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Occurrence of chloritoid-bearing metapelitic rocks and their significance in the metamorphism of the Silgará Formation at the Central Santander Massif

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Abstract
We report here for the first time the occurrence of chloritoid in Mg-Al-rich metapelitic rocks of the Silgará Formation at the Central Santander Massif, which was metamorphosed up to the amphibolite facies. These rocks contain an unusual mineral assemblage such as quartz + biotite + muscovite + garnet + staurolite ± kyanite ± chloritoid, with minor plagioclase and K-feldspar, and Fe-Ti oxides as the main accessory phases. Associated carbonate rocks containing the mineral assemblage tremolite + calcite. Chloritoid occurs as porphyroblastic tablets in graphite-bearing metapelitic schists highly tectonized that can be associated to the influence of the major tectonic structures in the study area. The occurrence of chloritoid as an index mineral in metapelitic rocks of the Silgará Formation is attributed to a thermal event (associated to the emplacement of small granitic masses) overimposed on the regional metamorphism.

Key words: Chloritoid, Metapelitic rocks, Silgará Formation, Central Santander Massif, Colombian Andes.

Ocurrencia de rocas metapelíticas con presencia de cloritoide y su significado en el metamorfismo de la Formación Silgará en la región central del Macizo de Santander

Resumen
En el presente estudio se reporta por primera vez la aparición de cloritoide en metapelitas ricas en Mg-Al de la Formación Silgará en la región central del Macizo de Santander, las cuales fueron afectadas por un metamorfismo hasta en facies anfibolita. Estas rocas contienen una asociación mineral inusual, tal como cuarzo + biotita + moscovita + granate + estaurolita ± cianita ± cloritoide, con menor plagioclasa y feldespato potásico, y óxidos de Fe-Ti como las principales fases accesorias. Rocas carbonatadas asociadas contienen la asociación mineral tremolita + calcita. El cloritoide ocurre como porfidoblastos tabulares en esquistos metapelíticos con grafito fuertemente tectonizados que pueden asociarse a la influencia de las principales estructuras tectónicas en el área de estudio. La ocurrencia de cloritoide como un mineral índice en las rocas metapelíticas de la Formación Silgará se atribuye a un evento térmico (asociado al emplazamiento de pequeñas masas graníticas) sobreimpuesto al metamorfismo regional.

Palabras clave: Cloritoide, Rocas metapelíticas, Formación Silgará, Región Central del Macizo de Santander, Andes Colombianos.

1. Introduction

The Santander Massif (Fig. 1) in the Colombian Andes context represents a key for interpreting the geologic and tectonic evolution of the northwestern continental margin of South America (Ríos et al., 2003). It comprises a northwest trending pre-Middle Devonian crystalline basement, which is composed by deformed and metamorphosed rocks of the Bucaramanga Gneiss Complex, Silgará Formation and Orthogneiss (Ward et al., 1973; Clavijo, 1994), all of which

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are cut by Paleozoic–Jurassic intrusive bodies of granite to diorite composition (Goldsmith et al., 1971; Banks et al., 1985; Boinet et al., 1985; Dörr et al., 1995; Restrepo-Pace, 1995; Ordóñez, 2003; Ordóñez and Mantilla, 2004) and smaller Cretaceous intrusive bodies. Metamorphism in the Santander Massif has been studied intensively during the last fifteen years (e.g., Schäfer et al., 1998; Ríos, 1999, 2001, 2005; Ríos and Takasu, 1999; Campos, 1999; Montenegro y Barragán, 1999; García y Campos, 2000; Ríos and García, 2001; Castellanos, 2001; Mantilla et al., 2001, 2002, 2003; Gélvez and Márquez, 2002; Ríos et al. 2003, 2008a, 2008b; Cardona, 2003; Castellanos et al., 2004, 2008, 2010; García et al., 2005; Gómez y Avila, 2006), which has contributed to modify the classic scheme of metamorphic zones and isograds proposed by Ward et al. (1969, 1970, 1973). However, the Central Santander Massif (CSM) is probably the most important region in this ancient massif. This region was chosen for detailed metamorphic study because it contains chloritoid-bearing metapelitic rocks in the low-grade Silgará Formation. Chloritoid is a nesosilicate mineral represented by the general formula $(Fe,Mg,Mn)_2Al_4Si_2O_{10}(OH)_4$. It is a widely distributed mineral, which has been described from several areas of regional metamorphism (e.g., Williamson, 1953; Atkinson, 1956; Halferdahl, 1961; Chinner, 1967; Cabanis, 1974, 1982; Baltatzis and Wood, 1977; Holdaway, 1978; Liou and Chen, 1978; Atherton and Smith, 1979; Lal and Ackermand, 1979; Labotka, 1981; Deer et al., 1982; Evirgen and Ashworth, 1984; Dickenson, 1988; Javkhlan et al., 2013) and from scarce areas of contact metamorphism (e.g., Atherton, 1980; Phillips, 1987; Kanekoand Miyano, 1990; Pattison and Tracy, 1991;Okuyama-Kusunose, 1994; Flinn et al., 1996; Likhanov et al., 2001). It has also been reported in hydrothermal environments (Ochoa et al., 2007). Chloritoid is not abundant in contact aureoles due to a narrow temperature interval at low pressures of contact metamorphism (Ganguly, 1969) and severe constraints imposed by specific bulk rock composition (e.g., Wang and Spear, 1991). The occurrence of chloritoid in this geological context has been focus of attention in previous studies (e.g., Atherton, 1980; Phillips, 1987; Kaneko and Miyano, 1990; Flinn et al., 1996), which discuses on the equilibrium relations of chloritoid with respect to the coexisting natural assemblages, providing valuable information on the chemistry, mineralogy and natural occurrence of chloritoid-bearing rocks to understanding the reactions controlling the appearance and disappearance of chloritoid-bearing assemblages during contact metamorphism. On the other hand, Likhanov et al. (2001) performed a detailed study on the mineral chemistry of chloritoid-bearing assemblages across contact-metamorphic isograds have been made. However, they consider that the chloritoid+biotite paragenesis has always been problematic in the construction of petrogenetic grids for pelites, in which this assemblage has markedly different stability limits. In this study, we report for the first time and discuss data concerning the occurrence of chloritoid and its significance in the metamorphism of the low-grade Silgará Formation metapelitic rocks at the CSM.

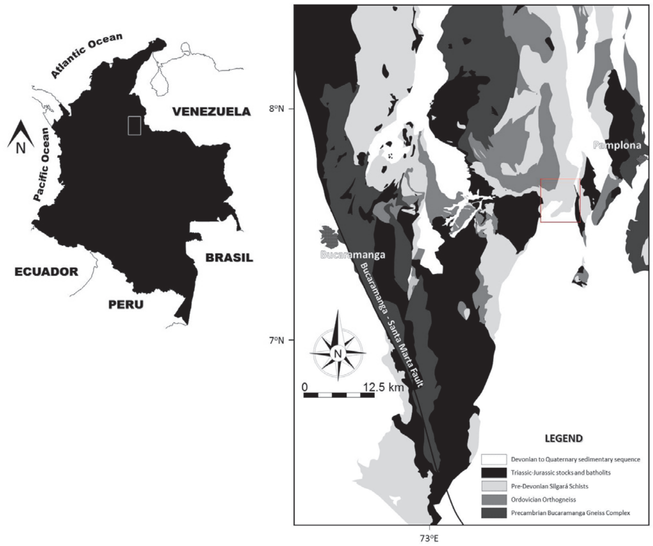

Figure 1. Regional geologic map of the Santander Massif. The rectangle marks the location of the study area at the CSM region.
Source: Modified from Goldsmith et al., 1971

2. Geological setting

The study area is located in the southern part of the CSM within a compressive tectonic zone between the Bucaramanga-Santa Marta and Chitagá fault systems, and corresponds to the Silos - El Cúcano sector (Fig. 2). The Silgará Formation crops out into several N-S trending strips, locally interrupted by the presence of dykes and sills of orthoamphibolites with banded to gabbroic structures. The metamorphic rocks of this metamorphic unit generally strike NE–SW and dip to the NW. These rocks been affected by multiple deformations, resulting in interference patterns. It is mainly composed of metapelitic rocks with minor intercalated psammitic, semipelitic, metabasic and, locally, metacarbonate rocks, which were affected by a metamorphism up to the amphibolite facies regional grade during the Caledonian orogeny and reveals a very complex tectonic and metamorphic history. These ancient rocks that make up the CSM were covered by a Upper Paleozoic to Mesozoic sedimentation developed (Julivert et al., l970), and constitute the limit between the Magdalena Middle Valley and Maracaibo Lake basins (Ward et al., l973) with a strong structural control and large Quaternary deposits. Ward et al. (1973) makes reference to the Silgará Formation as a cyclic megasequence of metamorphic rocks. Metapelitic rocks, displaying a well-developed schistosity, are the major constituents of the Silgará Formation, with minor intercalations of metamafic and metacarbonate rocks. However, in the study area, it is mainly composed by metapelitic schists with garnet, staurolite, kyanite and chloritoid, with minor layers of quartzites, metaconglomerates, calc-silicate-bearing metacarbonate rocks and marbles. Ríos et al. (2008b) also report metacarbonate and related rocks of the Silgará Formation close to the study area in the Mutiscua surroundings. Ward et al. (1970) based on our field observations defined the biotite

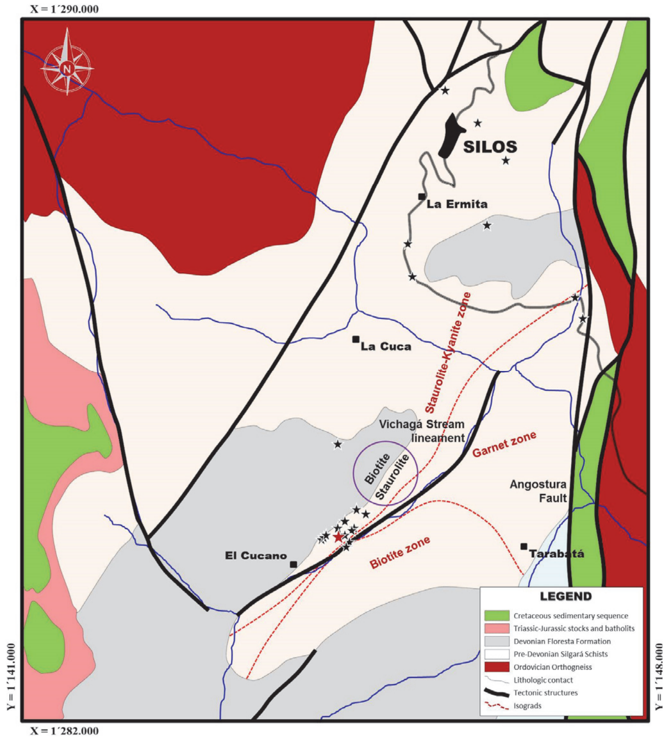

Figure 2. Geologic map of the study area at the CSM region, showing the distribution of the metamorphic zones; the sampling localities are indicated in black stars (the red star indicates the location of the chloritoid-bearing schists). The purple circle indicates the metamorphic zonal scheme proposed by Ward et al. (1970).
Source: Modified from Ward et al., 1970

and staurolite metamorphic zones in the area of interest, which were also recognized in the present study. However, our field observations and petrographic analysis reveal that this metamorphic sequence can be modified.

3. Field sampling and analytical methods

A research group of geoscientists from the Universidad de Pamplona y Universidad Industrial de Santander performed several fieldworks on the CSM, particularly in the Silos – La Cuca – El Cúcano sector, visiting several localities, taking into account the discovery of chloritoid-bearing schists. The sampling strategy consisted of collecting samples of chloritoid-bearing schists and associated rocks from several outcrops. The chloritoid-bearing schists object of the present study were collected in one outcrop on the way Silos – El Cúcano and close to the Vichagá Stream, and belongs to the staurolite-kyanite metamorphic zone. Mineralogical and petrographic analysis were performed in a trinocular Olympus BX-51 transmitted light microscope to establish the modal percentage of mineral constituents and mineral assemblages, with emphasis on textural relationships between mineral phases, and the photographs were taken using a NIKON NIS-elements BR microphotographic system of the Research Group in Geofísica y Geología (PANGEA), de la Universidad de Pamplona. Mineral abbreviations are after Whitney and Evans (2010). SEM-BSE/EDS imaging and analysis were carried out by environmental scanning electron microscopy (FEI Quanta 650 FEG) to examine the mineral phases' textures and cross-cutting relationships in the chloritoid-bearing schists, under the following analytical conditions: magnification = 130-350x, WD = 10.1 mm, HV = 20 kV, signal = Z CONT, detector = BSED.

4. Field occurrence

Metamorphic rocks of the Lower Paleozoic Silgará Formation at the CSM crops out as a NE trending strip. It is mainly composed of metapelitic rocks with minor intercalated psammitic, semipelitic and metacarbonate rocks, which include quartzites, metaconglomerates, calc-silicate-bearing metacarbonate rocks and marbles, which occur as scarce intercalations of centimeter up to meter scale of thickness and variable morphology (with sharp contacts) and thickness, developing discontinuous bands and lenticular bodies, within the metapelitic sequence of the Silgará Formation (FIG. 3). The rocks of interest in this study are referred as chloritoid-bearing schists. These rocks were affected by a Caledonian regional metamorphism that produced a metamorphic zonation ranging from the biotite zone through the garnet up to the staurolite-kyanite zone of the typical Barrovian zonal scheme under low- to middle-T and low-P conditions. We describe a metamorphic sequence cropping out along the Vichagá Stream, making emphasis on the chloritoid-bearing schists and associated rocks. A broad spectrum of physical conditions, varying from greenschist facies to amphibolite facies, have been attributed to the investigated metamorphic sequence. In general, these rocks appear highly tectonized that can be associated to the influence of the major tectonic structures in the study area. This fact, coupled with the capture and alignment of the Vichagá Stream allows us to infer a structural lineament along this stream. The metamorphic sequence (Fig. 3) is dominated by silicate (and locally quartz-rich) rocks composed of garnet, staurolite, kyanite and chloritoid, which display a schistosity structure. Metapelitic rocks are represented by three types of rocks. Grayish-silver micaschists with a well-developed foliation, which are mainly composed of muscovite, biotite, quartz, plagioclase, garnet, staurolite and chloritoid. They show at least two dominant foliation directions. The second type corresponds to quartzites, which may be quartz-rich (minor plagioclase) or mica-rich, the last of them containing muscovite, biotite, garnet, kyanite and staurolite. The third type is represented by folded phyllites, which are characterized by a crenulated cleavage. They locally show discordant quartz veinlets. Calcareous levels of white and pink marble are interbedded within these silicate rocks. Fine-grained white marbles show a tabular geometry, with thicknesses of up to 55 cm, and a strong tectonism as demonstrated by the occurrence of numerous blocks. These rocks display a banded structure characterized by the presence of fibro-radial and lenticular tremolite aggregates of approximately 10 x 5 mm, varying in color from yellowish-white to light brown. They are arranged correspondingly with the banding. Additionally, fractures perpendicular to the structure of these rocks occur, which are characterized by the presence of grayish-green tremolite of acicular habit. The origin of tremolite is associated with a metasomatic-hydrothermal event due to the infiltration and circulation of fluids rich in H_2O and CO_2, as well as SiO_2, which facilitate the mobilization of Ca, contributing to the development of a calc-silicate system. This process was favored by the strong fracturing and development of secondary porosity in marble. Fe-Ti oxides, such as rutile, ilmenite, titanite and leucoxene are the main accessory mineral phases. Marble layers (Figs. 3a) are locally folded (Fig. 3b). A typical outcrop of micaschist is shown in Fig. 3c. Gradational contacts between garnet-bearing metapelitic rocks to marbles were also observed, and are especially abundant in strongly deformed rocks, where calc-silicate zones may have a very irregular shape and variable thickness. Micaschists (Fig. 3d) typically present a regional cleavage. Graphite schists show scarce intercalations of quartzites (Fig. 3e). Quartzites display net foliation planes and multiple joint surfaces as shown in Fig. 3f. On the other hand, milky-white quartz of hydrothermal origin is commonly observed developing amoeboid fashion patches and aligned bands due to tectonism, a phenomenon that also deforms the polysynthetic twinning in calcite bands.

General features of the metamorphic rocks at hand-specimen scale are shown in Fig. 4. Very fine-grained garnet-bearing schists are illustrated in Fig. 4a, with euhedral garnet porphyroblasts. Fig. 4b illustrates a net contact between a fine-grained pink marble (lower part) and a epidote-group mineral-bearing Ca-pelite (upper part), which shows a boudinage structure. Porphyroblastic tablets of chloritoid occurs in graphite-bearing metapelitic schists (Fig. 4b). Fig. 4c illustrates an example of a middle-grained garnet-staurolite bearing schist, showing subhedral garnet and large and skeletal staurolite porphyroblasts. Large and elongated staurolite porphyroblasts partially including subhedral garnet porphyroblasts in middle-grained metapelitic schist are shown in Fig. 4d. These rocks are associated with hydrothermal veins of quartz and amphibolite accumulations with not defined foliation. The sequence described here is similar to that described by Ríos et al. (2008b). Marbles shows a banded structure and granoblastic texture; they are characterized by the presence of several fan aggregates of fibrous acicular tremolite (Fig. 4e) or veinlets of acicular tremolite (Fig. 4f).

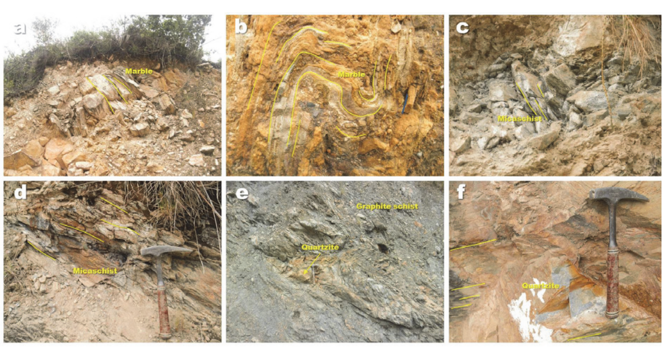

Figure 3. Field photographs of the metamorphic rocks of the Silgará Formation at the CSM.
Source: The authors.

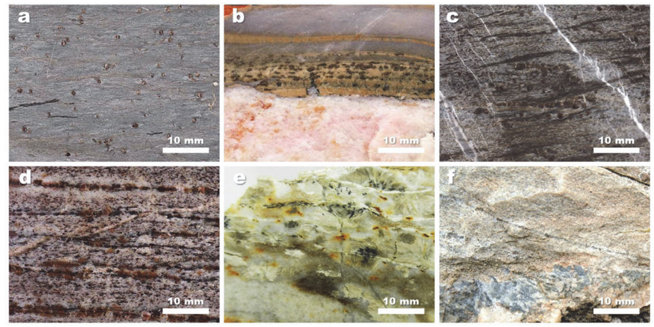

Figure 4. Hand-specimen photographs of the metamorphic rocks of the Silgará Formation at the CSM.
Source: The authors.

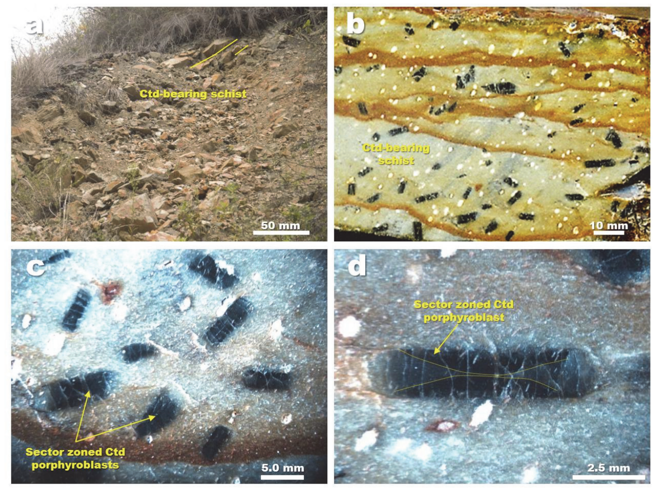

Figure 5. (a) Outcrop and (b)-(d) hand-specimen photographs of chloritoid-bearing schists of the Silgará Formation at the CSM.
Source: The authors.

The discovery of the chloritoid-bearing schists were done in an abrupt and highly tectonized area, where these rocks develop tectonic blocks surrounded by very fine-grained pelites (Fig. 5a). Numerous chloritoid porphyroblasts are easily recognizable with a naked eye. At hand-specimen scale (Figs. 5b-5d), chloritoid occurs in graphite-bearing metapelitic schists as small tabular porphyroblasts with a limited size range (long axes of 45-100 mm and widths of 5-15 mm), accompanied by porphydoblastic plagioclase (milky white ellipses), always significantly larger than the fine-grained groundmass mainly composed of quartz, chlorite and muscovite.

5. Petrography

Fig. 6 illustrates the main petrographic aspects of the chloritoid-bearing schists and associated rocks of the Silgará Formation at the CSM. A very fine-grained phyllite, displaying a crenulation cleavage, which is cross cut by a calcite vein, is shown in Figs. 6a-6b. It shows a lepidoblastic texture and is mainly composed of muscovite, biotite, chlorite and graphite. Metapelitic rocks are mainly composed of quartz, plagioclase, muscovite and biotite, and display a granoblastic to porphyroblastic texture. They contain metamorphic minerals, such as garnet, staurolite and kyanite, show a porphyroblastic and poiquiloblastic nature and reveal a syn-tectonic growth. They usually show an idioblastic to xenoblastic character, although they sometimes can show a skeletal character. Both garnet and staurolite are developing thin bands. These minerals show strong deformation and a subidioblastic to xenoblastic character. Fine-grained garnet-bearing schists showing a well-developed crenulation cleavage are illustrated in Figs. 6c-6d, with euhedral garnet porphyroblasts without mineral inclusions and with graphite as the main accessory mineral. Figs. 6e-6f illustrates another example of fine grained garnet-bearing schists with graphite as the main accessory mineral. Large staurolite porphyroblasts partially including subhedral garnet porphyroblasts in middle-grained metapelitic schist are illustrated in Figs. 6g-6h. A large staurolite porphyroblast with several ilmenite inclusions and displaying incipient alteration to chlorite is shown in Figs. 6i-6j. Marble with a nemato-granoblastic texture is characterized by the mineral assemblage calcite + quartz as shown in Figs. 6k-6l. Figs. 6m-6n illustrates a fan aggregate of fibrous acicular tremolite in marble, which display locally quartz veins with a striated appearance, due to the presence of numerous fluid inclusions which align, creating this particular aspect. A typical kyanite-bearing quartzite is illustrated in Figs. 6o-6p.

Fig. 7 illustrates the main petrographic aspects of the chloritoid, which occurs in graphite-bearing metapelitic schists that display a porphyroblastic texture. Chloritoid exhibits the typical fan tail morphology, poor cleavage, a greenish brown/blue pleochroism, and sector zoning (hourglass structure). It is usually found as isolated single crystals, although they can develop typical groups of two or more crystals. Chloritoid exhibits an interesting textural relationship with the aligned chlorite and muscovite, which define the main foliation of these rocks. Rarely, chloritoid is aligned parallel to the main cleavage and it is normally occurs as oriented with their long axes at an angle of 30-90º to the main foliation. There is evidence of chloritoid overgrowing the cleavage, because the main foliation is not deflected around the porphyroblasts

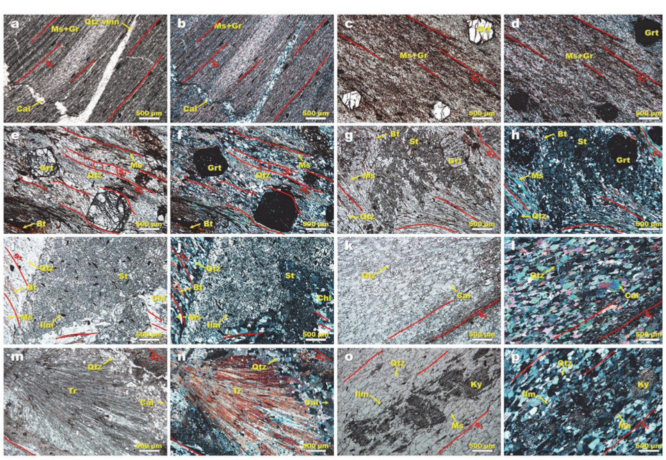

Figure 6. Photomicrographs showing representative textural relationship of chloritoid-bearing schists and associated rocks of the Silgará Formation at the CSM.
Source: The authors.

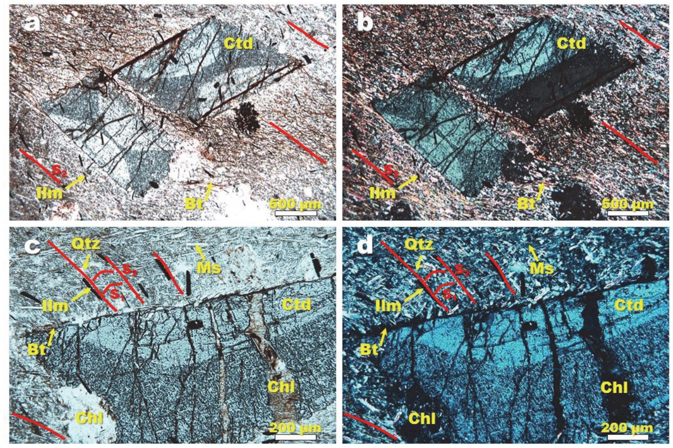

Figure 7. Photomicrographs showing representative textural relationship of minerals in chloritoid-bearing schists of the Silgará Formation at the CSM.
Source: The authors.

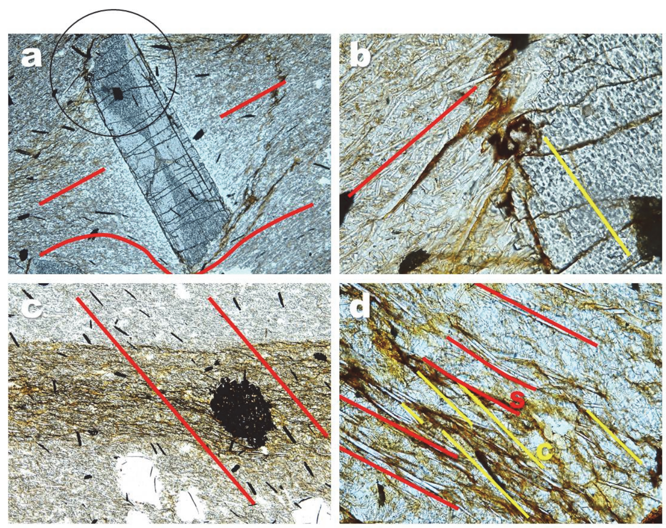

Figure 8. Microstructural features of the chloritoid-bearing schist. (a) Chloritoid rotated with respect to the main foliation of the rock. (b) Inclusions in chloritoid orthogonally oriented with respect to the main foliation of the rock. (c) Ilmenite and plagioclase overimposed on the main foliation of the rock. (d) S-C structures developed as the result of shearing in the rock.
Source: The authors.

and therefore not pressure shadows were observed on either side of the chloritoid porphyroblasts. These textural relationships suggest that the chloritoid porphyroblasts post-date the deformation event which produced the main foliation of these rocks.

Although the sampling carried out in this study was not done with exhaustive orientations of samples, their microstructural features provide valuable information on the occurrence of at least three deformational events associated to the mineralogical development of the host lithology of the chloritoid (Fig. 8): (1) Deformation event D_n that produced the main metamorphic foliation of the rock (S_n or S_2), which is responsible of the mineral assemblage Chl+Ms+Qtz. (2) Nucleation of chloritoid porphyroblasts within an inter-tectonic regime, with an evident orientation of quartz inclusions in the hourglass sectors nearly orthogonally to the main foliation of the rock (S_n). As noted and in accordance with Passchier and Trouw (1991), these inclusions probably grew passively on the fabric in the absence of deformation and protecting the pattern of inclusions resulting from subsequent deformation. (3) Deformation event D_{n+1} that promoted the formation of a late foliation (S_{n+1} or S_3), which generated S-C structures (C-type shear bands) and nucleation of ilmenite and plagioclase, which are observed overimposed on the main foliation of the rock (S_n). On the other hand, this late deformation event produced rotation of chloritoid porphyroblasts. The chloritoid-matrix relationship is governed by the expression: D_n < chloritoid < D_{n+1}.

The SEM image in Fig. 9 shows the textural relationships between chloritoid and associated mineral phases with semiquantitative energy dispersive spectrum (EDS) analysis at different points. An overview high resolution image mosaic of the textural relationships between chloritoid and associated mineral phases (left side) shows chloritoid porphyroblasts, displaying sector-zoning (hourglass structure), which are randomly distributed with regard to rock cleavage. Note the high-density ilmenite from the backscatter electron image contrast. Energy Dispersive Spectroscopy (EDS) allowed to identify what those particular elements are and their relative proportions in the mineral phases that constitute the chloritoid-bearing schist. EDS analysis of chloritoid (1) porphyroblasts reveals that this mineral phase is composed mainly of Si, Al, O and Fe elements (mass ratios of Si:Al:O:Fe = 13.40:26.05:34.41:20.68), with minor Mg (1.84 wt%). The matrix is constituted by biotite (2) and muscovite (3), which show the following mass ratios Si:Al:O:Fe:Mg = 13.33:15.53:33.68:25.04:8.09 for biotite, and Si:Al:O:K = 25.53:23.32:35.24:8.53 for muscovite, the last of them with minor Na (1.17 wt%), Mg (0.43 wt%) and Ti (0.31 wt%) elements. The EDS spectrum of quartz (4), which occurs as matrix or as inclusions in chloritoid, reveals the presence of Si and O elements (mass ratios of Si:O = 58.66:41.34). Ilmenite (5) represents the main accessory phase, occurring both as matrix or as inclusions in chloritoid, and its EDS analysis indicates the presence of Fe, Ti and O elements (mass ratios of Fe:Ti:O = 39.55:34.64:23.46). Magnetite (6) occurs as a secondary phase developing thin veinlets that penetrates chloritoid following a growth surface or fractures, and its EDS spectrum reveals that it mainly consists of Fe (63.51 wt%) and O (28.36 wt%); Al and Si are attributed to sample preparation. EDS spectra are in agreement with literature data (http://www.sfu.ca/~marshall/sem/mineral.htm).

X-rays generated by scanning the electron beam across the sample can be used to produce EDS mapping, which provides in addition to the BSE image a meaningful picture of the elemental distribution of a mineral phase. In Fig. 10, the different phases shown on the BSE image (Fig. 9) can be identified by elemental mapping (Figs. 10a-10d), which however will only give a qualitative image of the distribution of elements.

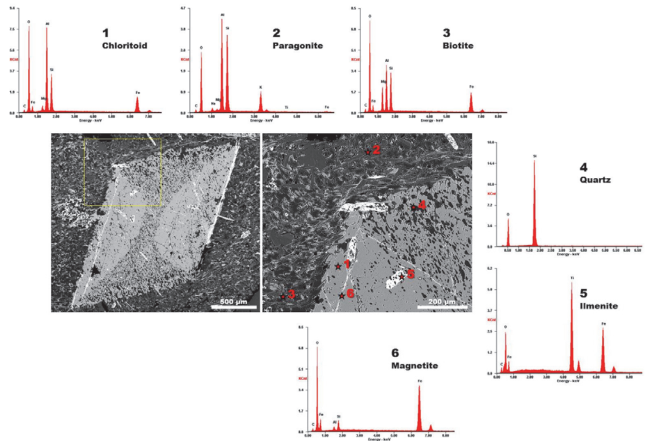

Figure 9. SEM photomicrograph and EDS spectra at the marked stars on the image of the mineral phases in the chloritoid-bearing schist. The appearance of C element is attributed to the carbon coating on the sample before SEM analysis.
Source: The authors.

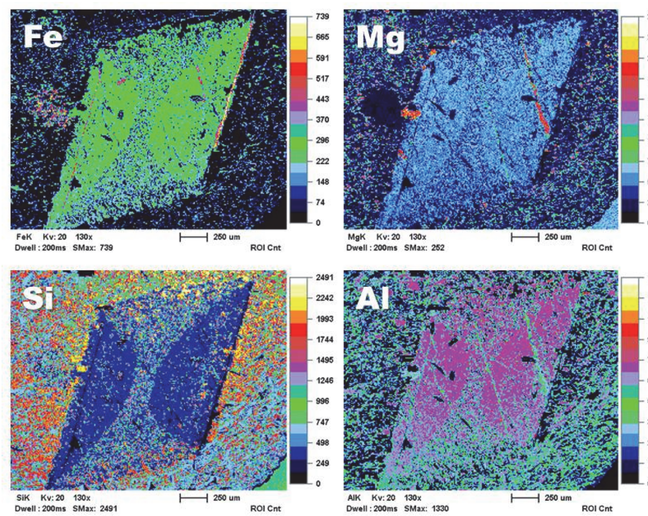

Figure 10. (a) Fe, (b) Mg, (c) Si and (d) Al compositional maps of sector-zoned (hourglass structure) chloritoid and associated mineral phases. Light colors show areas of high concentration while dark colors represent areas of low concentration (black is very low concentration).
Source: The authors.

6. Metamorphism

Mineral assemblages and their relationships suggest the occurrence of a low- to middle grade metapelitic sequence with intercalations of semipelitic, psammitic and carbonate rocks. The metamorphism of the Silgará Formation at the CSM is characterized by the occurrence of typical index minerals of Barrovian type metamorphism. Based on mineral assemblages, the Silgará Formation at the study area can be divided into a Barrovian-type facies series of biotite, garnet and staurolite-kyanite zones, modifying the metamorphic isograds reported by Ward et al. (1970) and revealing a complex metamorphic and deformational history for this geologic unit. According to mineral assemblages investigated by the authors, there are interesting petrological data that can be related from the northern to the southern parts of the CSM, with a decreasing in metamorphic zones from the core of the CSM to its peripheral parts, where an extensive staurolite-kyanite zone has been developed, with a strong structural control that produce a thinning of the garnet and biotite zone. Therefore, we don´t agree with the original zonal scheme, taking into account that Ward et al. (1970) suggest a reversal distribution of the metamorphic zones with a staurolite zone to the east and a biotite zone to the west, the last of them including the Floresta Formation. We document progressive changes in mineral assemblage zones in these rocks, although the regional distribution of assemblages has not yet been mapped. However, the isograds apparently were deflected by the presence of structural features.

6.1. Biotite zone

Metapelitic rocks from the biotite zone are phyllites or fine-grained schists characterized by a penetrative cleavage, which is affected by later crenulation cleavage. The typical mineral assemblage is Chl + Ms + Bt + Qtz + Pl with opaque accessory minerals. The slaty cleavage S_1 (formed during the first deformation D_1) is defined by chlorite and muscovite. S_2 (formed during D_2) represent the regional schistosity. The chemical reaction considered in semipelitic rocks is Kfs + Chl = Bt + Ms + Qtz + H_2O, whereas the chemical reaction considered in metapelitic rocks is Phe + Chl = Bt + Ms + Qtz + H_2O (Spear, 1993).

6.2. Garnet zone

Metapelitic rocks are typically foliated, fine- to medium-grained, metapelitic schists. The typical mineral assemblage is Qtz + Ms + Grt + Gr ± Cld. Garnet occurs as very small and euhedral porphyroblasts, which do not contain mineral inclusions. Sector zoned (hourglass structure) chloritoid randomly distributed overgrows the schistosity of the rock. The occurrence of chloritoid in this metamorphic zone can be also related to Al-rich pelites and probably near the biotite zone. The chemical reaction considered in metapelitic rocks is Chl + Ms = Grt + Bt + Qtz + H_2O (Whitney et al., 1996).

6.3. Staurolite-kyanite zone

Metapelitic rocks are typically foliated, medium- to coarse-grained, metapelitic to semipelitic schists that contain the following mineral assemblages Qtz + Bt + Ms + Grt + St ± Ky ± Cld, with minor plagioclase and K-feldspar, and Fe-Ti oxides as the main accessory phases. Carbonate rocks contain the assemblage Tr + Cal. Garnet occurs as porphyroblasts partially or totally included in large, poikiloblastic and elongated staurolite porphyroblasts parallel to the main schistosity of the rock. They contain several quartz and ilmenite inclusions. Staurolite grew after garnet. Kyanite occurs as scarce subhedral porphyroblasts, which are related to mica domains. The chemical reactions considered in this metamorphic zone are described below.

In the lower part of this metamorphic zone, staurolite probably grew at the expense of chloritoid by the reaction Cld + Qtz = St + Grt + H_2O (Whitney et al., 1996). On the other hand, chlorite persists and, therefore, the reaction Grt + Chl + Ms = St + Bt + Qtz + H_2O (at low T) should be considered, which takes place at a fixed temperature for any given pressure, because it is discontinuous and proceeds until one of the three reactants has been consumed (Yardley, 1989). According to Yardley (1989), when this reaction ceases, additional staurolite may be produced by a continuous reaction involving the remaining phases, such as Chl + Ms = St + Bt + Qtz + H_2O (at high T). Kyanite may have grown at the expense of staurolite by a reaction such as St + Chl + Ms = Ky + Bt + Qtz + H_2O (Whitney et al., 1996).

Chloritoid does not occur commonly in the Silgará Formation, due to the MnO content of garnet, which produces an expansion of the Grt–Chl stability field to lower temperatures or to Al poor bulk compositions that contain garnet + chlorite assemblages rather than chloritoid + biotite (Spear and Cheney, 1989).

7. Petrologic significance

The appearance of chloritoid is very difficult to understand with regard to other metamorphic index minerals and its relation to the Barrovian scheme defined at the CSM is still unclear. Chloritoid has been reported and described in many metamorphic terrains in which this mineral appears in low- and medium-P metapelites impoverished and enriched in Al and high-P metapelites with high contents of Mg. The PT conditions of chloritoid-bearing metapelites range from the sub-greenschist facies to the middle part of the amphibolite facies in the staurolite-kyanite zone. The occurrence of chloritoid in the lowest grade rocks are reported by Primmer (1985) in Upper Devonian epizone slates, and Robinson and Bevins (1986) close to the upper anchizone-epizone boundary. On the other hand, Spear (1993) reports the occurrence of the paragenesis chloritoid + pyrophyllite. At the greenschist facies, chloritoid is a common mineral associated with chlorite and muscovite in rocks enriched in Fe and with high contents of Al (Turner and Verhoogen, 1960; Cabanis, 1982, Johnson et al., 2003). The contents of Fe and Al must be greater than those recorded for the stability of chlorite and muscovite (Cabanis, 1982; Johnson et al., 2003). In this sense, it is not unusual the occurrence of chloritoid with high ottrelite component in low-grade metapelites of the greenschist facies as phyllites and schists (Kramm, 1973; Brindley and Elsdon, 1974). At the amphibolite facies, chloritoid has also been reported in rocks with andalusite, kyanite and staurolite (Cabanis, 1974; Spear, 1993). The construction of petrogenetic grids and stability diagrams of the paragenesis with chloritoid indicate that under certain conditions, a chloritoid zone analogous to the biotite zone can be considered (Spear, 1993). One is based on the KFMASH grid of Harte and Hudson (1979), in which chloritoid+biotite is stable over a narrow temperature interval at relatively low-pressure, and the other on the KFMASH grids of Spear and Cheney (1989) and Wang and

Spear (1991), in which this assemblage is stable over wide ranges of pressure and temperature conditions. The petrological study presented below provides a good opportunity to assess the validity of these alternative petrogenetic grids for pelites.

Taking into account the first occurrence of chloritoid in the Santander Massif, we propose two interpretations. (1) Chloritoid is associated with muscovite, chlorite and quartz in the staurolite-kyanite zone of the amphibolite facies in a highly deformed and sheared region. However, chloritoid porphyroblasts do not show evidence of deformation, which could be interpreted as a post-deformation growth and could correspond to the retrograde step of metapelites with low contents of Al, but somewhat enriched in Fe. (2) An almost isobaric thermal metamorphic event related to the emplacement of small granitoid masses without deformation has been superimposed on the Barrovian metamorphism previously defined at the Santander Massif, and particularly very well defined at the CSM.

The most probably origin of chloritoid, given its restricted occurrence within the Santander Massif, and more specifically within the metapelitic rocks of the Silgará Formation, can be attributed to heat fluxes associated to numerous felsic granitoid masses without deformation, many of which have not been mapped yet mainly due to their intense and advanced weathering and size (in general less than 1 km^2 in extension but with a distribution that covers nearly 2.000 km^2 in several sectors of the CSM). They occur as small bodies displaying intrusive contact with the three main metamorphic units of its crystalline basement of the Santander Massif, many of which were mapped and described by Ward et al. (1973). Compositionally, these granitoids are represented by moscovite and/or biotite quartzmonzonite and granite, with local variations in grain size and color, being important to note that they do not show evidence of deformation pre-, syn- or post-emplacement. However, the lack of thermobarometric and geochronologic data do not allow defining the PTt conditions of formation of chloritoid in the geological context of the Santander Massif.

It is argued that despite poverty and preservation of outcrops, the apparent restriction of chloritoid to a highly tectonized area at the southern part of the CSM is unusual and real. Two possible interpretations of this restriction are considered: Chloritoid occurs in graphite-bearing metapelitic schists highly tectonized that can be associated to the influence of the Vichagá Stream lineament in the study area. The occurrence of chloritoid as an index mineral in metapelitic rocks of the Silgará Formation makes it necessary to revise if chloritoid is definitively associated to a thermal event (associated to the emplacement of small granitoid masses without deformation) overimposed on the regional metamorphism or not. However, we consider the last of them as the most probably cause of the formation of chloritoid, in spite of Ríos and co-workers have reported petrologic evidences that related the emplacement of orthogneiss masses not only to the restricted appearance of textural and compositional sector-zoned garnets (Castellanos et al., 2004) and large porphyroblasts of andalusite, particularly in the peripheral regions of the Ordovician Orthogneiss. Chloritoid-bearing assemblages have been described from numerous areas of regional metamorphism and from scarce contact aureoles. The second case is due, in part, to a narrow temperature interval at low pressures of metamorphism (Ganguly, 1969) and severe constraints imposed by specific bulk rock composition (e.g. Wang and Spear, 1991). However, we have not evidence of a contact metamorphism and, therefore, we conclude that the origin of the chloritoid-bearing assemblages in the study area can be related to heat flow associated to the emplacement of small granitoid masses without deformation.

Additional evidences of the effect of the emplacement of orthogneiss masses have been reported by Ríos et al. (2008b), who consider that H_2O required to drive prograde CO_2 loss in metacarbonate rocks probably came from regional dehydration of surrounding metapelitic rocks, although the development of a H_2O-rich diopside reaction zone in the presence or absence of scapolite probably also required an external fluid contribution derived from syn-metamorphic intrusions (orthogneiss masses) emplaced during the final stage of metamorphism of the Silgará Formation. The widespread existence of “shimmer” aggregates of sericite alteration of aluminous minerals (e.g., staurolite or kyanite) in the staurolite-kyanite zone provides evidence of potassium transfer during the retrograde metamorphism.

8. Conclusions

Chloritoid is reported for the first time in metapelitic rocks of the Silgará Formation from the staurolite-kyanite zone of the amphibolite facies at the CSM. This mineral occurs as idioblastic sector zoned (hourglass structure) porphyroblasts in a matrix of muscovite, chlorite, quartz, ilmenite and graphite as major minerals. The lithologic context would indicate an almost isobaric thermal event superimposed on the Barrovian metamorphism caused by the emplacement of small granitoid masses without deformation. We conclude that the metamorphism may be characterized as a Barrovian type, developed in conditions of medium pressure and temperatures conditions reaching the amphibolite facies. The medium pressure metamorphism could result from thermal perturbation related to the calc-alkaline granitoid intrusions at middle to upper crustal depths. The zonal sequence of biotite, garnet and staurolite-kyanite is different to that original reported in the classic work of Ward et al. (1970). The first appearance of chloritoid differs from other regions of the Santander Massif, where this index mineral not appears to be developed.

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