

# Automated petrography analysis by QEMSCAN® of a garnet-staurolite schist of the San Lorenzo Formation, Sierra Nevada de Santa Marta massif

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## ABSTRACT

Automated petrographic analysis integrates scanning electron microscopy and energy-dispersive X-ray spectroscopy hardware with expert software to generate micron-scale compositional maps of rocks. While automated petrography solutions such as QEMSCAN® are widely used in the mining, mineral processing, and petroleum industries to characterize ore deposits and subsurface rock formations, it has not been used in metamorphic petrology. This study applies automated petrographic analysis using QEMSCAN® to a garnet-staurolite schist of the San Lorenzo Formation, Sevilla geological province (Sierra Nevada de Santa Marta massif), and demonstrates that this analytical technique has clear potential application in petrologic studies.

Key words: automated petrography; metamorphic rocks; garnet; schist; QEMSCAN®; San Lorenzo Formation; Sierra Nevada de Santa Marta, Colombia.

## RESUMEN

*El análisis petrográfico automatizado integra hardware de microscopía electrónica de barrido y espectroscopía de rayos X con software experto para generar mapas de composición de rocas a escala de micras. Si bien las soluciones de petrografía automatizada, como QEMSCAN®, se usan ampliamente en las industrias de minería, procesamiento de minerales y petróleo para caracterizar los depósitos minerales y las formaciones rocosas subsuperficiales, no se ha utilizado en petrología metamórfica. Este estudio aplica el análisis petrográfico automatizado utilizando*

*QEMSCAN® a un esquistó con granate y estaurólita de la Formación San Lorenzo, provincia geológica de Sevilla (macizo de la Sierra Nevada de Santa Marta), y demuestra que esta técnica analítica tiene una clara aplicación potencial en estudios petrológicos.*

*Palabras clave: petrografía automatizada; rocas metamórficas; granate; esquistó; QEMSCAN®; Formación San Lorenzo; Sierra Nevada de Santa Marta, Colombia.*

## INTRODUCTION

Petrology, as a Geoscience discipline, concerns the understanding of the origin of rocks, and petrography is a branch of this discipline that involves the macroscopic and microscopic description of mineral content and texture (microstructure) to support petrogenetic interpretations (Robinson, 1991). Conventional microscopic studies are routinely developed in a polarized optical microscope, used to identify minerals on the basis of their optical properties. However, due to its manual and laborious nature, the mining industry has found several problems, particularly in geometallurgy or mineral processing. Systems for automated petrography based on Scanning Electron Microscopy (SEM) have been developed since the 1980s at Australia's Commonwealth Scientific and Industrial Research Organization - CSIRO (Hoal *et al.*, 2009). Numerous automated petrography systems are in use worldwide, predominantly in the precious and base metal mining industries, which are used to measure ore properties such as ore typing, precious metal host mineralogy, mineral associations (*e.g.* mineral liberation) or phase purity from core samples or grinded mate-

rial (Van der Wal and Kruseman, 2011). The advantages of automated systems like the QEMSCAN® (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) are their statically robustness, reliable mineral identifications, round-the-clock operations, high throughput, multiple applications with high degree of flexibility, multiple measurements modes, built-in quality-control programs, and data/information (Fennel *et al.*, 2005; Ayling *et al.*, 2012) that can be used in several fields as forensics, environmental geology, coal and petroleum mineralogy, geopolymer development, meteorite investigations or archaeological research (*e.g.*, Al-Otoom *et al.*, 2005; Goodall and Scales, 2007; Chen-Tan *et al.*, 2009; Pirrie *et al.*, 2009; Segvic *et al.*, 2014; Menzies *et al.*, 2015; Dieterich *et al.*, 2016; Mackay *et al.*, 2016; McLeod *et al.*, 2016). The energy-dispersive X-ray spectroscopy (EDS)-SEM systems, such as the QEMSCAN®, have made great progress in speed and precision since the beginning of the 21st century, becoming a reference system for quantitative evaluation of minerals by scanning electron microscopy, which was originally designed for the mining industry (*e.g.*, Camm *et al.*, 2004; Liu *et al.*, 2005; Goodall and Scales, 2007; Pascoe *et al.*, 2007; Rollinson *et al.*, 2011; Santoro *et al.*, 2014; Anderson *et al.*, 2014), although it has been gaining recognition in other areas of research (*e.g.*, Butcher *et al.*, 2003; Pirrie *et al.*, 2004; Al-Otoom *et al.*, 2005; Sliwinski *et al.*, 2009; Šegvič *et al.*, 2014; Potter-McIntyre *et al.*, 2014). QEMSCAN® developed and distributed by Intellection Pty Ltd., located in Brisbane, Australia, and a registered trademark owned by FEI Company since 2009, is a fully automated microanalysis system that enables quantitative chemical analysis of materials and generation of high-resolution mineral maps and images as well as porosity structure (Gottlieb *et al.*, 2000). It uses a scanning electron microscopy platform (SEM) with an electron beam source in combination with four energy-dispersive X-ray spectrometers (EDS). QEMSCAN® creates phase assemblage maps of a specimen surface scanned by a high-energy accelerating electron beam along a predefined raster scan pattern. It preferentially uses low-count energy-dispersive X-ray mapping for mineral classification, which is done by comparison of the X-ray element-spectrum to existing dataset of mineral phases (Warlo *et al.*, 2019). The elemental composition in combination with back-scattered electron (BSE) brightness and X-ray count rate information is converted into mineral phases (Gottlieb *et al.*, 2000). QEMSCAN® data includes bulk mineralogy and calculated chemical composition. By mapping the sample surface, textural properties and contextual information such as particle and mineral grain size and shape, mineral associations, mineral liberation, elemental behavior, porosity, and matrix density can be calculated, visualized, and reported numerically. The general aim of the present work is to introduce an example of QEMSCAN® analysis to image and quantify the distribution of mineral phases in metamorphic rocks, particularly in a thin section of a garnet-staurolite schist of the San Lorenzo Formation, Sevilla geological province (Sierra Nevada de Santa Marta massif). Specific objectives comprise the determination of the modal mineralogy based on a robust statistical dataset and the description of the mineralogical variation within this type of rocks, based on X-ray mapping. Furthermore, this study explores the advantages and limitations of QEMSCAN® applied to petrography.

## ANALYSIS METHODOLOGY AND WORKFLOW

A polished thin section of the garnet-staurolite schist was carbon coated before analysis in order to avoid electrical charging. Petrographic analysis was made under a trinocular Nikon (Labophot2-POL) transmitted light microscope to identify the rock-forming mineral phases. Mineral abbreviations are after Kretz (1983). Data were generated and processed using FEI's QEMSCAN® technology and iDiscover™ off-

line image analysis software of FEI's Center of Excellence for Natural Resources in Brisbane, Australia. The analyses were performed using a QEMSCAN® 650 FEG. The software package iDiscover consists of four software modules: Datastore Explorer (data management module), iMeasure (measurement module, SEM and EDS control), iExplorer (data processing and classification tools, mineral database management, reports), and SIP (Species Identification Protocol) editor. A summary of the QEMSCAN® system and its various application modes is provided by several authors (*e.g.*, Gottlieb *et al.*, 2000; Pirrie *et al.*, 2004; Goodall *et al.*, 2005; Pirrie and Rollinson, 2011). This instrument has been used with several versions of the iMeasure software for the data acquisition, and iDiscover software for the spectral interpretation and data processing. The measurements were collected in field-scan mode and X-ray data were collected at 10 and 2 µm of resolution. The QEMSCAN® was operated using an accelerating voltage of 20 kV and a specimen current of approximately 5 nA. A mineral list was created to capture all the mineral phases in the sample. All data are reported in volume percentage (% by weight) per sample. The method of analysis used was Field Image with a resolution of 2×2 or 10×10 µm. However, some higher resolution measurements were conducted to highlight some textural characteristics and compare the resolution vs. analysis time. The measurements were made using different electron beam stepping intervals (pixel size) in order to show the powerful capabilities of QEMSCAN®. Post-measurement processing of the frames were performed to create mosaic images using iDiscover. The obtained images were used to extract quantitative mineral and petrological data, such as modal proportions (in volume %), and matrix density.

## PETROGRAPHY

The studied garnet-staurolite schists of the San Lorenzo Formation are foliated, medium- to coarse-grained, pelitic rocks that generally show a millimeter-scale compositional banding consisting of alternation of lepidoblastic muscovite-biotite bands and coarse-fine grained granoblastic quartz-rich bands. The schistosity is mainly due to the alignment of individual grains of phyllosilicates and Fe-Ti oxides. The typical mineral assemblage is quartz + muscovite + biotite + garnet + staurolite (with minor apatite, zircon, graphite and Fe-Ti oxides). Garnet occurs as porphyroblasts (up to 5 mm diameter) along with staurolite, which develop shattered porphyroblasts in which mica and ilmenite parallel to the regional foliation wrap around garnet and mica and quartz occur in strain shadows. The small scale folding of the schistosity plane has produced a crenulation cleavage, accompanied by segregation of quartz into horizontal layers. The presence of porphyroblasts of garnet and staurolite disturbed the schistosity. Multiple deformations affected these pelitic rocks giving rise to interference patterns. Petrographic and microstructural evidence indicates that they are multiply deformed with at least three deformational events ( $D_1$ ,  $D_2$ ,  $D_3$ ), which progressively generated three schistositities ( $S_1$ ,  $S_2$ ,  $S_3$ ), associated to the mineralogical development of the host lithology of garnet porphyroblasts, which is illustrated in Figure 1.

This relationship between deformation and development of progressive schistosity surfaces has been reported in different studies (*e.g.*, Bell and Rubenach, 1983; Ríos *et al.*, 2003; Chattopadhyay and Ghosh, 2007; Vinagre *et al.*, 2016; Castellanos *et al.*, 2001, 2004, 2016a, 2016b; García *et al.*, 2017). Our observations suggest that during a first step of deformation ( $D_1$ ), the original structure of the protholith was affected as revealed by a first metamorphic foliation ( $S_1$ ). The deformation event  $D_2$  produced the main metamorphic foliation of the rock ( $S_2$ ), which is responsible of the mineral assemblage muscovite + biotite + quartz, representing the conspicuous stretching lineation. Garnet

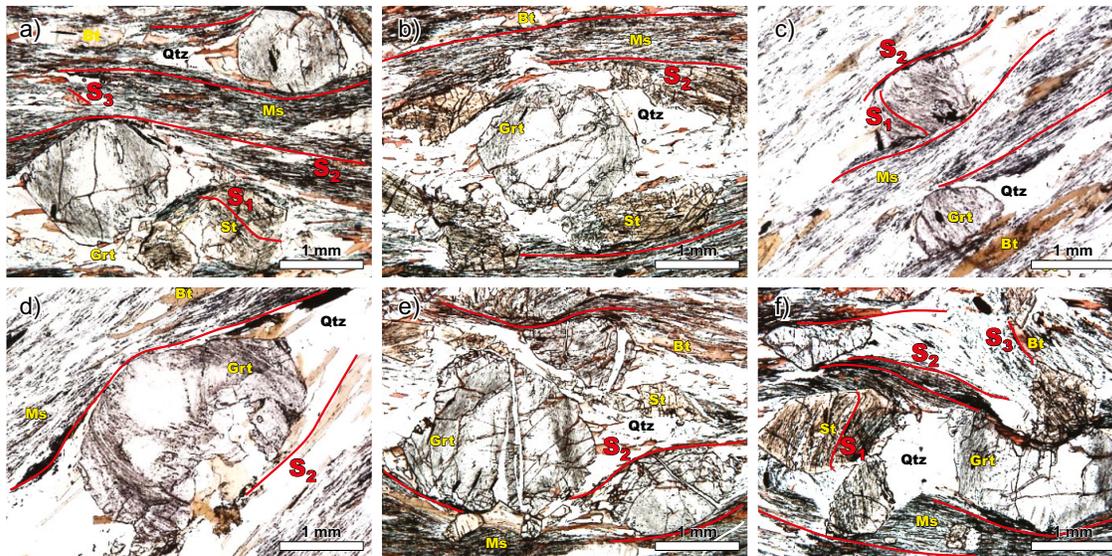


Figure 1. Photomicrographs to illustrate the structure and constituent minerals of a garnet-staurolite schist of the San Lorenzo Formation, Sierra Nevada de Santa Marta massif (Colombia), and the relationship of foliations and mineral growth. Qtz: quartz; Ms: muscovite; Bt: biotite; Grt: garnet; St: staurolite; S<sub>1</sub>: first schistosity; S<sub>2</sub>: second schistosity; S<sub>3</sub>: third schistosity.

porphyroblasts display a complex textural sector and sigmoidal zoning as reported by Castellanos *et al.* (2016a), with sectored core including radially arranged quartz without penetration of crenulated S<sub>1</sub> developed by quartz and ilmenite, which forms a low angle (approximately 30°) with the main foliation (S<sub>2</sub>). A large subhedral garnet porphyroblast, displays a penetrative crenulated S<sub>1</sub> (about 90° to the main schistosity - S<sub>2</sub>) and sigmoidal inclusion-pattern of quartz + ilmenite trails due to rotation during garnet growth. Garnet has been affected by tectonic dissolution. A deformation event D<sub>3</sub> promoted the formation of a late foliation (S<sub>3</sub>), which generated S-C structures (C-type shear bands) and nucleation of biotite, which were observed overimposed on the main foliation of the garnet-staurolite schists (S<sub>2</sub>).

## QEMSCAN<sup>®</sup> MINERAL MAPPING

### Mineral list

The Mineral List can be used to define the mineralogical data, simplify reporting or to highlight specific mineral phases (Rokosh *et al.*, 2016). Once the elemental concentration has been measured at each analytical point by the EDS detectors, the software automatically matches it with a library of mineral definitions, which are called Species Identification Protocols (SIPs) and are assembled in a SIP list (Worden *et al.*, 2018). A specific color is assigned to each mineral phase and the data points are combined to form a contiguous false color image of a specific mineral phase, and the quantification of mineral phases is carried out. Figure 2a shows the main mineral list used for mineral maps and quantification for the garnet-staurolite schist sample. QEMSCAN<sup>®</sup> can identify most rock-forming minerals in milliseconds by collecting their characteristic X-ray spectra, which are compared to entries in a dataset containing the SIPs. By providing quantitative and statistically reliable compositional information, automated mineralogy solutions such as QEMSCAN<sup>®</sup> have become important tools for characterizing rock-forming minerals. Table 1 summarizes measurements statistics for the QEMSCAN<sup>®</sup> analysis of the sample. For each pixel size a total of acquired X-ray data points of 6,285,575 for 10 μm and 2,342,991 for 2 μm were obtained to derive mineralogical data.

Mineral statistics were obtained from the sum of the number of pixels of each mineral phase and were normalised to provide a quantitative 2-D modal mineralogy (*e.g.*, Pirrie *et al.*, 2004; Ayling *et al.*, 2012; Worden *et al.*, 2018). Mineral mapping imposes a BSE grid with specific resolution (determined as “pixel spacing”) over the entire sample or specific mineral phase based on the BSE threshold (Hrstka *et al.*, 2018). Each pixel, which makes up the mineral map, represents an individual analysis point (Butcher *et al.*, 2000). The QEMSCAN<sup>®</sup> system scans a specific surface area, which is divided into a field grid. For each field, the electron beam performs the scan across the surface, collecting data at equidistant points in the X and Y directions. The system first takes an intensity reading of back-scattered electron (BSE) to measure the density of the mineral phases in the analyzed sample. The electron beam dwells at points where the BSE reading is above a certain threshold to allow the X-ray detectors to record a spectrum. Then, this spectrum is fed to the main mineral list used for mineral maps and quantification.

### Bulk modal mineral abundance

Prior to beginning this investigation, the garnet-staurolite schist sample was mineralogically characterized using conventional transmitted light microscopy (Castellanos *et al.*, 2016a). This work conducted in order to guide the setup of the phase identification parameters and to evaluate the accuracy of the final output. The imaging work conducted using a standard polished thin-section of the garnet-staurolite schist. Figures 2b and 2c show the QEMSCAN<sup>®</sup>-derived host rock mineralogy, highlighting the main features of the analyzed sample. The back-scattered electron image in Figure 2b illustrates the complex microstructural and textural features of the garnet-staurolite schist, whereas the false-colored image in Figure 2c reveals the distribution of the identified mineral phases. SEM-based automated mineralogy analysis includes the use of both BSE and X-rays signals, in conjunction with advanced image and pattern recognition analysis to successful provide quantitative mineralogical data. QEMSCAN<sup>®</sup> is a powerful technique that can be used in metamorphic petrology for identifying index minerals and describing the main microstructural and textural features, which is of great importance to determine the tectonic

history of metamorphic rocks. Index minerals may be few in number and present only as small inclusions making them difficult to identify by conventional petrography. On the other hand, the identification of relict minerals of earlier metamorphic assemblages and their relationship to the fabric of the metamorphic rocks is very important in thermobarometry and geochronology studies for deducing the previous segments of the pressure-temperature-time-deformation path (Fairhurst *et al.*, 2010).

The X-ray chemical composition map (Figure 3) of the garnet-staurolite schist reveals its typical regional metamorphic foliation, which is defined by platy minerals such as muscovite (dark pink) and biotite (green). Quartz (light pink) occurs in form of elongated, drawn-out grains. Locally, feldspars (dark turquoise) appear in granoblastic domains. Garnet porphyroblasts (moderated brownish red) are pseudo-hexagonal in cross-section. Staurolite porphyroblasts (brown) are elongated and show penetrating twinning. Ilmenite laths (brownish red) occurs as a matrix phase or as inclusions in garnet and staurolite porphyroblasts.

The quantification of modal phase abundances (modal mineralogy) presented in the legend of Figure 3 represents a quantum leap in the currently employed mineralogical analysis of the garnet-staurolite schist. The modal analysis (in wt %), which are presented in graphic and tabular form on the right side of Figure 3, reveals that the sample contains major quartz (33.53%) and muscovite (22.76 %) and minor staurolite (13.87 %), biotite (10.78 %) and garnet (8.59 %), feldspars (3.34 %) and other silicates (5.69 %). Trace amounts (< 1%) of ilmenite, phosphates, Fe-oxide/hydroxide and rutile/anatase are also present. There is a portion of the scan that is not classified (referred to as Other). It does not mean that the elemental composition of these points is unknown, simply that there was no mineral definition in the SIP that was consistent with the measured spectra (*e.g.*, Ayling *et al.* 2012; Qian *et al.* 2015). Typically, these points reflect boundary phases between mineral grains, where the X-ray spectra generated are composite signals, although it may represent mineral species that are not defined in the SIP library (Ayling *et al.*, 2012). This also demonstrates the spatial distribution of mineral phases over a defined area of a thin section, and provides quantitative

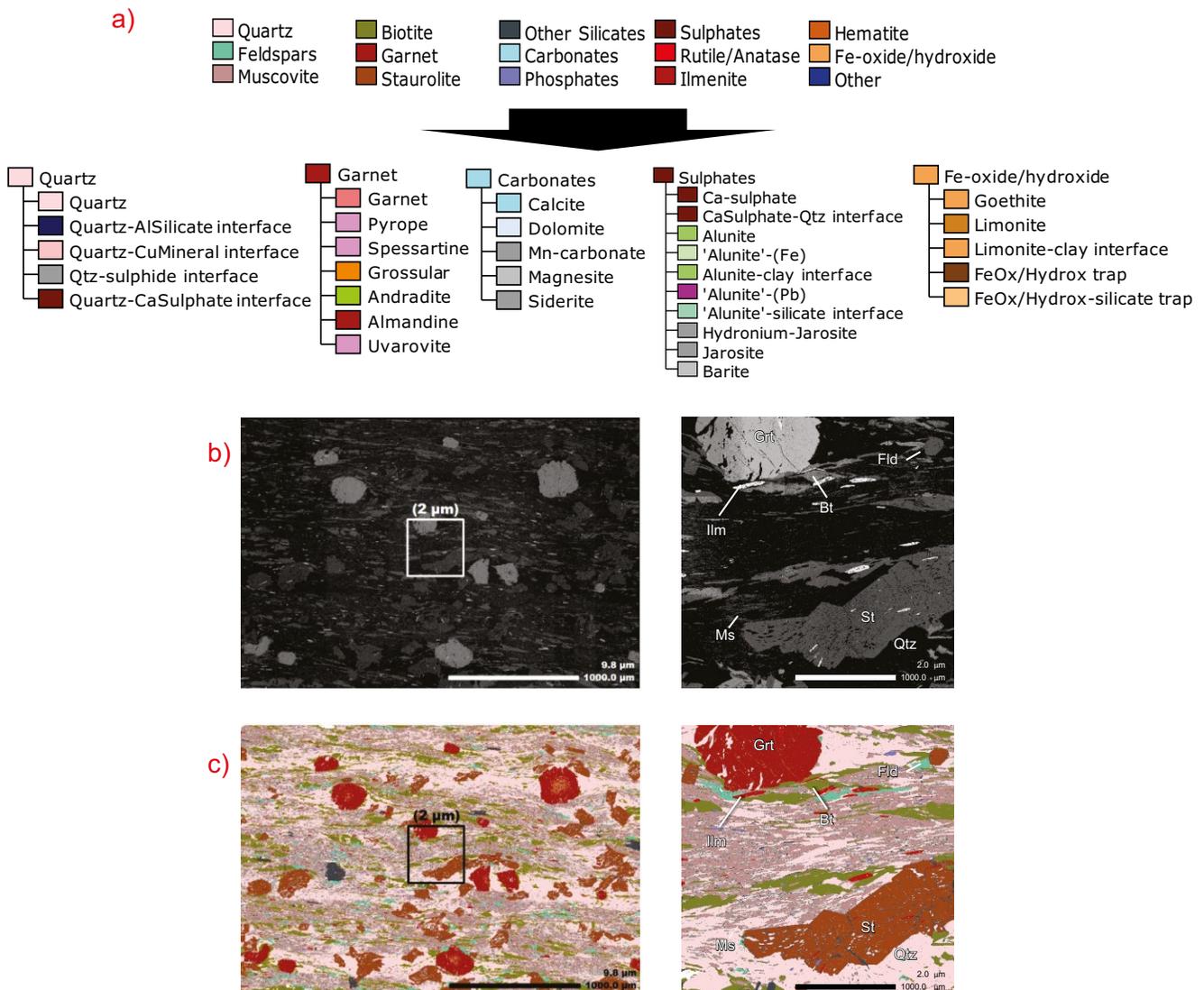


Figure 2. a) Main mineral list used for mineral maps and quantification. b) QEMSCAN backscattered electron image of the garnet-staurolite schist. (c) QEMSCAN false-colored image analysis of the garnet-staurolite schist. In (b) and (c) the images on the right side correspond to the box shown in the images on the left side. Qtz: quartz; Ms: muscovite; Bt: biotite; Grt: garnet; St: staurolite; Ilm: ilmenite; Fld: feldspar.

Table 1. Measurements statistics.

Measurement	Measurement mode	Elapsed (h:m:s)	Measured fields	Field height (points)	Field width (points)	Field size ( $\mu\text{m}$ )	X-ray counts	Total acquired X-ray (points)
10 $\mu\text{m}$	Field image	08:35:07	667	100	100	976.8	1000	6285575
2 $\mu\text{m}$	Field image	02:13:02	9	500	500	976.8	1000	2342991

modal abundance data. Information obtained from this study augments mineralogical results obtained by optical microscopy and by electron microprobe, and provides a quantification of the mineralogy for specific applications. The analysis software also determined that staurolite (115.19  $\mu\text{m}$ ) and quartz (52.72  $\mu\text{m}$ ) show the largest average grain sizes.

QEMSCAN<sup>®</sup>-based analysis procedure for characterizing minerals can provide a distinct advantage over techniques, where the detection limits do not allow for identification of most of the minor mineral phases (Benvie, 2007). However, according to Goodall and Scales (2007), QEMSCAN<sup>®</sup> as other analytical techniques are continuously challenged in order to obtain representative results, but a good understanding of their limitations can allow complementary techniques to be employed, validating the results and providing a comprehensive background of the mineralogy. In order to evaluate this, an additional quantitative elemental method like Electron-Probe Microanalysis (EPMA) should be considered, taking into account its tremendous impact on research in the geological sciences. QEMSCAN<sup>®</sup> analysis coupled with EPMA can be used to identify and quantify the mineralogy of metamorphic rocks and define the distribution of mineral phases. EPMA provides quantitative information about chemical composition of rock-forming minerals and allows estimating the relative mineral abundances (*e.g.*, Pirrie *et al.*, 2004; Reed, 2005; Goldstein *et al.*, 2018). However, EPMA can be time consuming, especially when looking for trace minerals.

### Element maps

The iDiscover software enables fast generation of single-element SIP. The element-percentages that are generated in this way are not

absolute concentrations and can only be used in a relative sense. Absolute concentrations of elements can be achieved once matrix effects on X-Ray generation have been resolved. Matrix effects include absorption (A) and fluorescence (F) in the sample, and electron backscattering and penetration, which vary with atomic number (Z) (Ayling *et al.*, 2012). These aspects form the basis of the ZAF corrections that are applied to raw X-ray data to extract quantitative elemental information, however, matrix effects and performance of ZAF corrections on mixed spectra will be addressed in a future study. Element maps show the spatial distribution of elements in a sample. Maps of different elements over the same area can help to determine what phases are present. Element maps give a complete 2D picture of the chemical zoning of a mineral, which is more informative than a simple traverse line. Element maps are recorded digitally and can be saved to use as sample maps for locating spot analyses. Software capacities aim at showing the variability and flexibility of information that can be delivered by QEMSCAN<sup>®</sup>. This in addition to the information provided above related to the garnet-staurolite schist.

Garnet is one of the most studied minerals in relation to chemical variations in metamorphic rocks (Ríos *et al.*, 2008), providing very valuable information on the mechanisms of crystal nucleation and growth because they usually contain internal textural zones and inclusion patterns that can help in correlating the timing of garnet growth with deformation and metamorphism (*e.g.*, Rice and Roberts, 1988; Williams, 1994). In addition, they show chemical zoning preserve a record of their growth history (*e.g.*, Takasu, 1986).

Chemical zoning maps of the elements iron (Fe) and calcium (Ca)

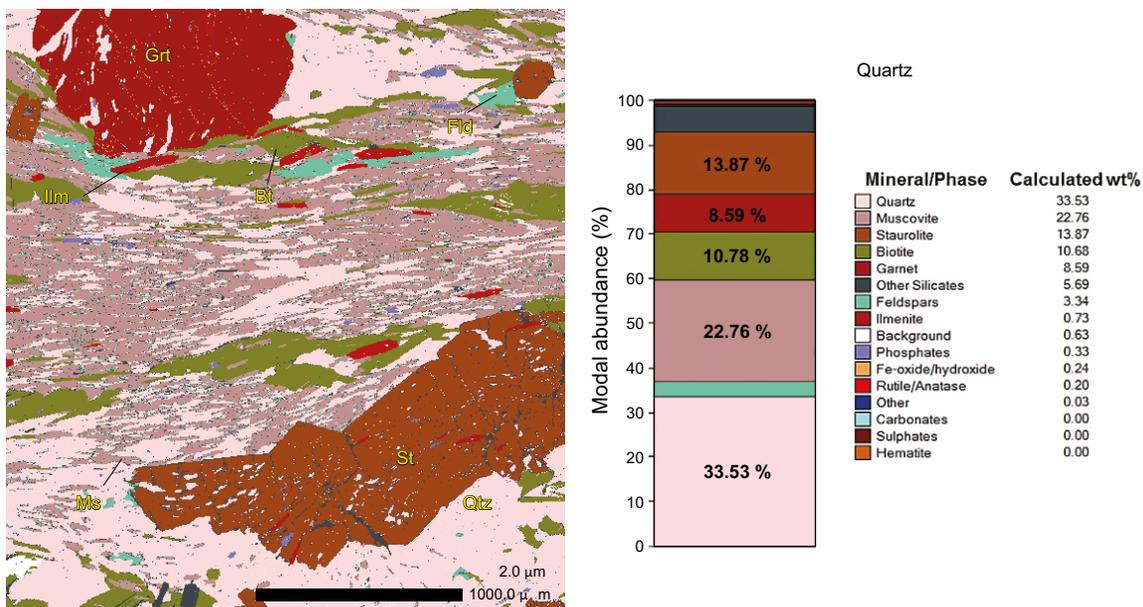


Figure 3. Mineral map of the garnet-staurolite schist thin section produced using a QEMSCAN (2  $\mu\text{m}$  pixel spacing). The legend indicates the identified phases, as well as their calculated modal abundances in wt%. Qtz: quartz; Ms: muscovite; Bt: biotite; Grt: garnet; St: staurolite; Ilm: ilmenite; Fld: feldspar.

for a garnet crystal are shown in Figure 4a. In general, garnet shows simple prograde zoning and simple shape. Each map includes the scale used as chemical zoning levels, and these can be adapted according to the requirements and/or conditions of the case. We consider that garnet displays normal zoning probably as result of growth under low- to medium-grade metamorphism during a progressive phase as suggested by several authors (e.g., Harte and Henley, 1966; Hollister, 1969; Ikeda, 1993; Spear, 1993; Castellanos *et al.*, 2008; Ríos *et al.*, 2003, 2008).

Chemical zoning maps of the elements iron (Fe) and calcium (Ca) and manganese (Mn) for the same garnet crystal are shown in Figure 4b. Unlike zoning maps presented above (which were based on the method of intensity and a X-ray peak count of 1000), we show now chemical zoning maps and elemental concentration measurement done with 10000 X-ray counts in a selected garnet from the garnet-staurolite schist. Garnet shows a complex zoning and shape, which reveals amoeba-like and sector zoning. Amoeba-like zoned garnet shows a similar chemical zoning for Mn as that reported by Ríos *et al.* (2010). According to Daniel and Spear (1998), it can reveal multiple nuclei formed simultaneously in the core region, with nuclei expanding by growth in amoeba-shape forms along preexisting mineral grain boundaries. However, it is not clear that there are distinct nuclei, taking into account the Ca distribution in garnet. Therefore, we agree with Ríos *et al.* (2010) in the sense that the zoning pattern of the core suggests dissolution, diffusion modification and overgrowth of a single grain at intermediate stages of metamorphism (*i.e.*, before the outer Mg-rich rim was formed). On the other hand, the occurrence of sector zoned garnets has been reported by several authors (e.g., Wilbur and Ague, 2006; Rice *et al.*, 2006; Stowell *et al.*, 2011). The origin of this type of garnet has been associated with a source of heat as a result of the syn-tectonic emplacement of intrusive bodies of different composition in the late stages of metamorphism (e.g., Shirahata and Hirajima, 1995; Castellanos *et al.*, 2004, 2016a). After a higher resolution analysis, we agree with Castellanos *et al.* (2016a) with respect to the nucleation and growth process of the textural sector- and sigmoidal-zoned garnet of interest in the present study, which reveal that it probably was developed during the late emplacement of gabbroic rocks of the Santa Marta Batholith close to the peak regional of metamorphism of the San Lorenzo Schists. It is significant for the discussion on the nucleation and growth mechanism of this type of garnets as a key piece for interpretation of the tectono-metamorphic history of this metamorphic unit.

#### ADVANTAGES AND DISADVANTAGES OF QEMSCAN®

The characterization techniques for geological materials have advanced every day in search of greater effectiveness when conducting different studies for integrating data at different scales. QEMSCAN® is used as a complementary tool to support conventional petrographic methods for mineralogical determinations, such as transmitted and reflected light microscopy, scanning electron microscopy, Electron Probe Microanalysis, and X-ray diffraction. It has several advantages over conventional methods of mineralogical determination due to its robust mineral recognition library and ability to perform numerous types of analysis per run with short yielding times (e.g., Pirrie *et al.*, 2004; Pirrie *et al.*, 2009; Knappett *et al.*, 2011; Allen *et al.*, 2012).

QEMSCAN® is very useful for quantitative evaluation of minerals by scanning electron microscopy from which it is possible to get several advantages when analyzing different materials with details that otherwise they may be overlooked with other techniques. However, such research facilities are more expensive and less affordable. QEMSCAN® is an automated system that allows the determination of the mineral

and chemical composition of a mineral (Jordens *et al.*, 2016), which traditionally cannot be carried out through conventional microscopy. In this study case, we highlight the use of QEMSCAN® as an automated mineralogy system in the characterization of metamorphic rocks, as well as the advantages offered by this type of research technology in the characterization of geological materials. We intend to put in context the diversity of characterization techniques that exist and the importance of not being satisfied with the traditional ones, given the knowledge about them and their usual use.

The novelty and scientific value of the present work is the use of QEMSCAN® as an automated mineralogy solution that integrates largely automated measurement techniques based on scanning electron microscopy and energy-dispersive X-ray spectroscopy, which can be applied in different fields of scientific knowledge. The advantages of automated systems, such as QEMSCAN®, are their statically robustness, reliable mineral identifications, round-the-clock operations, high throughput, multiple applications with high degree of flexibility, multiple measurements modes, built-in quality-control programs, and data/information that can be used by geologists, metallurgists, mining engineers, chemists, material scientists, and accountants (Fennel *et al.*, 2005). One of its most notable advantages is the preparation of mineral maps in order to represent the chemical composition of a mineral phase by assigning a specific color, which facilitates the visualization and management data.

One of the important points by the integration conventional analysis with QEMSCAN® is to address the limitations related the observation scale, working time and accuracy in order to provide reliable results in the mineralogical and chemical analysis of geological materials. Transmitted light microscopy of metamorphic rocks can reveal their mineralogy and microstructural and textural features, but is not effective in resolving or quantifying the mineralogy of this type of rocks. The principal problem when using transmitted light microscopy is that it is only possible to determine, with any certainty, links between a relatively small array of elements and most of the rock-forming minerals. On the other hand, the modal analysis by conventional petrography is normally based on 300 point counts or less, and there is always some uncertainty (approximately 5–10 % or more) regarding the data resolution and estimation of mineral content.

It is well known that the quantification of mineral phases can be performed by X-ray diffraction analysis using the Rietveld method, a rapid and accurate quantitative technique, which has been reported in several works (e.g., Taylor and Matulis, 1991; Weidler *et al.*, 1998; Henao *et al.*, 2010). Quantitative analysis by the Rietveld method (e.g., Rietveld, 1969) has huge advantages over traditional methods using integrated intensities of a small set of reflections in limited angular intervals, since the overlap of the lines of a pattern of powder diffraction, especially in mineralogically complex samples, make it virtually impossible to carry out a rigorous analysis by conventional methods (Henao *et al.*, 2010). However, the disadvantage of the X-ray diffraction analysis is that although the presence of specific mineral phases is frequently recorded with a high degree of certainty, the quantitative data will likely have low resolution and resolution. In other cases, the comparison of peaks of the X-ray diffraction patterns with the standard line patterns from the Powder Diffraction File database supplied by the International Centre for Diffraction Data (ICDD) can reveal mineral phases, for which the interpreter must determine whether or not they are present in the analyzed sample.

Scanning electron microscopy is a useful analytical technique for observing minerals in a high resolution. The main advantage of this type of microscopy is to achieve an extraordinary amplification of the sample image while maintaining a resolution power almost a thousand times greater than that of transmitted light microscopy. One

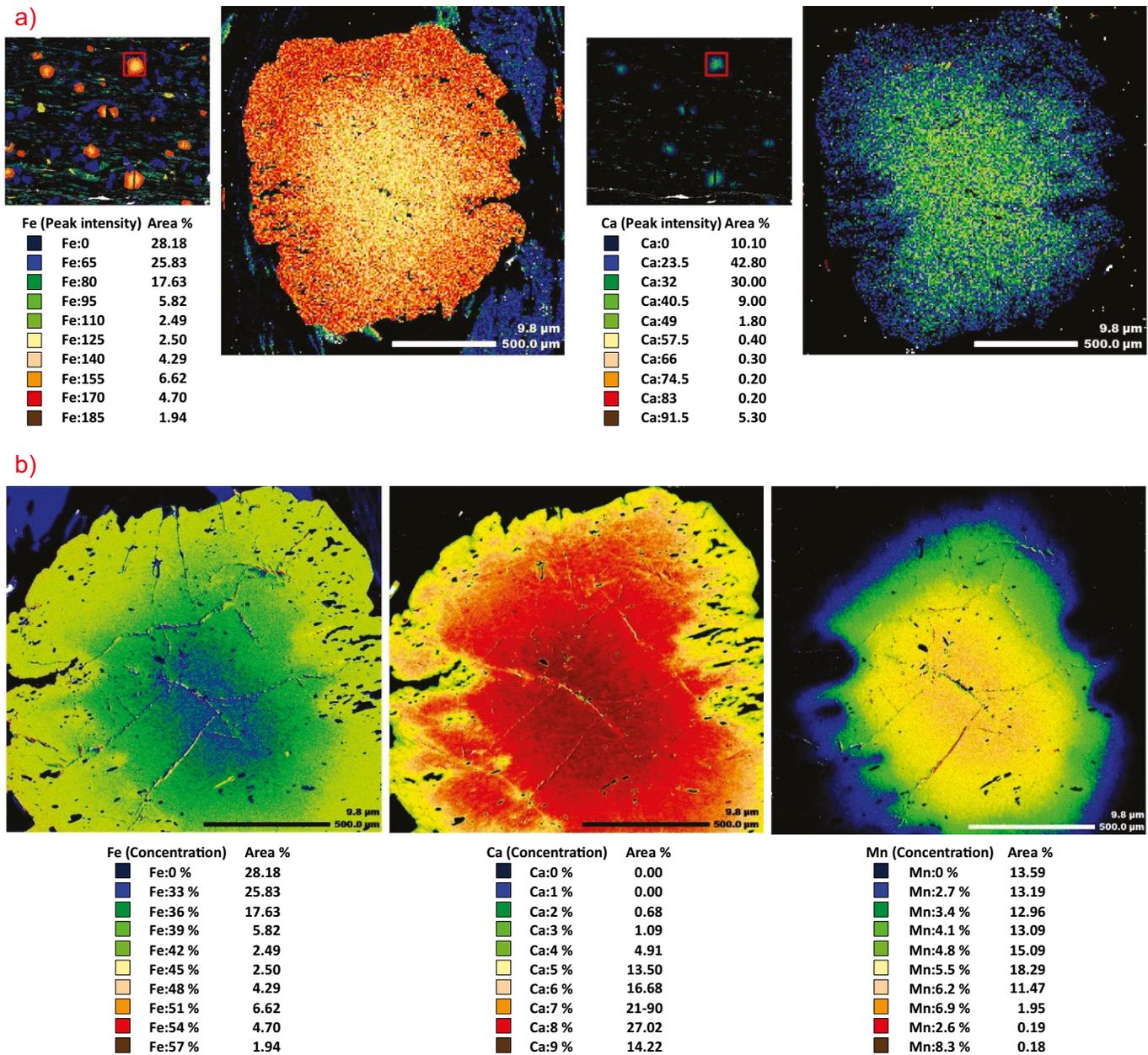


Figure 4. a) Fe (left) and Ca (right) chemical zoning in garnets. b) Fe, Ca and Mn chemical zoning in garnets. Image (a) reveals relative elemental concentrations based on peak intensities at a lower resolution, and image (b) shows absolute concentration at higher resolution. The blue colour represents low concentrations and the red colour represents high concentrations.

of the great advantages over other types of microscopy is the ease of sample preparation. The disadvantages of this analytical technique include environmental rigor for its correct operation, high acquisition and maintenance costs or the sample size that hinders its movement, among others. A disadvantage against the QEMSCAN<sup>®</sup> system is that the determination of the chemical composition of a mineral phase can only be carried out semi-quantitatively as well as the limits in the scale and size of the samples that can be analyzed.

QEMSCAN<sup>®</sup> gives the quantitative modal mineralogical data to trace mineral levels, calculated chemistry, mineralogical association, elemental behavior with mineralogical map of the sample (Pascoe *et al.*, 2007). It creates phase assemblage maps of a specimen surface scanned by a high-energy accelerating electron beam along a predefined raster

scan pattern. Low-count energy-dispersive X-ray spectra (EDX) are generated and provide information on the elemental composition at each measurement point. The elemental composition in combination with back-scattered electron (BSE) brightness and X-ray count rate information is converted into mineral phases (Gottlieb *et al.*, 2000). QEMSCAN<sup>®</sup> data includes bulk mineralogy and calculated chemical assays. By mapping the sample surface, textural properties and contextual information such as particle and mineral grain size and shape, mineral associations, mineral liberation, elemental department, porosity, and matrix density can be calculated, visualized, and reported numerically. The main benefit of the method exposed here is the spatially resolved mineralogical data inferred from chemical spectra, which provides increased information on mineral species (particularly with respect to

trace minerals), quantitative and statistically valid data on ore mineral abundances, particle size and shape distributions, and quantitative data on mineral associations (Rollinson *et al.*, 2011). No other analytical technique, or combination of techniques, can easily replicate the ability of QEMSCAN® to identify, image and quantify different mineral phase in thin section within relatively short times (Worden *et al.*, 2018). However, it is very important to perform a quantitative validation of the QEMSCAN® analyses, which despite offering significant advantages over traditional bulk compositional and mineralogical methods, should be compared by EPMA. The SIP can be calibrated to quantitative compositional data obtained by EPMA (Andersen *et al.*, 2009). The main disadvantage of QEMSCAN® is that it is a very expensive tool and there are few equipment available. The QEMSCAN® technique is not capable of differentiating diverse textural forms of the same mineral and, therefore, images need to be compared with the output of other techniques, such as optical microscopy or cathodoluminescence images, and it cannot differentiate mineral phases with the same chemical composition (Worden *et al.*, 2018).

EPMA provides enormous analytical advantages for mineralogists and petrologists (*e.g.*, McGee and Keil, 2001; Lisowiec, 2005). The impact generated by such analytical technique is evident not only by the abundant existing geological literature (*e.g.*, Hickmott and Spear, 1992; Chernoff and Carlson, 1997; Ríos and Takasu, 1999; Spear and Daniel, 2001; Spiess *et al.*, 2001; Ríos *et al.*, 2003, 2008, 2010; Meth and Carlson, 2005; Castellanos *et al.*, 2004, 2008; García *et al.*, 2017) but also by the proliferation of the technique in laboratory analytical facilities worldwide. Garnet is the most studied metamorphic mineral using EPMA due to its distinct chemical zoning and broad range of variability in terms of significant end-members of the solid solution, providing data to constrain the P-T-t evolution of metamorphism in orogenic belts (Florence and Spear, 1993). It is a non-destructive analytical technique, which allows qualitative and quantitative analysis of individual mineral grains a few micrometers in diameter; identification of mineral grains and textural features of interest for chemical analysis; characterization of chemical zoning in minerals, mineral inclusions, and exsolution lamellae; development of a large number of quantitative analyses in a relatively short time; addition of several wavelength dispersive spectrometers (WDS) to electron column. However, EPMA also has limitations (Thomas *et al.* 2017): it is unable to detect the lightest elements (H, He and Li) and, therefore, H<sub>2</sub>O in hydrated mineral phases cannot be analyzed; X-rays sometimes generate overlapping peak positions that must be separated; data are reported as oxides and not as cations, therefore, cation proportions and mineral formulae must be recalculated by stoichiometry; cannot distinguish between the oxidation states of Fe and, therefore, so the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio cannot be determined and must be determined by other techniques.

Although automated petrography systems are commonly used worldwide, only a few research facilities are equipped with a QEMSCAN® system. Nevertheless, it is expected that this technique will grow in popularity in such a way that it becomes more attractive for the geoscientific community, recognizing the need to appeal to this latest generation technology in the petrographic characterization of rocks. However, it is important to consider that the experience of the petrographer is necessary at the time of interpreting the data obtained in any of the cases since there may exist several discrepancies on the identification of a specific mineral phase.

## CONCLUSIONS

The present work shows how QEMSCAN® technology can be used as an input to metamorphic petrology. By studying the mineralogy and

getting quantitative data on mineral phases, petrological constrains can be determined. The QEMSCAN® can give information about mineral associations, elemental behavior to different minerals in a sample, mineral sizing information, and mineral assemblage of a sample. These analyses are over and above the visual mapping of particles in a sample. This paper presents a study case to illustrate the value of the technique to augment conventional microscopy analysis of metamorphic rocks. It is concluded that QEMSCAN® can be used as a powerful analytical technique can add value to petrology studies.

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