, then the combined k-ratio k_A obtained by the aggregate counting method can be calculated as (see Eq. (1.1)):

$$k_{\rm A} = \left(\frac{N_{\rm p,S}}{t_{\rm p}} - \frac{N_{\rm b,S}}{t_{\rm b}}\right) \left/ \left(\frac{N_{\rm p,S}^{\rm std}}{t_{\rm p}} - \frac{N_{\rm b,S}^{\rm std}}{t_{\rm b}}\right)$$
(2.1)

where

$$N_{p,S} = \sum_{i} N_{p,i} \text{ and } N_{b,S} = \sum_{i} N_{b,i}$$
(2.2)

$$N_{p,S}^{\text{std}} = \sum_{i} N_{p,i}^{\text{std}} \quad \text{and} \quad N_{b,S}^{\text{std}} = \sum_{i} N_{b,i}^{\text{std}}$$
(2.3)

and

$$t_{\rm p} = \sum_{i} t_{{\rm p},i}$$
 and $t_{\rm b} = \sum_{i} t_{{\rm b},i}$ (2.4)

As before, the superscript "std" in Eqs. (2.1) and (2.3) means that the corresponding quantity is evaluated in a reference standard. For simplicity, we assume that $t_{p,i} = t_{p,i}^{std}$ and $t_{b,i} = t_{b,i}^{std}$.

The precision σ_A of the k-ratio and detection limit DL_A are then obtained by using the same equations as those used for a single spectrometer (see Appendix 1). Expressing Eqs. (1.2) and (1.3) as a function of peak and background counts, we obtain:

$$\sigma_{k_{A}} = \sqrt{\left(\frac{N_{p,S}}{t_{p}^{2}} + \frac{N_{b,S}}{t_{b}^{2}}\right) \left/ \left(\frac{N_{p,S}}{t_{p}} - \frac{N_{b,S}}{t_{b}}\right)^{2} + \left(\frac{N_{p,S}^{\text{std}}}{t_{p}^{2}} + \frac{N_{b,S}^{\text{std}}}{t_{b}^{2}}\right) \left/ \left(\frac{N_{p,S}^{\text{std}}}{t_{p}} - \frac{N_{b,S}}{t_{b}}\right)^{2} \right.}$$

$$\times \left(\frac{N_{p,S}}{t_{p}} - \frac{N_{b,S}}{t_{b}}\right) \left/ \left(\frac{N_{p,S}^{\text{std}}}{t_{p}} - \frac{N_{b,S}^{\text{std}}}{t_{b}}\right)\right.$$

$$(2.5)$$

and

$$DL = 3\sqrt{2} \; rac{C^{ ext{std}}}{\left(N^{ ext{std}}_{ ext{p}, ext{S}} ig/ t_{ ext{p}} - N^{ ext{std}}_{ ext{b}, ext{S}} ig/ t_{ ext{b}}
ight)} \; ext{ZAF} \sqrt{rac{N_{ ext{b}}}{t}}$$

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