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OCCURRENCE AND SIGNIFICANCE OF THE POLYMORPHS OF Al_2SiO_5 IN METAMORPHIC ROCKS OF THE SANTANDER MASSIF, EASTERN CORDILLERA (COLOMBIAN ANDES)

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ABSTRACT

The pelitic and semipelitic rocks of the Santander Massif metamorphic basement have been affected by a Barrovian type of metamorphism, which has occurred under high-temperature and medium-pressure conditions. The polymorphs of Al_2SiO_5, kyanite, andalusite, and sillimanite, are each stable over a characteristic range of pressure and temperature and provide useful means of estimating conditions of metamorphism recorded by these rocks. In the staurolite-kyanite zone, in some cases the polymorphs of Al_2SiO_5 kyanite and andalusite, occur as porphyroblasts, the last one generally with a poikiloblastic character. Textural evidence indicates the formation of kyanite after andalusite, And → Ky. During the process of prograde metamorphism of the Santander Massif metamorphic rocks, the sillimanite first appears after kyanite or in muscovite adjacent to garnet, replacing biotite or garnet, and occurs as aggregates of fibrolite, sometimes penetrating quartz grains. A reaction such as staurolite + muscovite + quartz could produce the first appearance of sillimanite, as well as the disappearance of the staurolite from the chemical system.

Key words: Santander Massif, Barrovian, kyanite, andalusite, sillimanite

OCCURRENCIA Y SIGNIFICADO DE LOS POLIMORFOS DE Al_2SiO_5 EN LAS ROCAS METAMORFICAS DE EL MACIZO DE SANTANDER, CORDILLERA ORIENTAL (ANDES COLOMBIANOS)

RESUMEN

Las rocas pelíticas y semipelíticas del basamento metamórfico del Macizo de Santander han sido afectadas por un metamorfismo de tipo Barroviense, el cual ha ocurrido en condiciones de alta temperatura y media presión. Los polimorfos de Al_2SiO_5, cianita, andalusita, y silimanita, son estables en un rango característico de presión y temperatura y proporcionan información útil para estimar las condiciones de metamorfismo registradas por estas rocas. En la zona de la estaurolita-cianita, en algunos casos los polimorfos de Al_2SiO_5 cianita y andalusita, ocurren como porfidoblastos, los últimos generalmente con un carácter poiquiloblástico. Evidencia textural indica la formación de cianita después de andalusita, And → Ky. Durante el metamorfismo progrado de las rocas del Macizo de Santander, la silimanita aparece primero remplazando la cianita o la muscovita en zonas adyacentes al granate, remplazando la biotita o el granate y ocurre también como agregados fibroliticos algunas veces penetrando cristales de cuarzo. La reacción estaurolita + muscovita + cuarzo pudo haber producido la silimanita asi como la desaparición de la estaurolita del sistema químico.

Palabras clave: Macizo de Santander, barroviense, cianita, andalusita, silimanita

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INTRODUCTION

The presence of polymorphs of Al_2SiO_5 lets an approach in the determination of pressure and temperature (P-T) in metamorphic terrains. This study considers the occurrence of the polymorphs of Al_2SiO_5 in the Santander Massif metamorphic rocks, and their significance during the reaction history by which these rocks have evolved. The Santander Massif is characterized by a typical Barrovian zonal scheme, and evidences and interpretations on the occurrence of such polymorphs are presented here, besides studying the transition from the staurolite-kyanite zone to the sillimanite zone, which will mark the disappearance of the staurolite from the chemical system, and the first appearance of sillimanite. The nature and meaning of polymorphs of Al_2SiO_5 have been discussed in different works (e.g., Yardley 1977, Yardley *et al*. 1989, Spear 1993, and Spear *et al*. 1995).

The P-T conditions of the invariant equilibrium in the Al_2SiO_5 system are not well defined, which is related to small differences of free energy that exist between kyanite, andalusite and sillimanite near the equilibrium (e.g., Holdaway 1971). Experimental studies carried out near the phase equilibrium between the Al_2SiO_5 polymorphs show some differences respect to the location of the triple point of Al_2SiO_5 (e.g., Newton 1966a, Newton 1966b, Holdaway 1971, Bohlen *et al*. 1991, Hemingway *et al*. 1991, and Pattison 1992). On the other hand, Grambring (1981) shows geological evidences that support the coexistence of the three polymorphs of Al_2SiO_5 in conditions near the equilibrium in the Truchas Peaks region to the north of New México. The metastable persistence of a polymorph in the stability field of another one is a very common phenomenon due the polymorphic transitions involve only small changes in the free energy, suggesting that the water needs to be present in the rock as a solvent and catalizator, although not as a specie in the stoichiometric reaction (Bucher and Frey 1994).

Facies series with kyanite at middle grade and sillimanite at high grade represents metamorphism at pressures greater than that of the triple point and is referred to as the Barrovian facies series.

The metamorphic rocks that crop out in the Santander Massif are studied by mineralogical, petrographical, chemical and thermobarometric methods in order to determine both the pressure-temperature conditions of these rocks, and discuss the meaning of the occurrence of the aluminosilicates as part of their reaction history, integrating also textural and microstructural observations, as well as previously published data.

GEOLOGY OF THE SANTANDER MASSIF

The Santander Massif forms part of the Eastern Cordillera of the Colombian Andes, and is situated where this cordillera is divided within the NE-SW-trending Perijá Range and the ENE-WSW-trending Mérida Andes of Venezuela (FIGURE 1). The study area comprises three regions: Southwestern (from Pescadero to Aratoca), Central (from California to Mutiscua) and Eastern (west of Pamplona).

The Proterozoic and Paleozoic metamorphic basement of the Santander Massif has been classically divided within three metamorphic units; Bucaramanga Gneiss, Silgará Formation, and Orthogneiss (FIGURE 2), which are cut by intrusive bodies mainly of Paleozoic to Jurassic ages (e.g., Goldsmith *et al*. 1971), see FIGURE 1. The metamorphic rocks that crop out in the massif correspond to gneisses, amphibolites and migmatites of the Bucaramanga Gneiss, schists, quartzites and marble of the Silgará Formation and gneisses and amphibolites of the Orthogneiss.

During the metamorphism of the Silgará Formation, a sequence of metamorphic zones was developed (biotite, garnet, staurolite-kyanite and sillimanite) of the typical Barrovian zonal scheme. However, a migmatite zone is reported here. According to Miyashiro (1994), it belongs to the kyanite-sillimanite series (medium-P/T type). The mineral zones developed in pelitic and semipelitic rocks have defined the regional thermal structure and the boundaries between the mineral zones were defined on basis of the first appearance of such minerals. For mapping of isograds, some noticeable differences have been established in this study, such as the occurrence of the first sillimanite isograd and the second sillimanite isograd. The regional grade of metamorphism decreases towards the southwestern from the Páramo de Santurbán area (on the northeast) to the Aratoca area (on the southwest). The regional metamorphism has occurred under high-temperature and medium-pressure conditions. The metamorphic sequence ranges from the greenschist facies up to the upper amphibolite facies and was affected by a

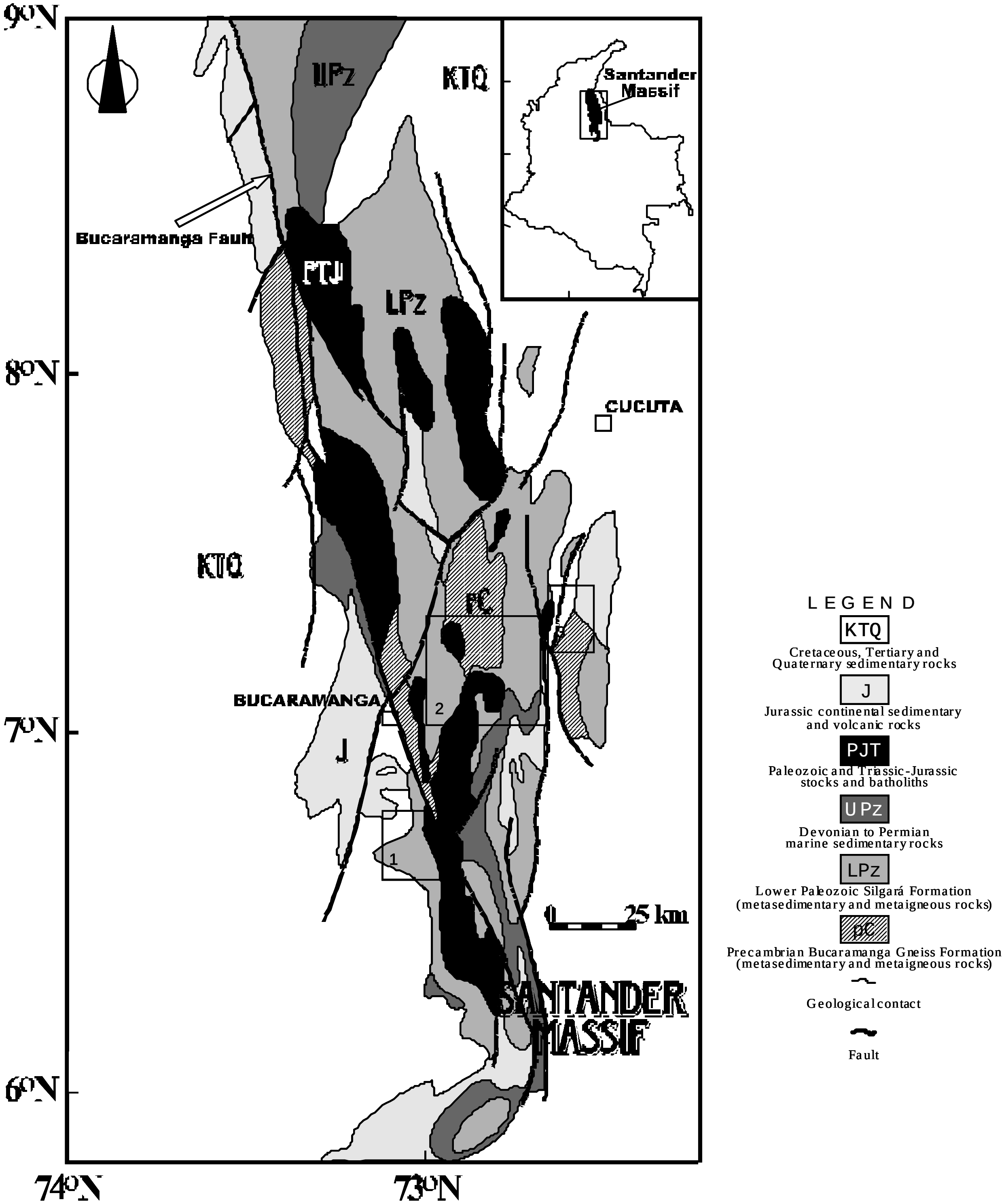

FIGURE 1. Generalized geologic map of the Santander Massif (modified after Goldsmith et. al, 1971), showing the study area, indicated by numbers 1, 2 and 3.

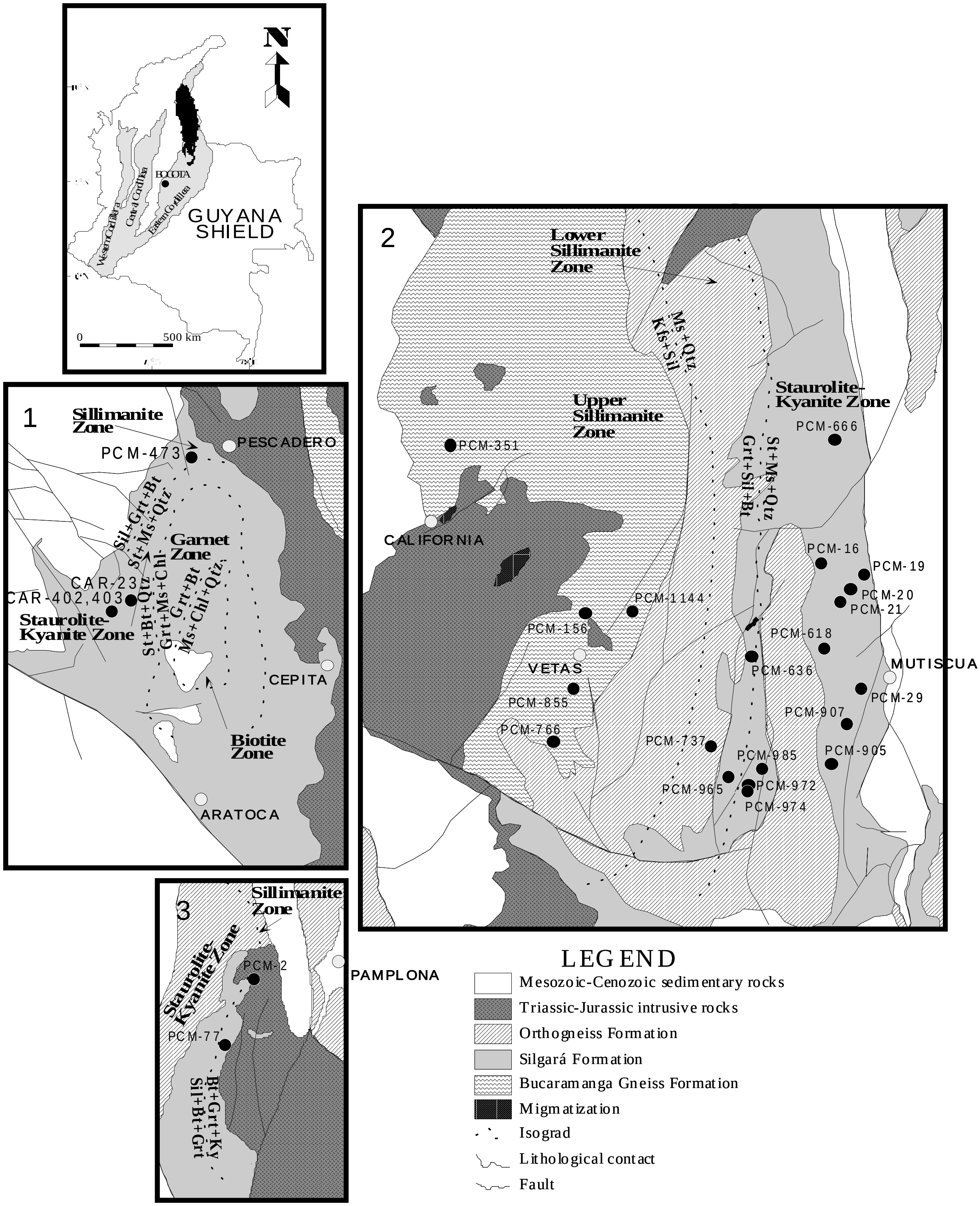

FIGURE 2. Geological map of the study area at the Santander Massif, modified after Ward et al. (1973): (1) southwestern region, (2) central region, and (3) eastern region. The sample localities with occurrence of Al_2SiO_5 polymorphs in the Silgará Formation metapelitic rocks are indicated by black dots.

retrograde metamorphism maybe within the epidote-amphibolite facies. Retrogressive effects appear to be stronger in rocks near to the contact with intrusive bodies in the massif.

OCCURRENCE OF POLYMORPHS OF Al_2SiO_5 AND REACTION TEXTURES

The occurrence of the polymorphs of Al_2SiO_5 is illustrated in FIGURES 3 and 4. The mineral assemblages and the occurrence of the aluminosilicates in the study area are described as follows. Mineral abbreviations are after Kretz (1983).

Southwestern Santander Massif

The southwestern region extends from Pescadero to Aratoca and is limited by the Bucaramanga Fault on the northeast and the Los Santos - Aratoca Fault on the southwest. In this region is reported the presence of kyanite, andalusite and sillimanite, defining a staurolite-kyanite zone. The more abundant mineral assemblage in pelitic and/or semipelitic rocks of the *staurolite-kyanite zone* is Bt + Ms + Qtz + Pl + Grt ± St ± Ky ± And. Here, the occurrence of the of the three Al_2SiO_5 polymorphs (see FIGURE 3) has been reported for the first time by Ríos and García (2001). On the other hand, the diagnostic assemblage in the transition between the staurolite-kyanite zone and sillimanite zone is Bt + Ms + Qtz + Pl ± Grt ± St ± Sil.

Andalusite is xenoblastic, and nearly half of its volume may contain numerous inclusions, so that individual grains look like a sponge. It occurs as elongated porphyroblasts around garnet, which has been replaced in its rim by sillimanite. Kyanite, which is the more abundant polymorph of Al_2SiO_5 in this region, occurs as small porphyroblasts, which display a well-marked cleavage and partition, and is apparently surrounding andalusite (FIGURE 3c). In some places kyanite relicts in muscovite are observed. Staurolite occurs as big porphyroblasts (up to 1.20 cm in cross section) with a poikiloblastic character, which contain numerous inclusions of quartz and ilmenite that define a internal schistosity (S_{int}) parallel to the external foliation (S_{ext}) of the rock, and many of these staurolite porphyroblasts are replaced by muscovite and chlorite, sometimes developing pseudomorphs. However, the staurolite usually occurs as corroded relicts within muscovite or showing aggregate of muscovite+chlorite surrounding and replacing them along irregular cracks. The first appearance of sillimanite is as knots of fibrous grains, called *fibrolite*, that have the appearance of matted wet brown hair. Fibrolite commonly occurs within muscovite that is associated to garnet porphyroblasts (FIGURE 4a) or as a replacement at their rims (FIGURE 3c), sometimes developing reaction rims. There is not regularity in the orientation of the minute crystals of sillimanite, because they cut cross the muscovite sheets to variable angles with respect to their cleavage. The sillimanite occurs as minute crystals sometimes penetrating quartz grains, which develop embayment in garnet, within which the polymorph of Al_2SiO_5 also occurs.

Central Santander Massif

The Central region is extended from California to the Mutiscua Fault. The mineral assemblages in the *staurolite-kyanite zone* and semipelitic rocks are Grt + Bt + Ms + St + Qtz ± Ky, Bt + Ms + Qtz ± Grt + St, Bt + Ms + Ky + And ± Pl + Qtz, and Ms + Ky + Qtz in pelitic rocks; Pl + Bt + Ms + Qtz, and Pl + Ms + Grt + Qtz + St in semipelitic rocks. On the other hand, the *sillimanite zone* is characterized by the following mineral assemblages: Grt + Bt + Ms + Sil + Qtz, and Grt + Bt + Sil + Pl + Qtz in pelitic rocks and Pl + Mc + Qtz + Ms + Bt in semipelitic rocks after the lower sillimanite isograd, and Grt + Bt + Sil + Kfs + Qtz in pelitic rocks and Grt + Pl + Sil + Kfs + Qtz in semipelitic rocks after the upper sillimanite isograd.

Subidioblastic porphyroblasts of kyanite and staurolite are concentrated in thin layers of foliated muscovite. Staurolite occurs as nearly euhedral porphyroblasts. It commonly has abundant quartz inclusions, but may be, as most grains here, inclusion-free.

The kyanite occurs as subidioblastic crystals, although it is commonly observed developing corroded relicts into muscovite. This mineral shows a good cleavage in one direction, as well as partition almost to right angles. It is associated to quartz and, sometimes, staurolite in quartz-rich bands, in which kyanite occurs surrounding staurolite (FIGURE 3d). Kyanite also occurs in mica-rich bands, along with muscovite and biotite. The microstructural development of the kyanite-bearing rocks reflects that this mineral has grown along two schistosity surfaces (S_n and S_{n+1}) approximately to 90º each other. Some reaction rims of muscovite have been developed around kyanite (FIGURE 3e). These reaction rims have nucleate between kyanite and quartz.

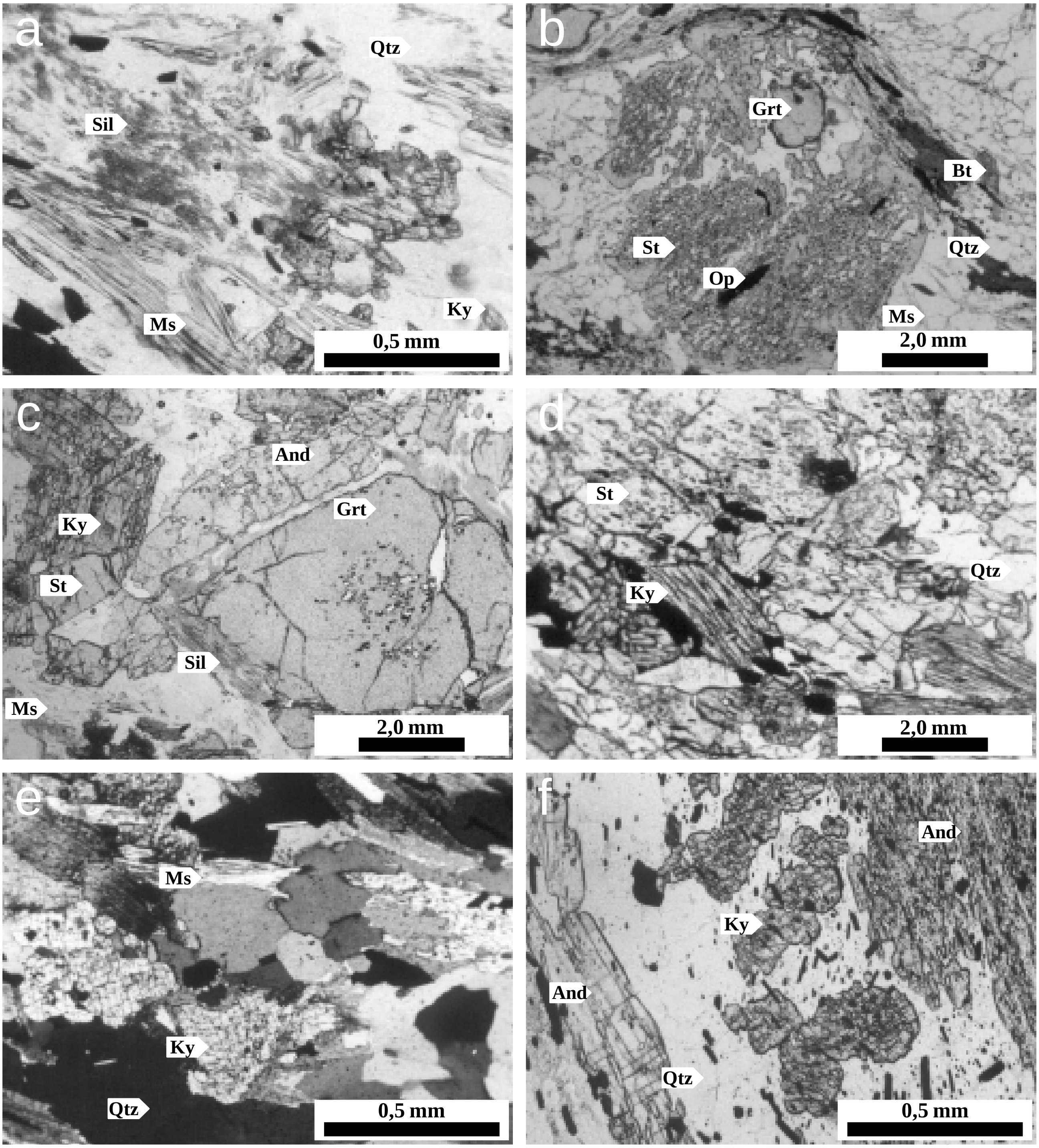

FIGURE 3. Ocurrence of staurolite and kyanite in metamorphic rocks of the Silgará Formation. (a) Sillimanite (fibrolitic variety) replacing kyanite. Photomicrograph, plane-polarized light. (b) Porphyroblast of staurolite including a relict of garnet. Photomicrograph, plane-polarized light. (c) Apparent equilibrium occurrence of the Al_2SiO_5 triple point. Photomicrograph, plane-polarized light. (d) Kyanite crystals surrounding porphydoblast of staurolite. Photomicrograph, plane-polarized light. (e) Muscovite developing a reaction rim around kyanite. Photomicrograph, crossed polars. (f) Kyanite crystals have overgrown a large and poiquiloblastic andalusite porphyroblast on the right side, which displays numerous opaque mineral inclusions. Observe the occurrence of a large andalusite porphyroblast on the left side. Photomicrograph, plane-polarized light.

The kyanite in some cases (sample PCM-985) is replaced by sillimanite (FIGURE 3a), and in other cases is found as relicts in muscovite.

Andalusite porphyroblasts are idioblastics, with rectangular shape, elongated in the sense of the main foliation and, many of them poikiloblastic, with numerous inclusions of quartz and opaque minerals. Small crystals of kyanite surround some of the andalusite porphyroblasts (FIGURE 3f).

Different stages of recrystallization of sillimanite have been recognized, from a fine and felted fibrolite appears to be the sillimanite of earliest formation, to coarse growth of prismatic crystals commonly as stellate aggregates enclosed in biotite. The texture in which coarse sillimanite occurs within biotite may reflect its growth either contemporaneously or subsequent to the recrystallization of the sillimanite (FIGURE 4b). The prismatic sillimanite, in some cases, showing diamond-shape cross sections and good cleavage, develops a strong orientation (FIGURE 4c). A fine fibrolitic sillimanite commonly shows a meandriform aspect through the micaceous bands of the rock, and occurs as intergrowths with, and apparently replacing, biotite. It develops a progressive replacement along the trace of cleavage in biotite, and relicts of biotite within sillimanite are common. The association sillimanite-muscovite also occurs, although there is no regularity of the orientation, because numerous small needle-like crystals of sillimanite traversing muscovite at different angles to the cleavage. Chinner (1961) supposes that if a sillimanite-muscovite texture originally existed, extensive recrystallization and growth of muscovite have destroyed it during the later phases of metamorphism. An acicular variety of sillimanite occurs as minute and isolated crystal across quartz (FIGURE 4d), plagioclase and, less frequently, garnet, as well as along the contact between quartz grains or between quartz and plagioclase grains. The sillimanite also develops pseudomorphs along with biotite and, maybe with leucoxene, replacing garnet (FIGURE 4e), although is possible to think that a previous replacement biotite+muscovite after garnet may occur.

Kyanite probably is absent in such rocks in which sillimanite is abundant and occurs as coarse-grained prismatic crystals. Some textures involving staurolite, kyanite and muscovite indicate growth of these minerals after the main period of sillimanite development, which shows that the recrystallization of coarse sillimanite has been followed by a retrograde process to staurolite-kyanite zone conditions (Chinner 1961). However, we have no evidences of the occurrence of idioblastic kyanite or staurolite within sillimanite, apparently replacing or including it.

In some case staurolite porphyroblasts, which present numerous quartz inclusions, include relicts of garnet (FIGURE 3b). The recrystallization of muscovite after staurolite or kyanite commonly occurs, and typical textures of this recrystallization are corroded relicts of kyanite or staurolite, and remnants of sillimanite, found within muscovite. This growth of muscovite appears to be related to a high activity of water and potassium in the fluid phase at the staurolite-kyanite zone (Chinner 1961).

Eastern Santander Massif

This region is located to the west of Pamplona city and extends from this to the Morro Negro Fault on the west. In the *staurolite-kyanite zone* mineral assemblages are represented by Bt + Ms + Qtz ± Grt ± Ky in pelitic rocks, and Pl + Mc + Qtz + Ms + Bt in semipelitic rocks. The following are mineral assemblages that occur in pelitic rocks of the *sillimanite zone*: Grt + Bt + Ms + Sil + Qtz, and Pl + Ms + Grt + Qtz.

The occurrence of kyanite is restricted to the appearance as corroded relicts within muscovite.

Sillimanite occurs as fibrolite aggregates randomly oriented within the garnet porphyroblasts, sometimes developing pseudomorphs along with biotite (FIGURE 4f), as well as to minute crystals non regularly dispersed penetrating quartz grains or associated with biotite in the matrix.

MINERAL CHEMISTRY AND GEOTHERMOBAROMETRY

Electron microprobe analyses for this study were performed on the constituent minerals, using a JEOL JXA 8800M electron microprobe analyzers from the Research Center for Coastal Lagoon Environments at Shimane University and the Center of Electron Microscopy at Universidad Complutense de Madrid, under the following analytical conditions: accelerating voltage and specimen current are 15 kV and 2.0×10^{-8} Å, respectively. Data acquisition and reduction were

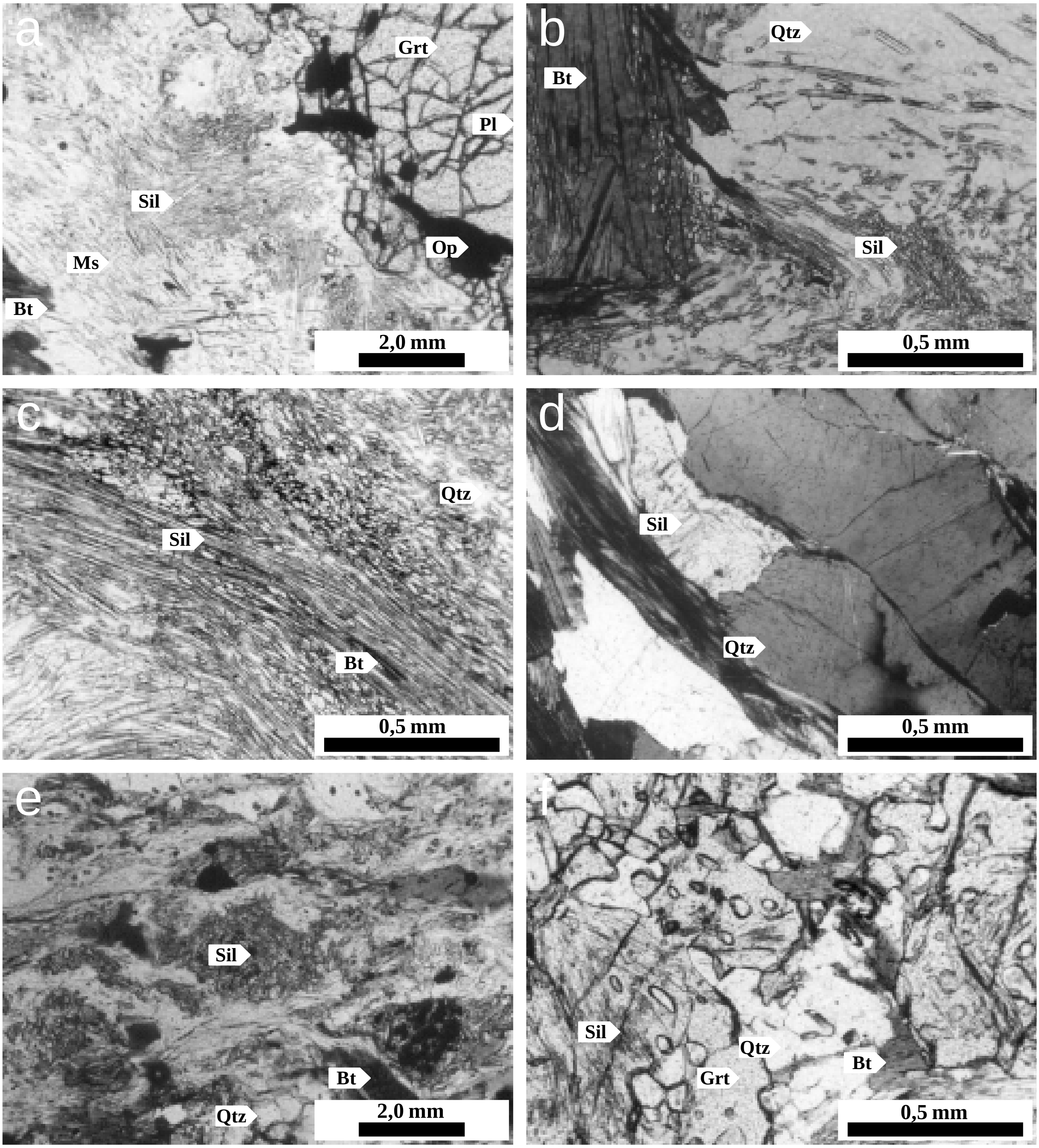

FIGURE 4. Ocurrence of sillimanite in metamorphic rocks of the Silgará Formation. (a) Fibrolitic sillimanite occurs as inclusions in muscovite and quartz near a garnet porphydoblast. Photomicrograph, plane-polarized light. (b) Prismatic sillimanite, associated to biotite, developing a crenulation schistosity. Photomicrograph, plane-polarized light. (c) Sillimanite (prismatic variety), in which some crystals are cut perpendicular to their length and show cross sections with a diamond-shape and show cleavaje after (010). Photomicrograph, plane-polarized light. (d) Fibrolitic sillimanite included into quartz. Photomicrograph, crossed polars. (e) Pseudomorphs of sillimanite+biotite after garnet. Photomicrograph, plane-polarized light. (f) Fibrolitic sillimanite included into garnet and quartz. Photomicrograph, plane-polarized light.

TABLE 1. Representative chemical compositions of minerals of pelitic schist of Southwestern region, Santander Massif (Silgara Formation, sample PCM-473).

COMPONENT	MINERAL			
	GARNET	BIOTITE	MUSCOVITE	PLAGIOCLASE
SiO2	37.00	34.67	45.22	62.27
TiO2	0.00	1.60	0.67	0.00
Al2O3	20.34	18.88	32.87	23.37
FeO	31.16	21.32	3.15	0.06
Fe2O3	-----	---	---	---
MnO	7.26	0.03	0.00	---
MgO	2.75	8.26	0.69	---
CaO	1.57	---	---	4.98
Na2O	---	0.22	0.89	8.99
K2O	---	10.14	10.64	0.29
Cr2O3	---	---	---	---
TOTAL	100.08	95.12	94.13	99.96
Cations/O	12	22	22	8
Si	3.001	5.371	6.184	2.765
Ti	0.000	0.186	0.069	0.000
Al	1.944	3.447	5.298	1.223
Fe+2	2.113	2.762	0.360	0.002
Fe+3	---	---	---	---
Mn	0.499	0.004	0.000	0.000
Mg	0.333	1.908	0.141	0.000
Ca	0.136	---	---	0.237
Na	---	0.066	0.236	0.774
K	---	2.004	1.856	0.016
Cr	---	---	---	---
TOTAL	8.026	15.748	14.144	5.019
XMg	0.14	0.41		
Xalm	0.69			
Xsps	0.16			
Xprp	0.23			
Xgrs	0.04			
XAn				0.23

X_{Mg}=Mg/(Fe+Mg), X_{alm}=Fe^{2+}/(Fe^{2+}+Mn+Mg+Ca), X_{sps}=Mn/(Fe^{2+}+Mn+Mg+Ca), X_{prp}=Mg/(Fe^{2+}+Mn+Mg+Ca), X_{grs}=Ca/(Fe^{2+}+Mn+Mg+Ca), X_{an}=Ca/(Na+Ca+K).

performed using the ZAF correction. Natural and synthetic minerals were used as standards. Mineral compositions were determined by multiple spot analyses. Representative chemical compositions of minerals, which were used to calculate pressures and temperatures are shown in TABLES 1, 2, 3, 4 and 5. García and Ríos (1999) consider that the chemical composition of the metamorphic rocks in the Santander Massif shows very complex relationships, which reflects a strong control of the chemical compositions of the constituent minerals by the bulk-rock chemistry control, masking the chemical changes produced by pressure and temperature.

The P-T conditions of equilibrium among the rims of major minerals in these rocks were estimated by Berman's TWQ program, the results of pressure and temperature estimates are summarized in TABLE 6.
In the southwestern region, Ríos and García (2003) calculated P-T conditions (495-518°C and 4.4-5.5 kbar from garnet zone; 590-612°C and 6.6-7.5 kbar from staurolite zone; 660-700°C and 5.5-7.2 kbar from

sillimanite zone) using different thermometers and barometers. P-T determinations using TWQ in the sample PCM-473 with sillimanite were 5.7Kb and 614°C respectively. On the other hand, the TWQ program was applied in the other regions in order to estimate the pressure and temperature conditions, mainly in the staurolite-kyanite and sillimanite zones. In the eastern region was obtained a temperature of 778°C with pressures of 7.5 kbar; in the sillimanite zone. In the central region, P-T conditions are as follows: 9.5 kbar and 630°C in the staurolite-kyanite zone, and 6.6 – 7.5 Kbar and 690-727°C in the sillimanite zone. The P-T conditions are consistent with phase equilibrium deductions. However they are far away from the experimental determinations of the invariant equilibrium in the Al_2SiO_5 system reported by some authors (e.g., Holdaway, 1971).

TABLE 2. Representative chemical compositions of minerals in pelitic schist of Central region, Santander Massif (Silgara Formation, sample PCM-28).

COMPONENT	MINERAL			
	GARNET	BIOTITE	MUSCOVITE	PLAGIOCLASE
SiO_2	37.74	36.54	47.51	59.31
TiO_2	0.06	0.96	0.00	0.00
Al_2O_3	22.25	19.07	34.13	26.19
FeO	28.78	16.64	2.10	0.02
Fe_2O_3	-----	---	---	---
MnO	1.57	0.01	0.03	0.02
MgO	3.20	11.56	0.61	0.01
CaO	6.66	0.12	0.08	7.72
Na_2O	---	0.34	0.07	7.00
K_2O	---	8.42	10.88	0.07
Cr_2O_3	0.00	0.00	0.01	0.00
TOTAL	100.26	93.66	95.42	100.34
Cations/O	12	22	22	8
Si	2.976	5.536	6.329	2.635
Ti	0.004	0.109	0.000	0.000
Al	2.067	3.405	5.358	1.371
Fe^{+2}	1.897	2.108	0.234	0.001
Fe^{+3}	---	---	---	---
Mn	0.105	0.001	0.003	0.001
Mg	0.376	2.611	0.121	0.001
Ca	0.563	0.019	0.011	0.367
Na	---	0.100	0.018	0.603
K	---	1.627	1.849	0.004
Cr	0.00	0.000	0.001	0.000
TOTAL	7.987	15.516	13.925	4.983
X_{Mg}	0.17	0.55		
X_{alm}	0.65			
X_{sps}	0.04			
X_{prp}	0.33			
X_{grs}	0.19			
X_{An}				0.38

X_{Mg}=Mg/(Fe+Mg), X_{alm}=Fe2+/(Fe^{2+}+Mn+Mg+Ca), X_{sps}=Mn/(Fe^{2+}+Mn+Mg+Ca), X_{prp}=Mg/(Fe^{2+}+Mn+Mg+Ca), X_{grs}=Ca/(Fe^{2+}+Mn+Mg+Ca), X_{an}=Ca/(Na+Ca+K).

TABLE 3. Representative chemical compositions of minerals in pelitic gneiss of Central region, Santander Massif (Bucaramanga Gneiss, sample PCM-855).

COMPONENT	MINERAL		
	GARNET	BIOTITE	PLAGIOCLASE
SiO_2	38.15	35.92	56.60
TiO_2	0.00	2.73	0.00
Al_2O_3	21.80	16.20	27.30
FeO	26.56	17.50	0.16
Fe_2O_3	-----	---	---
MnO	4.51	0.20	0.00
MgO	3.52	12.91	0.00
CaO	5.49	0.03	9.10
Na_2O	---	0.27	6.50
K_2O	---	9.41	0.08
Cr_2O_3	0.00	0.02	0.00
TOTAL	100.03	95.19	99.74
Cations/O	12	22	8
Si	3.012	5.452	2.548
Ti	0.000	0.312	0.000
Al	2.028	2.898	1.448
Fe^{+2}	1.753	2.221	0.006
Fe^{+3}	---	---	---
Mn	0.302	0.026	0.000
Mg	0.414	2.921	0.000
Ca	0.464	0.005	0.439
Na	---	0.079	0.567
K	---	1.822	0.005
Cr	0.00	0.002	0.000
TOTAL	7.974	15.737	5.013
X_{Mg}	0.19	0.57	
X_{alm}	0.60		
X_{sps}	0.10		
X_{prp}	0.28		
X_{grs}	0.16		
X_{An}			0.43

X_{Mg}=Mg/(Fe+Mg), X_{alm}=Fe^{2+}/(Fe^{2+}+Mn+Mg+Ca), X_{sps}=Mn/(Fe^{2+}+Mn+Mg+Ca), X_{prp}=Mg/(Fe^{2+}+Mn+Mg+Ca), X_{grs}=Ca/(Fe^{2+}+Mn+Mg+Ca), X_{an}=Ca/(Na+Ca+K).

TABLE 4. Representative chemical compositions of minerals in pelitic gneiss of Central region, Santander Massif (Bucaramanga Gneiss, sample PCM-156).

COMPONENT	MINERAL		
	GARNET	BIOTITE	PLAGIOCLASE
SiO_2	37.82	35.10	59.81
TiO2	0.00	3.62	0.00
Al_2O_2	21.90	18.07	25.30
FeO	28.04	20.36	0.02
Fe_2O_2	-----	---	---
MnO	7.36	0.31	0.00
MgO	3.05	8.06	0.01
CaO	1.77	0.01	6.98
Na_2O	---	0.12	7.41
K_2O	---	9.86	0.38
Cr_2O_2	0.02	0.04	0.00
TOTAL	99.96	95.55	99.91
Cations/O	12	22	8
Si	3.016	5.387	2.669
Ti	0.000	0.418	0.000
Al	2.058	3.268	1.330
Fe^{+2}	1.869	2.613	0.001
Fe^{+3}	---	---	---
Mn	0.497	0.040	0.000
Mg	0.363	1.844	0.001
Ca	0.151	0.002	0.334
Na	---	0.036	0.641
K	---	1.930	0.022
Cr	0.001	0.005	0.000
TOTAL	7.955	15.542	4.997
X_{Mg}	0.16	0.41	
X_{alm}	0.65		
X_{sps}	0.17		
X_{prp}	0.24		
X_{grs}	0.05		
X_{An}			0.34

X_{Mg}=Mg/(Fe+Mg), X_{alm}=Fe^{2+}/(Fe^{2+}+Mn+Mg+Ca), X_{sps}=Mn/(Fe^{2+}+Mn+Mg+Ca), X_{prp}=Mg/(Fe^{2+}+Mn+Mg+Ca), X_{grs}=Ca/(Fe^{2+}+Mn+Mg+Ca), X_{an}=Ca/(Na+Ca+K).

REACTION HISTORY

Chemical reactions that take place during metamorphism produce mineral assemblages stable under the new conditions of temperature and pressure. A metamorphic reaction is an expression of how the minerals got to their final state, but a reaction does not necessarily tell us the path that was actually taken to arrive at this state. Special attention was focussed on Al_2SiO_5-bearing assemblages, their relationships, reaction textures and mineral chemistry. All three Al_2SiO_5 polymorphs can be observed at a given locality as reported Ríos and García (2001), although this does not necessarily mean that the rocks have been metamorphosed at or near the aluminosilicate triple point.

The sequence of mineral reactions found in the metamorphic rocks of the Santander Massif, under intermediate pressure conditions, from the staurolite-kyanite isograd-in to the sillimanite isograd-in are described below.

TABLE 5. Representative chemical compositions of pelitic schist of Eastern region, Santander Massif (Silgara Formation, sample PCM-77).

COMPONENT	MINERAL			
	GARNET	BIOTITE	MUSCOVITE	PLAGIOCLASE
SiO2	37.67	30.99	45.19	61.33
TiO2	0.01	1.87	0.58	0.00
Al2O3	21.88	27.41	33.82	24.39
FeO	32.34	17.71	2.37	0.05
Fe2O3	-----	---	---	---
MnO	3.11	0.09	0.02	0.00
MgO	3.76	7.64	0.64	0.00
CaO	1.16	0.17	0.02	5.32
Na2O	---	0.10	0.53	8.69
K2O	---	8.29	10.55	0.03
Cr2O3	0.02	0.00	0.00	0.00
TOTAL	99.95	94.27	93.72	99.81
Cations/O	12	22	22	8
Si	3.002	4.699	6.165	2.726
Ti	0.001	0.213	0.060	0.000
Al	2.055	4.898	5.438	1.278
Fe+2	2.155	2.245	0.270	0.002
Fe+3	---	---	---	---
Mn	0.210	0.012	0.002	0.000
Mg	0.447	1.727	0.130	0.000
Ca	0.099	0.028	0.003	0.253
Na	---	0.029	0.140	0.749
K	---	1.603	1.836	0.002
Cr	0.001	0.000	0.000	0.000
TOTAL	7.969	15.455	14.044	5.010
XMg	0.17	0.43		
Xalm	0.74			
Xsps	0.07			
Xprp	0.46			
Xgrs	0.03			
XAn				0.25

X_{Mg}=Mg/(Fe+Mg), X_{alm}=Fe^{2+}/(Fe^{2+}+Mn+Mg+Ca), X_{sps}=Mn/(Fe^{2+}+Mn+Mg+Ca), X_{prp}=Mg/(Fe^{2+}+Mn+Mg+Ca), X_{grs}=Ca/(Fe^{2+}+Mn+Mg+Ca), X_{an}=Ca/(Na+Ca+K).

In the staurolite-kyanite zone there is textural evidence to support the first appearance of kyanite (*kyanite-in isograd*) in metapelitic rocks of the Silgará Formation, by the polymorphic reaction andalusite → kyanite

Staurolite is a common mineral in pelitic and/or semipelitic rocks. We assume that the following discontinuous reaction may be very important in the production of staurolite:

(1) garnet + muscovite + chlorite = staurolite + biotite + quartz + H_2O,

which is a very important reaction for low-Al pelitic rocks because marks the first appearance of staurolite (*staurolite-in isograd*). Garnet has been partially resorbed by this reaction and a significant amount of chlorite will be removed along with the production of abundant staurolite and new biotite. Garnet commonly occurs as inclusions in staurolite porphyroblasts, which show a post-tectonic character respect to that mineral, although pre-tectonic respect to the main foliation of the rock, indicating the occurrence of reaction (1), which takes place at a fixed temperature for any given pressure since it is a discontinuous reaction and proceeds until one of the three reactants has been consumed (Yardley 1989). When this reaction has ceased some further staurolite may be produced by continuous reaction involving the remaining phases, such as

TABLE 6. Pressure and temperatures of the polymorphs of Al_2SiO_5 bearing metamorphic rocks using TWQ program.

Study Area	Southwestern region	Central region			Eastern region
Metamorphic zone	Sillimanite	Staurolite-Kyanite	Sillimanite	Sillimanite	Sillimanite
Sample N°	PCM-473	PCM-28	PCM-855	PCM-156	PCM-77
Temperature, (°C)	614	630	690	727	778
Pressure, (Kilobars)	5.7	9.5	7.5	6.6	7.5

(2) chlorite + muscovite = staurolite + biotite + quartz + H_2O.

According to Spear (1993), it is very probable that all chlorite and partially staurolite were consumed in these type of rocks, producing a new generation of biotite and the first appearance of kyanite by the reaction:

(3) staurolite + chlorite + muscovite = kyanite + biotite + H_2O.

In the transition between the staurolite-kyanite zone to the sillimanite zone a first generation of sillimanite first appears within muscovite immediately adjacent to garnet and occurs as aggregates of fibrolite, which may be together or penetrate biotite or quartz grains. Fibrolite is probably the result of a tie-line switching reaction that also produces biotite. In rocks that contain both kyanite and sillimanite, direct textural evidence for the polymorphic inversion from kyanite to sillimanite is rare. Instead, it occurs as clusters of minute, needle-shaped crystals embedded in biotite or quartz.

In the sillimanite zone as staurolite becomes less abundant, it may be preserved as inclusions or corroded relicts in muscovite and, therefore, something of the muscovite growth is clearly post-staurolite, suggesting the reaction

(4) staurolite + biotite = garnet + muscovite.

Muscovite is replaced by fibrolitic sillimanite in the mineral assemblage before the final disappearance of staurolite. According to Yardley (1977), sillimanite could appear as result of the univariant reaction:

(5) staurolite + muscovite + quartz = garnet + sillimanite + biotite + H_2O,

which marks the first appearance of sillimanite (fibrolite) and is very important in the disappearance of staurolite. In the case of garnet was not involved in the consumption of staurolite, this mineral reacts by the following reaction:

(6) staurolite + muscovite + quartz = Al_2SiO_5 + biotite + H_2O.

However, if garnet breaks down as sillimanite is produced, so the initial growth of sillimanite may be considered to result from two separate continuous reactions operating simultaneously:

(7) staurolite + muscovite + quartz = sillimanite + biotite + H_2O

(8) garnet + muscovite = biotite + sillimanite + quartz

Chinner (1961) suggests that sillimanite appears to have formed within biotite, which is thought to have been a nucleating agent, the trigonally arranged oxygen octahedra and tetrahedra in the alternate mica layers acting as nuclei for the growth of the octahedral Al-O and the tetrahedral (Al,Si)-O chains that constitute the sillimanite structure. Chemical zoning and sillimanite inclusions in muscovite and quartz may indicate decrease in pressure after the formation of sillimanite by reaction (6) and during staurolite-consuming reactions with increasing temperature. According to Carmichael (1969), in the small domains of the rock where sillimanite is found within flakes of muscovite, the following reaction was occurring:

(9) $2KAl_3Si_3O_{10}(OH)_2 + 2H^+ \rightarrow 3Al_2SiO_5 + 3SiO_2 + 2K^+ + 3H_2O$.

We may deduce from a textural relationship that kyanite reacted to form sillimanite by the polymorphic reaction kyanite → sillimanite.

However, recent studies in different metamorphic terrenes suggest that the development of sillimanite is a very complex process, often involving growth in both muscovite and biotite and rarely showing any connection with kyanite (e.g., Chinner 1966, and Kerrick 1987). For example, Ríos (1999) has reported for the first time the occurrence of fibrolite in the southwestern Santander Massif from a metapelitic rock lacking other Al_2SiO_5 phases near the contact with the Pescadero Pluton and, according to Kerrick (1987), the textural evidence reveals that fibrolite probably formed from the breakdown of biotite by a reaction such as

(10) $2K(Mg_xFe_{1-x})AlSi_3O_{10}(OH)_2 + 14HCl = Al_2SiO_5 + 5SiO_2 + 2KCl + 6(Mg_xFe_{1-x})Cl_2 + 9H_2O$,

and fibrolite can be considered to have formed in the waning stages of a thermal event. Therefore, this fibrolitization process is not always considered here as a polymorphic reaction.

On the other hand, Carmichael (1969) suggested that local closed-system ionic equilibria linking two Al_2SiO_5 phases for the kyanite → sillimanite transformation be precluded for rocks with fibrolite as the sole aluminum silicate.

A second generation of sillimanite (coarse prismatic crystals) appears at higher grade than fibrolite, commonly as a result of the muscovite breakdown reaction

(11) muscotite + quartz = K-feldspar + sillimanite + H_2O.

This dehydration reaction has been commonly defined as "the second sillimanite isograd", because it is responsible not only of the appearance of potassium feldspar but also the production of abundant sillimanite (Spear 1993). The resulting sillimanite + K-feldspar isograd is commonly termed "the second sillimanite isograd", because in addition to produce K-feldspar, it is responsible for the production of abundant sillimanite. The loss of platy muscovite and the production of alkali feldspar result in the transformation of mica-rich schist within foliated or massive feldspathic gneiss. Alkali feldspar is usually untwined orthoclase. It may have slight wavy extinction due to very fine-scale exsolution of albite-rich feldspar (cryptoperthite).

Some authors (e.g., Le Breton and Thompson 1988, and Vielzeuf and Holloway 1988) discuss about the pelite melting and it has been experimentally shown that liquids produced by the melting of metapelitic rocks are probably not saturated with respect to H_2O (*vapor absent melting*). In these rocks minerals such as muscovite and biotite are the best candidates for vapor absent melting, because the H_2O released by the dehydration of these minerals can react with quartz and feldspar to produce melts of granitic composition. According to Spear (1993), the elimination of muscovite can be attributed to either dehydration or melting reactions. At pressures between »3 and 14 kbar melting is favored over dehydration and, therefore, muscovite should dehydrate first, producing an initial quantity of melt by the following vapor absent melting reaction:

(12) muscovite + plagioclase + quartz = biotite + K-feldspar + Al_2SiO_5 + melt,

which could be followed by the breakdown of biotite at higher temperature.

CONCLUSIONS

The polymorphs of Al_2SiO_5 that occurre in the pelitic and semipelitic rocks of Silgara Formation and Bucaramanga Gneiss let to define the staurolite-kyanite and sillimanite zones in the Santander Massif. The apparition and abundance of these polymorphs were used for determining P-T metamorphic conditions as well as the reaction history. The reaction Ky = Sil was observed in pelitic rocks of Silgara Formation and it indicates the first isograde of sillimanite. The second sillimanite isograde refers to presence of prismatic crystals of sillimanite and disappear of muscovite.

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