

## X-ray color maps of the zoned garnets from Silgará Formation metamorphic rocks, Santander Massif, Eastern Cordillera (Colombia)

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### ABSTRACT

The metamorphic rocks of the Lower Paleozoic Silgará Formation of the Santander Massif, Eastern Cordillera (Colombia), were affected by a Barrovian-type metamorphism under low to high temperature and medium pressure conditions. These rocks contain garnet porphyroblasts, which show several kinds of chemical zoning patterns. The garnet grains behave as closed systems with respect to the rock matrix. Most of the observed zoning patterns are due to gradual changes in physicochemical conditions during growth. However, some garnet grains show complex zoning patterns during multiple deformation and metamorphic events.

*Keywords:* Metamorphic rocks, Silgará Formation, Santander Massif, zoned garnets, physicochemical conditions

### RESUMEN

Las rocas metamórficas de la Formación Silgará del Paleozoico Inferior del Macizo de Santander, Cordillera Oriental (Colombia), fueron afectadas por un metamorfismo tipo Barroviano bajo condiciones de temperatura baja a alta y presión intermedia. Estas rocas contienen porfiroblastos de granate, los cuales muestran varios tipos de patrones de zonación química. Los granos de granate se comportan como sistemas cerrados con respecto a la matriz de la roca. La mayoría de los patrones de zonación observados son debidos a cambios graduales en las condiciones fisicoquímicas durante el crecimiento. Sin embargo, algunos granos de granate muestran patrones de zonación complejos durante múltiples eventos de deformación y metamorfismo.

*Palabras clave:* Rocas metamórficas, Formación Silgará, Macizo de Santander, granates zonados, condiciones fisicoquímicas.

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### Introduction

Chemical zoning in metamorphic rocks has been widely studied since it preserves a chemical record of its growth history in rocks of very different chemical compositions and over a wide spectrum of metamorphic conditions. Garnet often shows a distinct chemical zoning and a 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). Previous studies reveal that the growth zoning of garnet is controlled by several processes: (1) diffusion-controlled growth (Chernoff and Carlson, 1997; Spear and Daniel, 2001; Meth and Carlson, 2005), (2) differences in the degree of achievement of equilibrium for different elements (i.e., partial equilibrium) and heterogeneities in rock composition (i.e., local equilibrium) (Meth and Carlson, 2005), and (3) effect of multiple nuclei (Daniel and Spear, 1998; Spiess et al., 2001). All these processes occur during crystal growth.

Diffusional reequilibration is the only post-growth process that leads to zoning in minerals (Schwandt et al., 1996; Fraser et al., 2000; Ríos et al., 2008). Garnet zoning may also be affected by fluid-infiltration (open systems) and deformation (Erambert and Austrheim, 1993; Skelton et al., 2002), and these processes may be coupled for deformation changes grain size and reorganizes grain boundaries, affecting rates and pathways for fluid-mediated diffusion (Kim, 2006). Williams (1994) suggested a metamorphic/deformation-controlled porphyroblast growth model where the growth-rate changes are controlled by microstructure development that is manifested by compositional and textural zoning. Garnet zoning patterns can be symmetrical or asymmetrical (Hickmott and Spear, 1992). Duebendorfer and Frost (1988) suggested that an original zoning pattern can be modified and truncated by development of schistosity due to selective dissolution during shearing, and Kim (2006)

indicated that zoning in garnet porphyroblasts can be modified by the development of surrounding foliations and by associated preferential dissolution and precipitation effects. Therefore, truncated/overgrown zoning patterns may provide crucial information to elucidate the growth-deformation history of garnet and the mechanism by which they develop in (poly)metamorphic rocks.

Garnets of metapelitic rocks from the Silgará Formation of the Santander Massif provide an opportunity to study the nature of crystal growth, taking into account that they are chemically heterogeneous and retain a record of their growth history, and chemically heterogeneous and retain a record of their growth history, and contain microfabrics that aid in relating periods of garnet growth/dissolution to periods of deformation. Several types of garnet chemical zoning have been reported in these rocks, which, in addition to microfabrics, were used for reconstruction of P-T-deformation paths during orogenesis (Ríos, 1999; Ríos and Takasu, 1999; Castellanos, 2001; Ríos et al., 2003a, 2003b, 2008; García et al., 2005; Castellanos et al., 2004, 2008). This paper focuses on the relationship between microfabrics and chemical zoning patterns of garnets of the metamorphic rocks of the Silgará Formation.

## Geological setting

The Santander Massif (Eastern Cordillera of Colombia) comprises an early Paleozoic metamorphic complex composed of the following geological units: Bucaramanga Gneiss Complex, Silgará Formation and Orthogneiss, which are intruded by several igneous bodies, most of them of Triassic-Jurassic age (Goldsmith et al., 1971; Boinet et al., 1985; Dörr et al., 1995). Figure 1 shows a generalized geological map of the Santander Massif. The metamorphic history of this massif is important for interpretation of the geologic and tectonic evolution

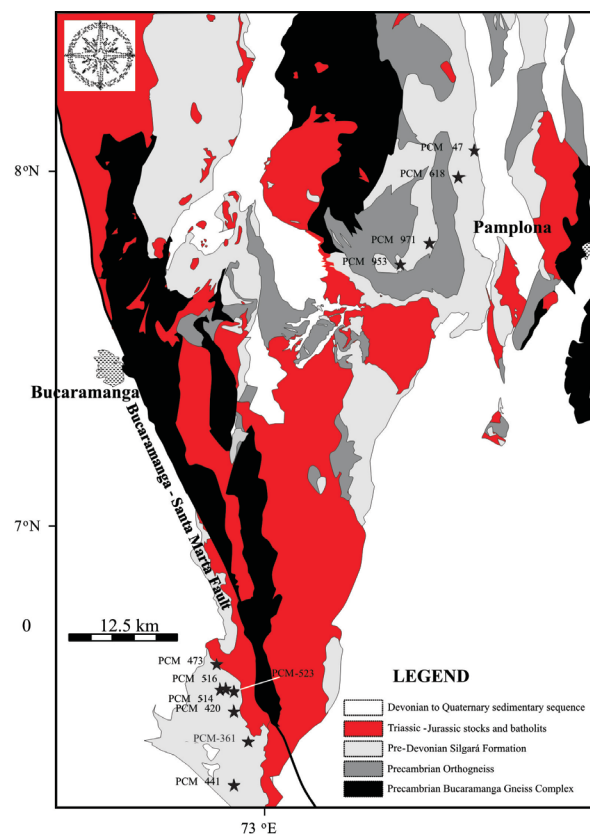
of the northwestern continental margin of South America (Ríos et al., 2008). The rocks of interest in this study are garnet-bearing pelites of the Lower Paleozoic Silgará Formation, which has been studied in detail by Ríos and co-workers (Ríos, 1999; Ríos and Takasu, 1999; Castellanos, 2001; Ríos et al., 2003a, 2003b, 2008; García et al., 2005; Castellanos et al., 2004, 2008). The Silgará Formation was affected by Caledonian regional metamorphism under low- to high-temperature and medium-pressure conditions (400-700 °C and 4.0-7.5 kbar), with the distinction of the biotite, garnet, staurolite-kyanite and sillimanite zones (Ríos et al., 2003a, Castellanos et al., 2008). Well-exposed sections of this metamorphic unit crop out at the Santander Massif (Figure 1), which is long established as classic area for the study of rock metamorphism and deformation caused by continental collision during the Caledonian orogeny (Ríos et al., 2008).

## Analytical procedures

X-ray maps were collected using the JEOL 8800 electron probe microanalyzer of the Geoscience Department at the Shimane University (Japan). The analytical conditions were as follows: 15 kV accelerating voltage, 25-75 nA beam current, 40-80 msec/pixel dwell time. Full details on garnet analyses and continuous traverses for elemental distribution were presented in previous studies (Ríos, 1999; Castellanos, 2001; Ríos et al., 2003a; García et al., 2005; Castellanos et al., 2008).

## Chemical zoning maps

In this study, we reveal a number of important observations regarding the major element zoning and its correlation with microfabrics in garnet-bearing



**Figure 1.** Generalized geological map of the Santander Massif modified after Ward et al. (1973), showing the regional distribution of metamorphic rocks of the Silgará Formation, showing locations of the investigated garnet-bearing pelites (white stars).

pelites of the Silgará Formation at the Santander Massif. Representative analyses of garnet are given by Ríos (1999) and Castellanos (2001). Garnet is almandine rich with minor pyrope, grossular and spessartine. Most garnet grains exhibit typical growth zoning patterns, except for the sillimanite zone sample, which shows a diffusion dominated zoning profile. Garnet in amphibole-bearing assemblages is richer in grossular than that in amphibole-free assemblages. X-ray color maps reveal that Mn and Mg zoning is likely related with to smooth changes in P-T conditions during prograde and retrograde metamorphism and, hence, the distribution of these elements are controlled by local equilibrium. However, zoning in Ca exhibits variable trends. In some cases, Ca and Mn-Mg zoning patterns are spatially related, suggesting that the main process that controlled the distribution of Ca is equilibrium. In most cases, however, it is generally unrelated to zoning patterns in Mn and Mg, in agreement with observations by Spear and Daniel (1998), suggesting additional processes. In these cases, we interpret the distribution of Ca as a result of the complex interplay of equilibrium and the diffusive transport of Ca from the rock matrix to the growing grains of garnet. A discussion of examples of chemical zoning in garnet, which are illustrated in Figures 2-13, is presented below.

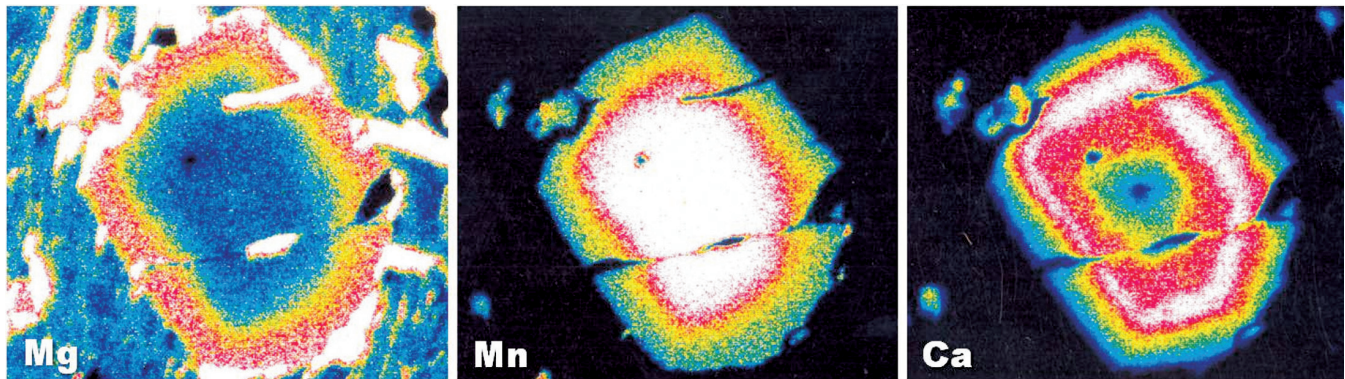
### Garnet zone

As shown in Figure 2 (sample PCM-441), the most striking characteristic of garnet is the high Mn concentration, which from core to rim varies from 52,2 to 24,9 mol% spessartine. Mg increases from core to rim (3,9 to 9,7 mol%).

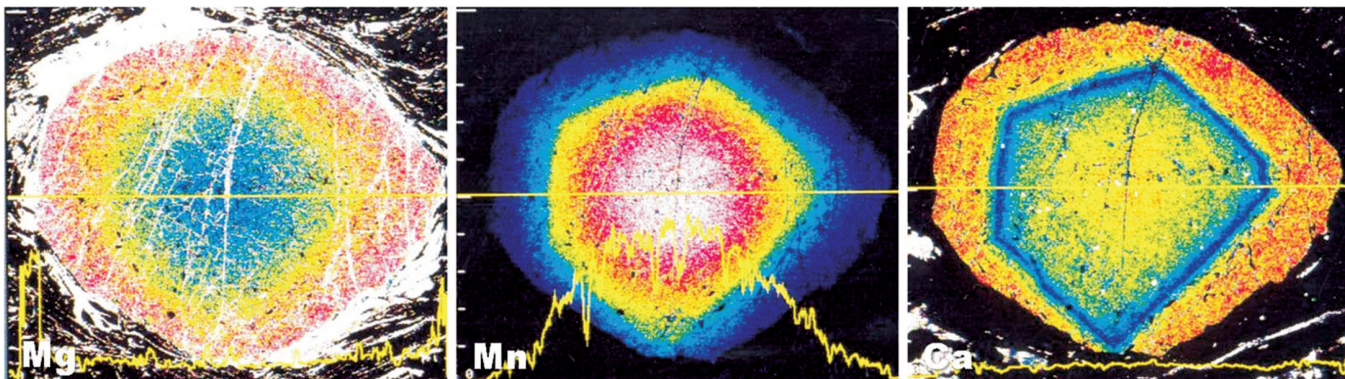
Garnet has a low-Ca core (7,2 mol%) with an inflection midway (13,9 mol%), developing a pseudo-hexagonal band, between core and rim, decreasing towards the rim (7,8 mol%). According to Spear (1993), a change in chemical zoning character from growth zoning to diffusion zoning by progressive homogenization is attributed to diffusion with increasing metamorphic grade.

### Garnet-Stauroilite zone

As shown in Figures 3-4, Ca and Mn-Mg zoning patterns are spatially related. Garnet from sample PCM-361 (Figure 3) is strongly zoned in Mn, which decreases from 20,1 mol% in the core to 1,6 mol% in the rim. Mg increases from core to rim (6,4 to 10,8 mol%). Ca decreases from core (5,0 mol%) towards a low-Ca annulus (1,8 mol%) with a sharp pentagonal outline, developing a slight discontinuity in the zoning midway between core and rim; then increases towards the rim (5,5 mol%). At the lower end of the garnet grain, the low-Ca annulus is truncated against the matrix (biotite), suggesting dissolution during foliation development, although this feature is not observed in the opposite upper end of the garnet grain. The qualitative line scan through the interior of the grain suggests that zoning in Ca is smooth whatever the process that formed this zoning pattern, the consequences for garnet zoning were mild. The high Ca / low Mn rim zone contains apatite, monazite and ilmenite aligned parallel to the margins of the garnet, whereas the cubedral low-Ca annulus within the garnet corresponds to a change in mineral inclusion abundance, but does not correspond to a change in the mineral inclusion assemblage itself. The low-Ca annuli should be assumed as a reaction boundary,



**Figure 2.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the smallest garnet porphyroblast in sample PCM-441, which is a pelitic schist from the garnet zone characterized by a mineral assemblage of muscovite + quartz + plagioclase + garnet ± biotite, with minor K-feldspar, tourmaline, apatite, zircon, epidote, calcite and Fe-Ti oxides.



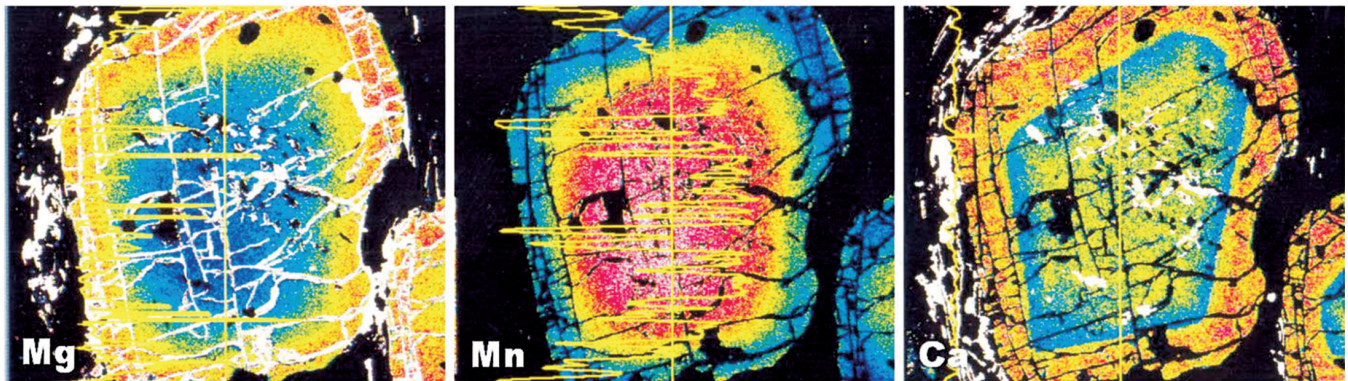
**Figure 3.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-361, which is a pelitic schist from the garnet-stauroilite zone characterized by the peak metamorphic assemblage of quartz + plagioclase + muscovite + biotite + garnet + stauroilite, with minor phases such as ilmenite, apatite, monazite, xenotime, zircon and rutile. Numerous inclusions of ilmenite define different patterns of distribution. Garnet diameter = 3.25 mm. Warm colors correspond to higher concentrations.

which is a function of P-T-X. If the variation in Ca is related to episodic reaction (consumption) of Ca-bearing minerals the nature of inclusion may change. Garnet from sample PCM-516 (Figure 4) shows a decrease in Mn from core (22,5 mol%) to rim (15,3 mol%). Note a small reversal in zoning near the rim. Mg increase from core to rim (12,0 to 16,1 mol%). Mg and Mn distributions show strongly negative correlation each other, whereas Ca distribution is not. Ca decreases outwards (5,3 to 3,6 mol%) and reaches a low-Ca annulus with sharp pentagonal outline at mid-region (3,6 mole %); then increases towards the rim (6,3 mol%).

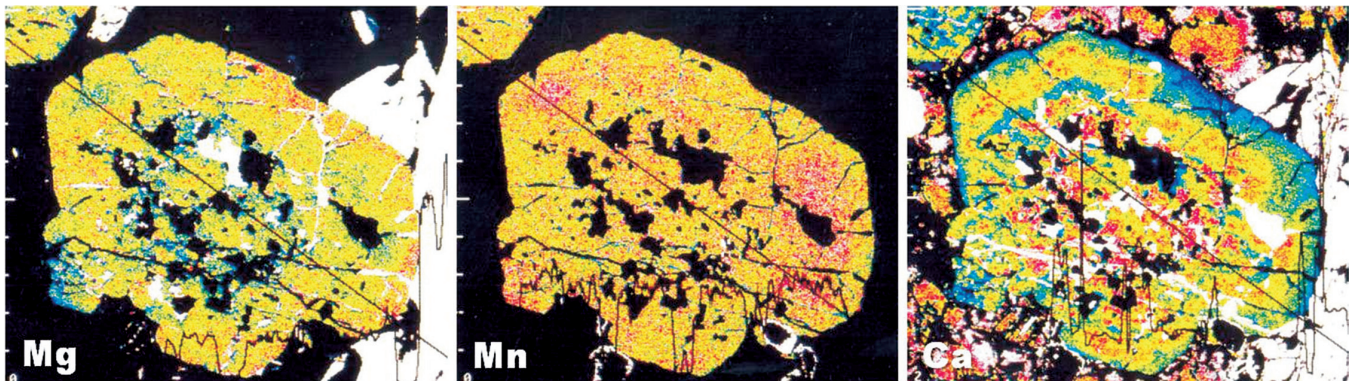
It is well known that changes in the reactant and product assemblages occur at different times and at different sites during the reaction history of garnet crystals of different size and, therefore, their effects they cannot only be the result of events affecting the entire rock, such as a change in pressure, temperature or fluid composition. These effects reflect kinetic factors that cause elements (notably Ca) to fail achieving full chemical equilibrium during garnet growth (i.e., partial equilibrium, Ríos et al., 2008). We consider that inclusion-free rims and inclusion-rich cores, supported by the occurrence of low-Ca annuli lacking inclusions in garnet (e.g., PCM-361, Figure 3, and PCM-516, Figure 4), cannot be assumed as representing variable growth rates. The problem is diffusion of a given element (Ca), and garnet can grow (high or low growth rates) with or without Ca (i.e., even if diffusion of Ca is hampered, Fe-Mn-Mg garnet can grow fast/slow). Texturally, although garnet outlines in these samples are slightly rounded, it is possible to observe that their rims were basically parallel to the euhedral low-Ca annuli and that the majority of garnet

consumption occurred at the corners or intersections of growth crystal faces of garnet. The abrupt variations in Ca distribution from core to rim are probably due to the consumption of Ca-enriched mineral phases in garnet-producing reactions, developing zoning patterns with euhedral low-Ca annuli parallel to the garnet outlines. According to Chernoff and Carlson (1997), this is typical of growth zoning and suggests that very little volume diffusion took place after growth, which is not a surprise, taking into account that the diffusion coefficient of Ca in garnet is smaller than that of Mg-Mn-Fe.

Oscillatory zoned grains display a concentric rhythmic layering with distinct composition. It is frequently recorded from metasomatic fluid-dominated environments and mineralized hydrothermal systems such as skarn deposits (Smith et al., 2004). Oscillatory zoning has been reported in calc-silicate rocks (e.g., PCM-514, Figure 5). In these rocks, garnet shows a complex oscillatory zoning in Ca, fluctuating between 17,0 and 23,2 mol%, opposite to the trend displayed by Mg (8,9 to 11,2 mol%) and Mn (19,4 to 22,6 mol%) zoning. Mg and Mn show a negative correlation. Note at least two high-Ca annuli with sharp hexagonal outlines. The variable grossular content may be related to reactions involving other calcic phases. A change in mineral assemblage may account for some of the oscillatory zoning trends observed, but, to explain this type of complex zoning, appearance/disappearance of Ca-rich phases is needed. Alternatively, other process (variation in fluid composition and/or infiltration of fluid) controlling the fluctuations in the availability of elements must be involved. The Ca-rich bands in garnet may correlate with the breakdown of epidote, plagioclase and/or calcic amphibole



**Figure 4.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-516, which is a pelitic schist from the garnet-staurolite zone characterized by a mineral assemblage of quartz + plagioclase + K-feldspar + muscovite + biotite + garnet, with minor ilmenite and calcite. Garnet diameter = 1.20 mm. Warm colors correspond to higher concentrations.



**Figure 5.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-514, which is a calc-silicate rock from the garnet-staurolite zone characterized by a mineral assemblage of quartz + plagioclase + K-feldspar + garnet + Ca-amphibole, with minor epidote, calcite, biotite, ilmenite, rutile and magnetite. Garnet diameter = 0.65 mm. Warm colors correspond to higher concentrations.

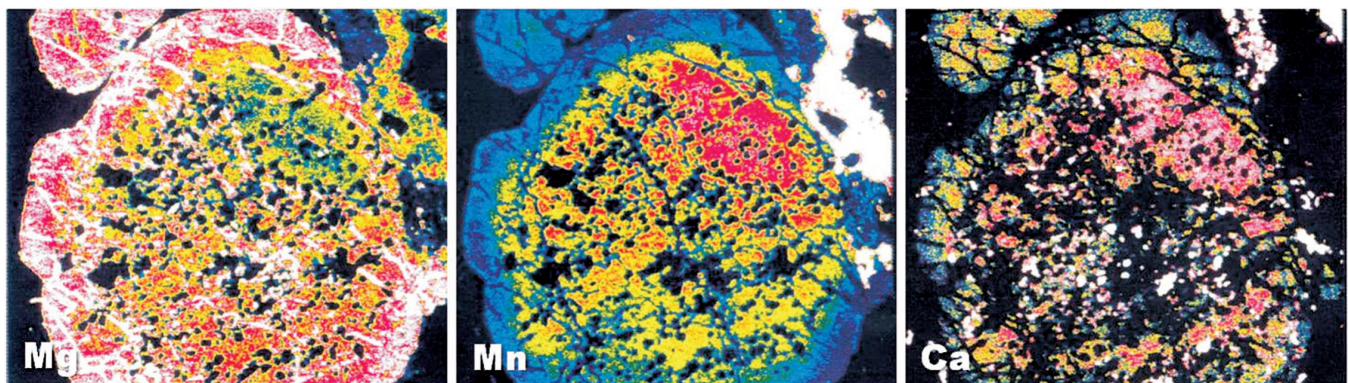
or with the presence of a Ca-rich fluid; garnet growth continued with decreasing grossular content after each of these events, with Ca fractionating into garnet, plagioclase and/or calcic amphibole (Ríos et al., 2008). A complex oscillatory zoning as described here has a controversial origin and it is difficult to explain it by a cyclic addition and loss of mineral phase(s) from the chemical system. Abrupt compositional shifts are interpreted to reflect sudden changes in the parameters controlling garnet growth as a result of episodic injections in the P–T path (García-Casco et al., 2002) or changes in the garnet-producing reactions (Jamtveit and Anderson, 1992).

Garnet usually shows a normal zoning with Mn content decreasing from core to rim, although a minimum Mn content near rim sometimes is observed, revealing a reversal zoning, which in many cases reflects post-peak resorption and reequilibration during cooling by elemental diffusion during retrograde metamorphism. As shown in Figure 6 (e.g., sample PCM-420), garnet exhibits growth zoning: from core to near rim, there is an increase in Mg (from 3,1 to 12,0 mol%) and a decrease in Mn (from 43,2 to 5,6 mol%) and in Ca (from 18,0 to 7,6 mol%). Note the Mn distribution showing a small reversal zoning at rim. Reversal in Mn (from 5,6 to 9,7 mol%) is accompanied by reversal in Mg (from 12,0 to 10,6 mol%). Concentrations of Mg and Mn in the core of the smaller garnet (upper left side) correspond with near-rim compositions in the larger crystal, although Ca composition is not similarly systematic. However, even if Ca in the core of the grain does not reach similar concentration as in the core of the larger grain, it should be systematic because Ca increases in the core. This can be explained due to the fact that the garnet was not cut through the core or that the core of the smaller grain started growth after the core of the larger grain.

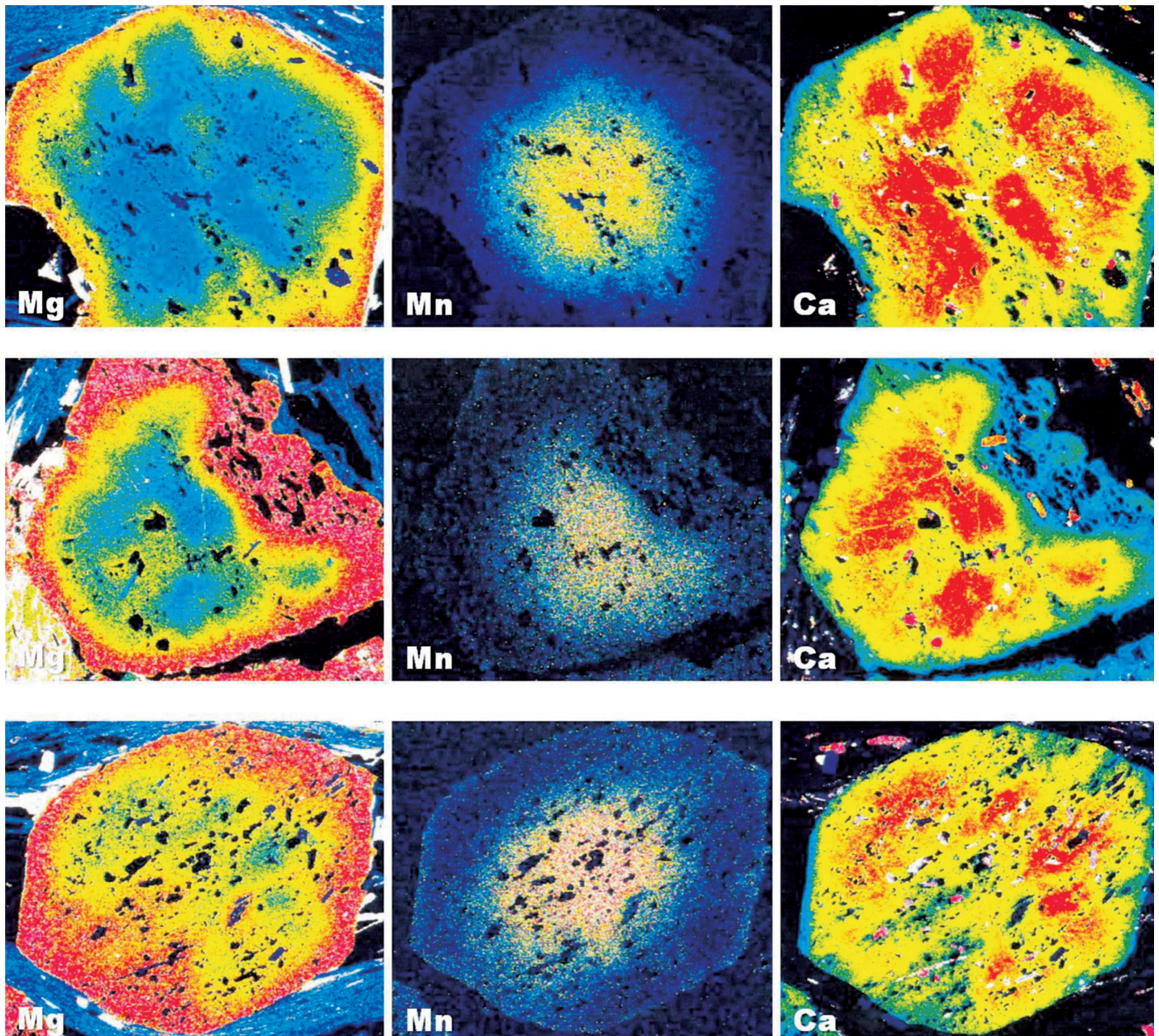
A more complex chemical zoning is observed in sample PCM-618 (Figures 7 and 8), which reveals amoeba-like and sector zoning in garnet. Amoeba-like zoned garnet (Figure 7) shows a similar chemical zoning as that reported by Daniel and Spear (1998) for Mn, which reveals multiple nuclei formed simultaneously 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, 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). To identify various nuclei, distinct concentric zoning about them should have developed until the crystals merge into a single grain with continuous overgrown bands. The distribution of Mn, with a localized maximum, suggests a single nucleus. Note the strong negative correlation between Mg and Ca, with Mg-poor and Ca-rich regions in the core compared to adjacent regions. Garnet shows normal zoning up to mantle, with a reversal chemical zoning from mantle to

rim, revealing a retrograde metamorphism. Sector-zoned garnet occurs in graphite-bearing pelites (e.g., PCM-618, Figure 8) and involves the preferential inclusion of graphite and quartz with a crystallographic control. Garnet displays variable patterns of zoning. It reveals that distribution of elements follows a radial (sector) trend, but in other cases distribution follows patchy and concentric trends. Note the strongly correlated distributions of Mg and Ca, with Mg-poor and Ca-rich regions compared to adjacent garnet. Mg from core (9,9 mol%) to rim (11,4 mol%), accompanied by a decrease of Mn (from 1,8 to 0,7 mol%) and Ca (from 8,2 to 7,94 mol%). As mentioned above, a localized maximum in Mn suggests a single nucleus for the garnet grain. The formation of sector-zoned garnets generally is related to rapid increase of temperature during metamorphism, which that may be due to enhanced heat flow related to an extensional event associated with coeval magmatism and thermal metamorphism and/or maybe due to strong strain in high temperature shear zones as suggested by Kleinschmidt et al. (2008). Castellanos et al. (2004) discuss in detail the occurrence and growth history of chemically sector-zoned garnets. Garnet zoning patterns can change due to dissolution, solution transfer, and diffusional modification (Spear, 1993). However, garnet zoning may have been influenced not only by metamorphic processes but also by deformation.

Additional examples of resorption are illustrated in Figures 9 and 10. Meth and Carlson (2005) suggest that Mn reversal zoning may have resulted from partial disequilibrium at millimeter scale. The core, represented by a high Mn concentration, is not situated in the geometrical center of the grain, which according to Ríos et al. (2008) suggests either asymmetrical growth or that a significant amount of resorption has taken place. Mn is not concentric about individual parts of the garnet, but rather is zoned in irregular, amoeba-like shapes, a pattern that reflects fast growth along grain boundary surfaces and slower dissolution and replacement of quartz inclusions (Spear and Daniel, 1999). Garnet in sample PCM-47 (Figure 9) shows normal zoning through the core to the inner rim, but in the outer rim the chemical zoning is reversed, revealing a retrograde metamorphism. From core to outer rim, there is an increase in Mg (from 1,8 to 3,1 mol%) and a decrease in Mn (from 4,5 to 1,5 mol%) and in Ca (from 3,4 to 2,7 mol%). Garnet in sample PCM-523 (Figure 10) shows normal zoning from core to rim. It displays an increase in Mg (from 9,0 to 13,1 mol%) and a decrease in Mn (from 32,2 to 20,9 mol%). Ca shows an irregular distribution (from 12,6 to 17,7 mol%). Garnet is interpreted as broken by dissolution. An alternative explanation is that the grain was affected by a process of replacement by chlorite, as indicated by the high Mg areas adjacent to the lower garnet rim. The chlorite grains seem to be larger than those in the matrix and not fully oriented along the main foliation, suggesting a replacement



**Figure 6.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-420, which is a quartz-feldspatic pelitic rock from the garnet-staurolite zone characterized by a mineral assemblage of quartz + plagioclase + K-feldspar + biotite + garnet, with minor ilmenite and magnetite. Garnet diameter = 1.75 mm. Warm colors correspond to higher concentrations.



**Figure 7.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of amoeba-like zoned garnet in sample PCM-618, which is a pelitic schist from the garnet-staurolite zone. Garnet shows patch and amoeba-like shapes of the Ca zoning. Garnet diameter = 2.50 mm. Warm colors correspond to higher concentrations.

of garnet by retrogression(+fluid infiltration). The (apparent) lack of orientation of chlorite suggests that the process took place with little, if any, deformation.

Zoning patterns of garnet reflect alteration due to dissolution/resorption induced by deformation. A truncation of chemical zoning is not only an evidence of tectonic dissolution in progressive shear zones but also an excellent indication of subsequent garnet resorption. Truncation has to do with dissolution, but tectonic dissolution is not demonstrated in this study. Static replacement (as indicated by biotite or quartz) seems to have been important in the development of the truncation. Anomalies in the chemical zoning have occurred adjacent to boundaries of the textural zones and within the zone as suggested by Vollbrecht et al. (2006). Data reported by Rios (1999) and Castellanos (2001) revealed that the compositions of the garnet at the textural boundaries are different for different traverses, which can be attributed to dissolution. According to Vollbrecht et al. (2006), this supports the suggestion

that zoning reversals within garnet porphyroblast and asymmetrical zoning patterns can be explained by (1) preferential dissolution and precipitation under partial/local chemical disequilibrium and (2) changes of bulk shortening direction.

#### *Sillimanite zone*

As shown in Figure 11 (sample PCM-953), garnet shows normal zoning, which is broken by dissolution. Garnet shows normal zoning up to mantle, with a reversal chemical zoning from mantle to rim, revealing a diffusion modification during retrogression. There is an increase in Mg (from 2,0 to 3,1 mol%) and in Ca (from 3,0 to 3,1 mol%) from core to mantle, with Mg and Ca decreasing to 2,6 and 1,7 mol%, respectively, from mantle to rim. Mn decreases from core (6,3 mol%) to mantle (2,1 mol%), increasing from mantle (2,1 mol%)

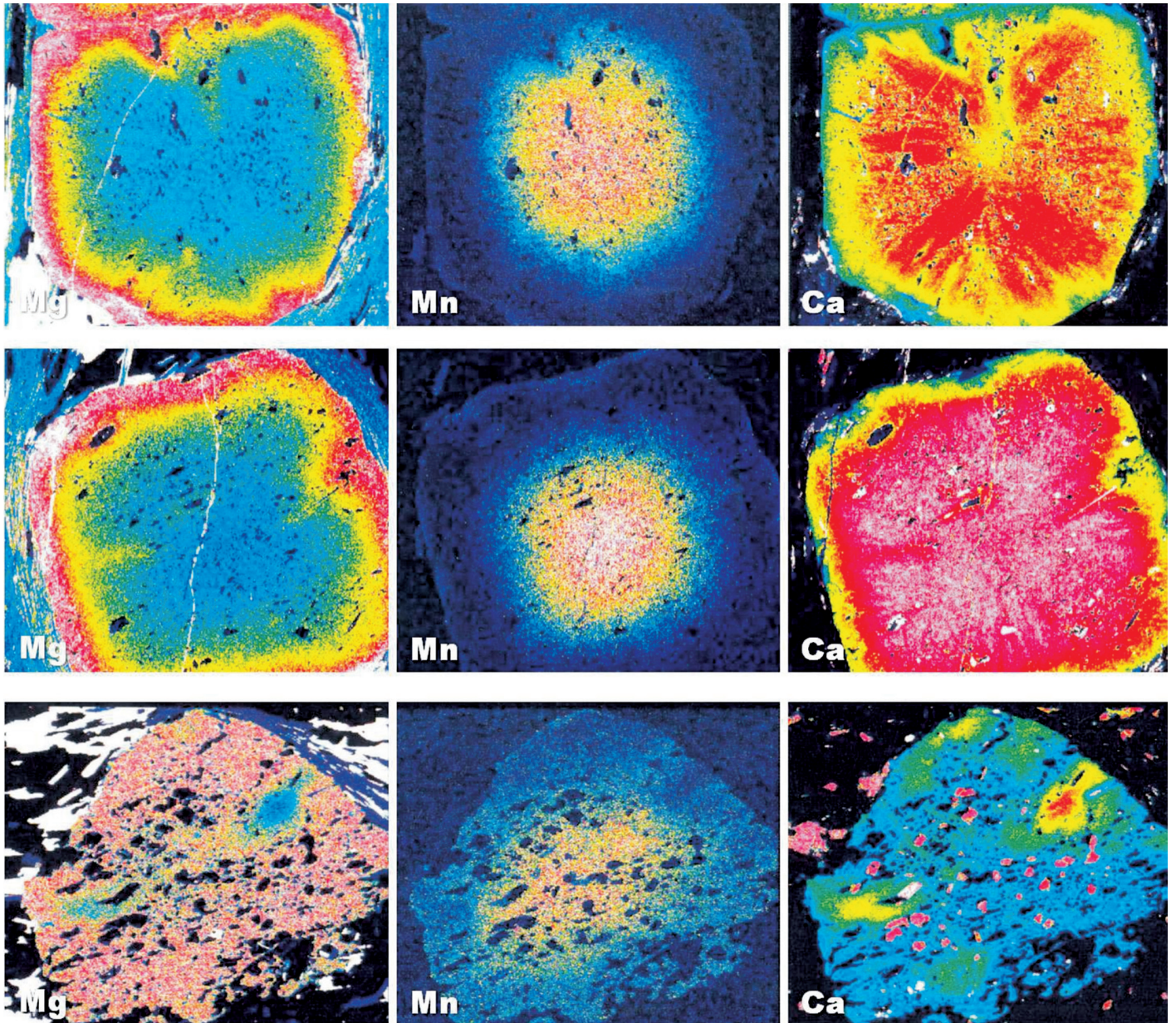


Figure 8. X-ray maps of Mg, Mn, and Ca showing compositional zoning of sector-zoned garnet in sample PCM-618, which is a pelitic schist from the garnet-staurolite zone. Garnet diameter = 2.25 mm. Warm colors correspond to higher concentrations.

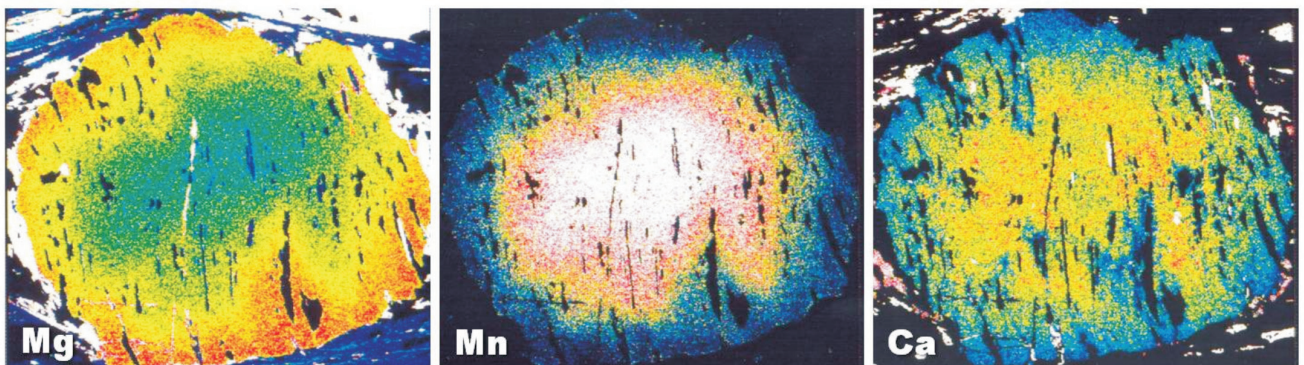


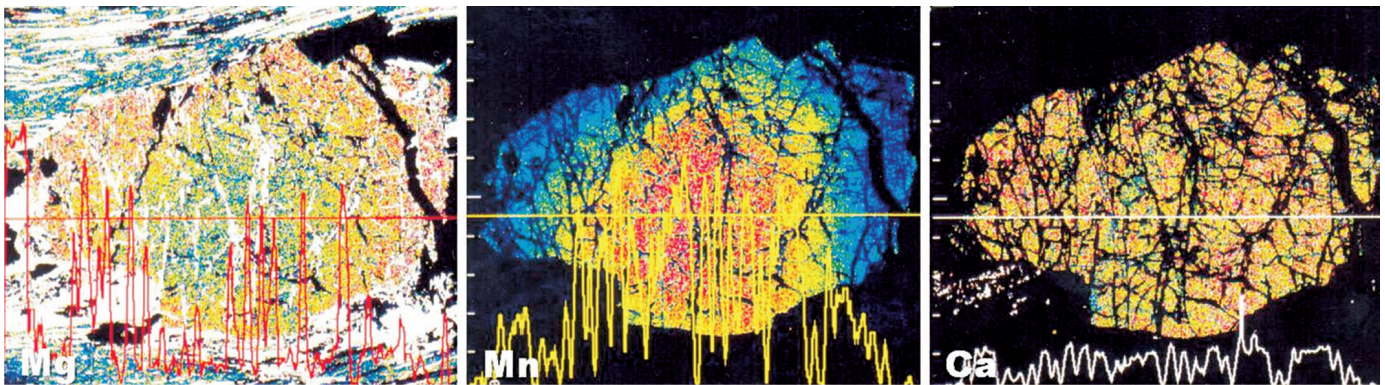
Figure 9. X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-47, which is a pelitic schist from the garnet-staurolite zone. Garnet diameter = 1.40 mm. Zoning is mild. It seems that diffusion at near peak conditions relaxed the original growth pattern. Warm colors correspond to higher concentrations.

to rim (7,0 mol%). Chlorite clearly replaces garnet. Hence, it seems that the dissolution (replacement) process took place during retrogression (+fluid infiltration). The (apparent) lack of orientation of chlorite suggests that the process took place with little, if any, deformation. This textural evidence also suggests that it was related to cooling as demonstrated by the high Mn rim (produced either by diffusion modification). On the other hand, it is clear that Ca behaves independently and does not mimic Mg and Mn zoning but it should be taken into account that the variation in Ca in the core-mantle region is smooth.

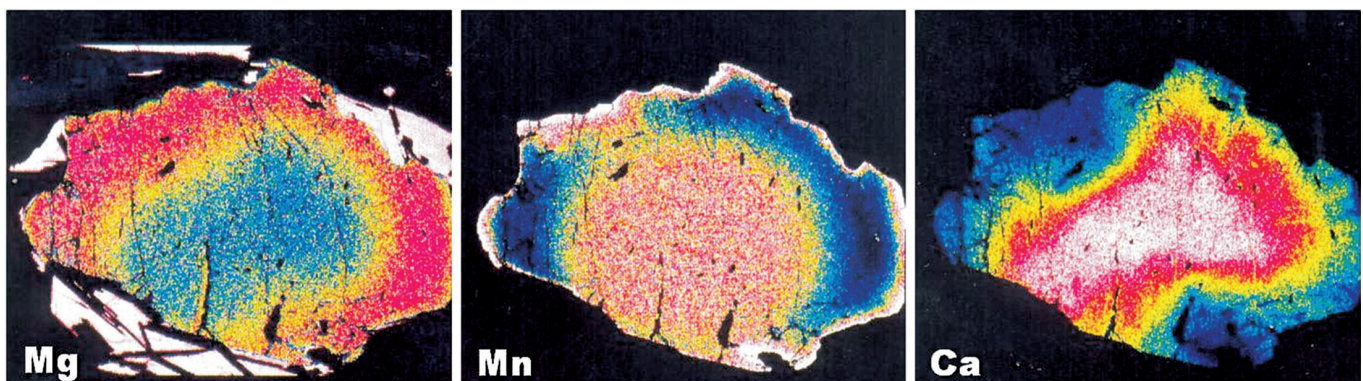
Garnet resorption would be expected to produce an irregular, embayed garnet margin and an overgrowth on such irregular boundary should produce a subhedral to anhedral low-Ca annulus, as observed in the studied garnets (e.g., PCM-473, Figure 12). Garnet exhibits reverse zoning, with a decrease in Mg (from 11,0 to 6,0 mol%) and increase in Mn (from 6,9 to 9,3 mol%) from core to rim. Composition is more homogenous in the interior of the crystal and Ca content increases slightly within the outer core (4,6-7,0 mol%), where it reaches a maximum, then decreases to 4,5 mol% at rim, developing a low-Ca annulus. A sharp decrease of grossular content from core to the mid-region has been interpreted by Menard and Spear (1993) as produced by resorption of garnet during production of staurolite, which is unlikely because the garnet core is euhedral. Chemical zoning does not follow the shape of the marked embayments (filled by quartz, biotite and ilmenite), indicating that it is broken by dissolution. The garnet grain was probably dissolved (and replaced), but tectonic-drive dissolution is not demonstrated. The classical theory of pressure-driven dissolution predicts dissolution at the interfaces (mechanical

discontinuities) orthogonal to the larger main principal stress and precipitation at the interfaces parallel to the smaller main principal stress. This is not clearly seen in the above images. An alternative is that it breaks apart in different pieces during non-coaxial deformation. In this case, the growth zoning is broken, but dissolution does not necessarily take place. After breaking apart, the pieces may experience further growth or they may experience retrogression (dissolution). It also suggests resorption or partial breakdown of the garnet (Spear et al., 1995) during the P-T decreasing probably linked to the exhumation of the rock. However, embayments along the garnet grain originally interpreted as a result of a resorption process, can be also interpreted as growth features, resulting from pinning of garnet grain boundaries adjacent to quartz (Pyle and Spear, 1999). We suggest, however, that garnet affected by progressive shear displays tectonic dissolution features, as revealed by the chemical zoning of garnet, which is abruptly truncated against the main metamorphic foliation of the rock. As previously stated, it seems that dissolution of garnet is related with replacement under (apparently) static conditions during retrogression rather than with tectonic dissolution.

Figure 13 (sample PCM-971) shows a pattern of quartz inclusions in garnet that tends to form a sigmoidal arrangement or snowball structure, which is known as synkinematic growth structure (e.g., Schoneveld, 1977). Microstructure of garnet shows different features between inner and outer parts of the grain. The inner part contains a sigmoidal arrangement of inclusions whereas the outer part has not inclusions. Garnet exhibits normal zoning, with Mn decreasing from 5,8 to 0,4 mol% and Mg increasing from 1,0 to 2,9 mol% from core to rim. Ca also decreases from core (4,8 mol%) to rim

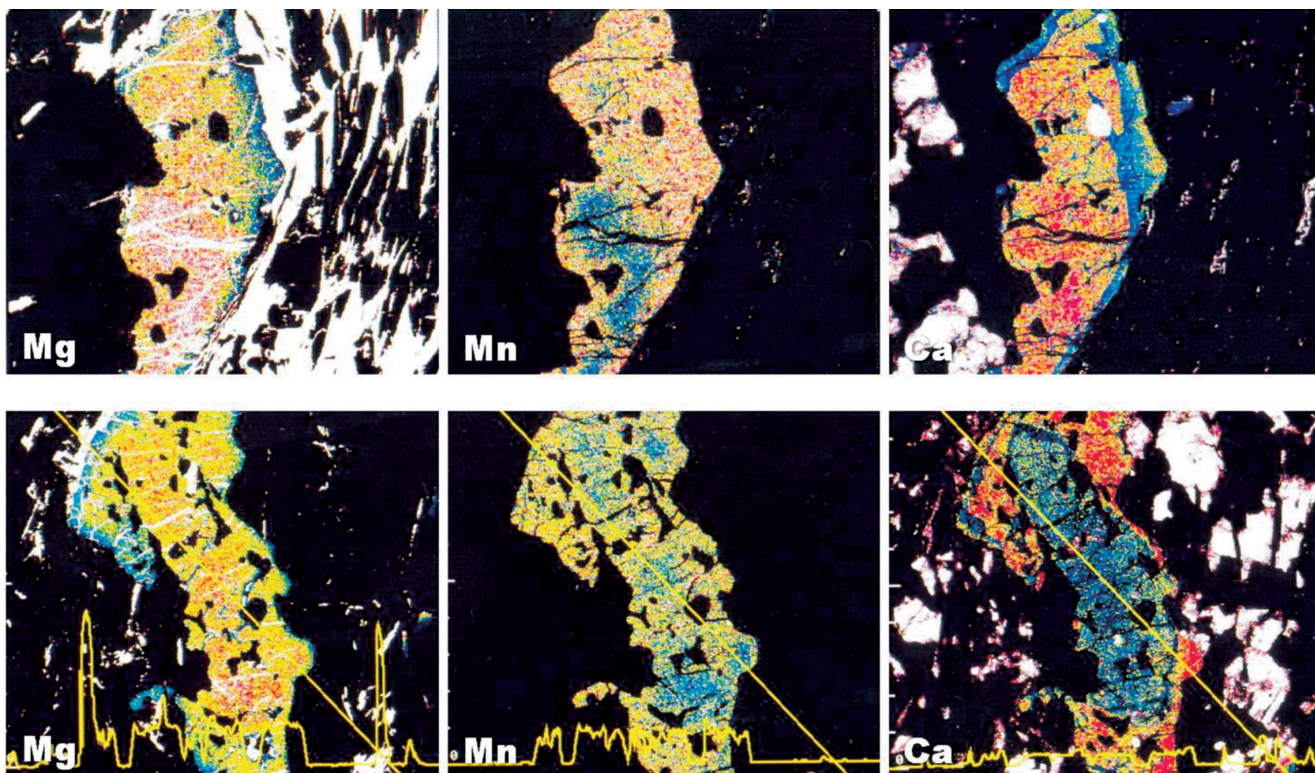


**Figure 10.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-523, which is a pelitic schist from the garnet-staurolite zone sillimanite zone. Garnet diameter = 2.00 mm. Warm colors correspond to higher concentrations.



**Figure 11.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-953, which is a pelitic schist from the sillimanite zone. Garnet diameter = 2.00 mm. Warm colors correspond to higher concentrations.





**Figure 12.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the garnet porphyroblast in sample PCM-473, which is a pelitic schist from the staurolite-kyanite zone characterized by a mineral assemblage of quartz + plagioclase + muscovite + biotite + garnet + staurolite, with minor sillimanite, ilmenite and magnetite. Garnet diameter = 2.50 mm. Warm colors correspond to higher concentrations.

(1.8 mol%). Therefore, it is characterized by a gradual decrease of Mn and Ca from core to rim, counterbalanced by a simultaneous increase of Mg. The strong correlation in the zoning of Mn, Ca and Mg suggests that these elements achieved local equilibrium during garnet growth. However, some authors (e.g., Ikeda et al., 2002) suggest to study in detail the microstructure, crystallographic orientation, chemical composition and three-dimensional shape of sigmoidal garnet in order to establish evidences that can be used to discuss its origin, and in particular to distinguish between non-rotational versus non-rotational models.

Chemical zoning of garnet from metapelitic rocks of the Silgará Formation can be summarized as follows: (1) garnet is almost pure almandine end member, with very low content of Mg, Mn and Ca. In addition, only a slight increase of Mn was observed at the core; (2) garnets exhibits normal zoning with increasing Mg components from core to rim and decreasing Mn and Ca components from core to rim, suggesting prograde metamorphism; (3) garnet exhibits normal zoning through to the inner rim, but in the outer rim the chemical zoning is reversed, reflecting the effects of retrogression, (4) sector-zoned garnet, with very different models of zoning; (5) amoeba-like zoned garnet; (6) anomalies in the chemical zoning at the textural boundaries reveals not only a modification by metamorphic processes but also deformation. Patterns can deviate from normal growth zoning in garnet (e.g., euhedral bands concentric about the garnet core, patches or spiral to curving patterns). Although the zoning in all elements is broadly concentric, detailed examination of the X-ray maps reveals a more complex pattern as occurring in sector zoned garnet, where a strong negative correlation between Mg and Ca is observed. Chemical zoning of garnet is generally asymmetric and core compositions do not always coincide with the geometric center of the garnet. Zoning patterns of garnet reflect alteration due to dissolution/resorption induced by deformation. A truncation of chemical zoning is not only an

evidence of tectonic dissolution in progressive shear zones but also an excellent indication of subsequent garnet resorption.

## Conclusions

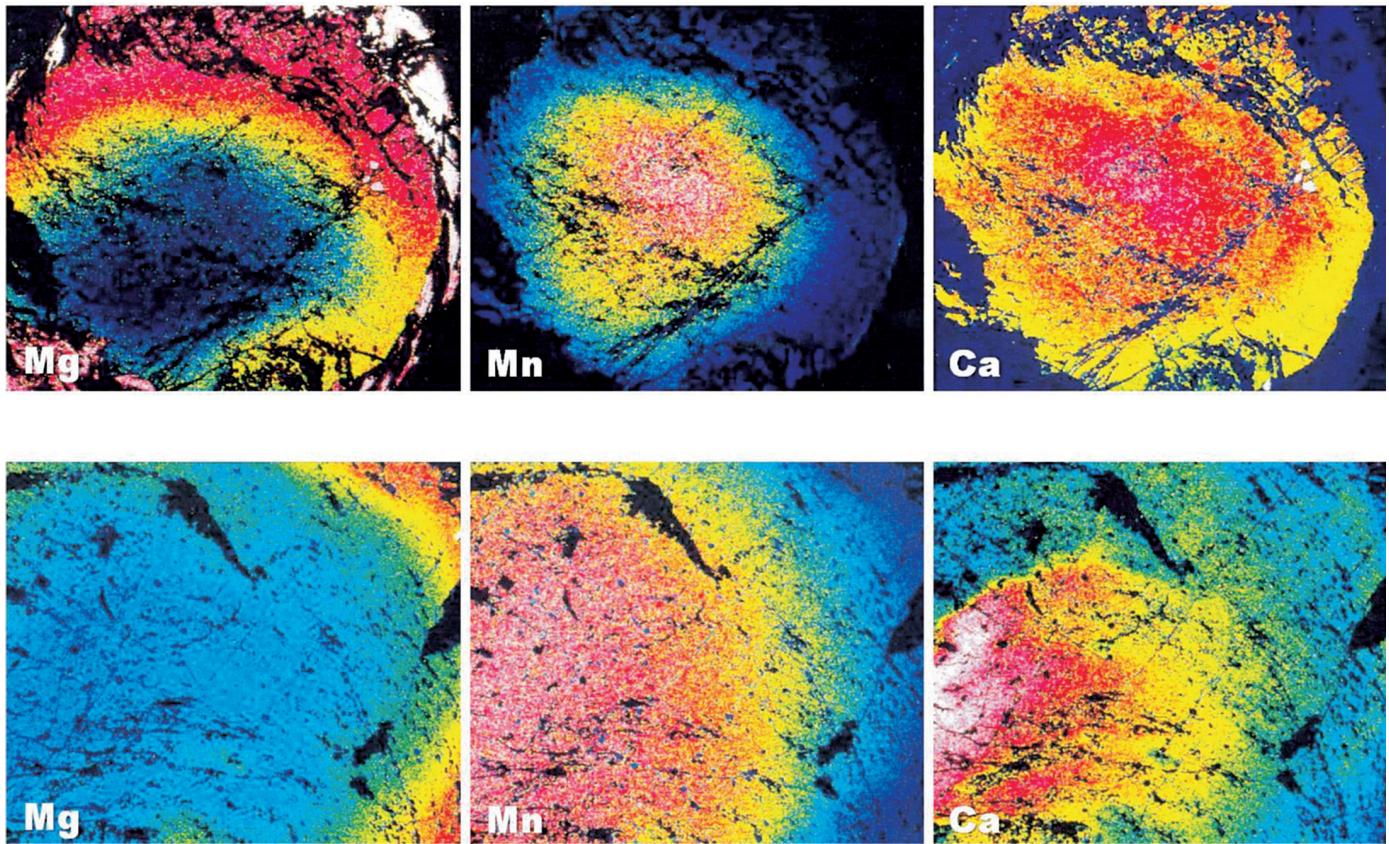
X-ray color maps of garnet in pelitic rocks of the Silgará Formation reveal complex patterns of nucleation and growth that probably were strongly affected by processes of dissolution, solution transfer (non demonstrated) and diffusion modification (during retrograde metamorphism). However, even if dissolution occurred, simultaneous precipitation is not clear.

Mg and Mn is interpreted to reflect equilibrium with the rock matrix, whereas Ca appears to be controlled by diffusive transport between garnet and rock matrix, which however cannot be demonstrated here largely because Ca-bearing minerals have not been described in detail and their reaction history (fluxes) not analyzed.

Mn reversal zoning is the result of partial reequilibration at the millimeter scale during retrogression, and oscillatory zoning of Ca appears to have been generated from slow intergranular diffusion in local chemical heterogeneities in the distribution of nutrients (Ca-bearing phases).

Inclusion-free rims and inclusion-rich cores likely resulted from variable growth rates, which is supported by the occurrence of garnet showing low-Ca annuli lacking inclusions and high-Mn inclusion-rich cores, which is not demonstrated here. Therefore, low- and high-Ca concentrations can be explained by Ca-bearing reacting phases rather than by growth rate, even if Ca-bearing phases do not react, taking into account that growth rate has to do with overstepping of equilibrium reaction boundaries.

The low- and/or high-Ca annuli should be assumed as reaction boundaries (a function of P-T-X) during garnet growth history, and truncation of the annuli is



**Figure 13.** X-ray maps of Mg, Mn, and Ca showing compositional zoning of the largest garnet porphyroblast in sample PCM-971, which is a pelitic schist from the sillimanite zone. Garnet diameter = 8.00 mm. Warm colors correspond to higher concentrations.

not only an evidence of tectonic dissolution in progressive shear zones but also an excellent indication of subsequent garnet dissolution/resorption.

Anomalies in the chemical zoning at the textural boundaries are different for different traverses, revealing not only a modification by a diffusion process but also the influence of microfabrics (non demonstrated) that promoted a dissolution/resorption process.

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