Petrological evolution of silica-undersaturated sapphirine-bearing granulite in the Paleoproterozoic Salvador–Curaçá Belt, Bahia, Brazil

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ABSTRACT

The Salvador–Curaçá Belt, located in São Francisco Craton, Brazil, was subjected to granulite facies metamorphism during the Paleoproterozoic orogeny (c. 2.0 Ga). Well preserved in enclaves of silica-undersaturated sapphirine-bearing granulite occur in a charnockite outcrop located along a kilometric-scale shear zone. The sapphirine-bearing granulite preserves domains with distinct mineral assemblages that record interactions between melt and peritectic phases (orthopyroxene₁ + spinel₁ + biotite₁). Sapphirine was crystallized in the Si-poor cores of the enclaves, sillimanite and spinel–cordierite symplectites in the intermediate Si-rich domains between cores and margins, and garnet and quartz-bearing cordierite/biotite symplectites in Si-rich margins of the enclaves. Melt–rock interactions and metamorphism occurred at ultrahigh temperatures of 900–950 °C at 7.0–8.0 kbar pressures. The mineralogical evolution of the domains reflects not only the influence of changes in bulk composition in the equilibrium volume of the reactions but also *P–T* changes during orogeny evolution. Electron microprobe dating of monazite both in the sapphirine-bearing granulite and charnockite indicates UHT metamorphism timing at c. 2.08–2.05 Ga that is related to global Paleoproterozoic UHT metamorphic events that occurred during the Columbia supercontinent assembly.

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1. Introduction

Sapphirine-bearing granulite rocks are useful to study the evolution of Earth's continental lithosphere since they contain metamorphic assemblages that might develop as a consequence of ultrahigh-temperature (UHT) conditions (Harley, 1998; Kelsey et al., 2004, 2005; Kelsey, 2008). Microstructures of sapphirine-bearing granulite and the related mineral-forming reactions are attributed to different causes: (a) isochemical metamorphism (e.g. Ellis, 1980; Droop and Bucher-Nurminen, 1984; Hensen, 1986; Harley, 1989; Sengupta et al., 1990; Kriegsman and Schumacher, 1999; Santosh et al., 2007); (b) retrograde melt interactions with peritectic phases (e.g. Hensen and Harley, 1990; Mouri et al., 1996; Kriegsman and Hensen, 1998; Kriegsman, 2001; Moraes et al., 2002; White and Powell, 2002); (c) Si and/or Al-diffusion metasomatism between spinel and melt (Dunkley et al., 1999; Sarkar et al., 2003).

The Salvador–Curaçá Belt (SCB) is a Paleoproterozoic granulite terrain located in the São Francisco Craton, Brazil (Almeida, 1977), that provides a good opportunity to study the process related to the development of sapphirine-bearing assemblages. In the SCB three occurrences of sapphirine-bearing granulites are known (Fujimori and Allard, 1966; Stormer, 1973; Fujimori, 1985; Ackermann et al., 1987; Leite, 2002). The older studies do not present discussions and interpretations which place the sapphirine-bearing mineral assemblages in the context of UHT metamorphism nor do they relate the formation of these assemblages to the tectono-thermal evolution of the SCB. In one of these occurrences the sapphirine-bearing granulite forms enclaves in a charnockite outcrop (Leite, 2002).

Our study focuses on the evolution of the sapphirine-bearing mineral assemblages and discusses the processes and mechanisms for UHT mineral-forming reactions in this occurrence. We investigate the effects of bulk composition as well as the *P–T* changes on the formation and consumption of Al–Mg minerals in the presence of charnockitic magma. The age of the UHT mineral–melt-reactions was also obtained by the U–Th–Pb electron microprobe (EMP) dating of monazite (Montel et al., 1996) and is discussed in the context of the Paleoproterozoic SCB tectonic evolution and in the Columbia supercontinent assembly (Rogers and Santosh, 2002; Zhao et al., 2002, 2004).

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2. Regional geological setting

The Salvador–Curaçá Belt (SCB) represents the northern part of the regionally extensive Paleoproterozoic Rhyacian Orogen (Barbosa and Sabaté, 2002, 2004) that evolved during the collision of Archaean blocks at c. 2.0–2.1 Ga (Sabaté et al., 1990; Ledru et al., 1994; Barbosa

and Sabaté, 2002, 2004). In the north-eastern region of Bahia State (Fig. 1a), the SCB is juxtaposed to the Archaean Gavião and Serrinha blocks (Fig. 1b).

In the study area (Figs. 1b and 2), the Gavião block has a basement composed of orthogneisses (Melo et al., 1995; Teixeira, 1997) and the Mundo Novo greenstone belt (Mascarenhas and Silva, 1994) with

Fig. 1. (a) Map of Brazil with location of Bahia State. Box in Bahia map marks the study area. (b) Geological sketch map of the region containing the study area and related tectonic domains in Bahia State (modified from Sabaté et al., 1990; Teixeira et al., 2000). 1 – Paleoproterozoic granites; 2 – Metasedimentary sequences; 3 – Greenstone Belts; 4 – Paleoproterozoic granulite belt; 5 – Archaean granulite cratonic block (Jequié); 6 – Archaean gneissic-migmatitic cratonic blocks (Gavião and Serrinha).

Fig. 2. Geological sketch map of the study area (modified from Melo et al., 1995; Sampaio, 1995; Mascarenhas et al., 1998).

prevailing metamorphic grade in the amphibolite facies. This basement is dated at c. 3.4–3.2 Ga (Mougeot, 1996; Peucat et al., 2002). Metasedimentary sequences and peraluminous granites cover or intrude this basement (Fig. 2). The metasedimentary sequences constitute the Saúde Complex and the 2.0–1.8 Ga Jacobina foreland basin (Ledru et al., 1997).

The Salvador–Curaçá Belt (SCB) is composed of three lithological units (Fig. 2): (a) the Caraíba Complex, comprising granulites derived from tonalite–trondhjemite–granodiorite protoliths (Teixeira, 1997); (b) the Tanque Novo–Ipirá Complex (Kosin et al., 2003), comprising predominantly leptynitic gneisses and leucogranites together with minor sedimentary derived granulites in the southern part of the study area, or by charnockite–enderbite plutons in the northern part of the area; and (c) the São José do Jacuípe Suite, a gabbro–peridotite granulitic association that probably represents an ophiolitic sequence (Teixeira, 1997).

At least two main episodes of ductile deformation are recorded in the SCB, both contemporaneous with Paleoproterozoic high-grade metamorphism (Sabaté, 1996; Leite, 2002). The first episode (D_1) is characterized by compositional layering and flat-lying foliations (S_1), relict isoclinal folds with approximately N–S horizontal axes related to west-verging shear ramps and east–west plunging to the east stretching lineation (L_1). The second episode (D_2) evolved in a transpressional tectonic regime and its deformation geometric pattern is partitioned between a network of NNW-trending folded and steep-dipping oblique to strike-slip sinistral shear zone domains. The kinematic indicators (S – C structures, asymmetric foliation trajectories and oblique to subhorizontal L_2 stretching lineations) outline tectonic transport from ESE toward WNW.

U–Pb SHRIMP ages obtained on tonalitic and enderbite granulites from the Caraíba Complex show two distinct age populations at ca. 2.7–2.6 Ga and at 2.08–2.07 Ga preserved in cores and rims of zircon respectively (Silva et al., 1997, 2002). The 2.7–2.6 Ga are interpreted as the age of magmatism in an island-arc setting while the younger 2.08–2.07 Ga age population is related to the high-grade metamorphism (Silva et al., 1997, 2002). Another tonalite from the Caraíba Complex has been dated at 2.1 Ga suggesting that crustal growth in the SCB occurred during the Paleoproterozoic (Carvalho and Oliveira, 2003).

3. Outcrop description

The sapphirine-bearing granulite is exposed in the Lajedo farm, 8 km northeast of Capim Grosso city (Fig. 2) in the Tanque Novo–Ipirá Complex. It occurs as 10–40 cm-wide discontinuous layers and boudins (Fig. 3a, b), within a charnockite pluton in a regional NW–SE trending subvertical D_2 shear zone. Sapphirine is in close spatial association with orthopyroxene and spinel, but sapphirine and spinel only occurring within the internal parts of the layer and boudins where quartz is absent. Sillimanite is restricted to the outer parts of the layer and boudins. Garnet only occurs at the contact between sapphirine-bearing granulite and charnockite where it constitutes spherical zones surrounded by biotite selvages (Fig. 3a).

4. Petrography

4.1. Sapphirine-bearing granulite

Samples were collected using a portable drill along perpendicular sections across the layer and one of the boudins (Fig. 3a, b). The petrographic analyses demonstrate that the sapphirine-bearing granulite shows both compositional and textural variations from the centre to the margins of the layer and the boudin (Fig. 4a, b). Three distinct domains have been identified based on their petrography and locations across the studied layer and boudin.

Domain I is located in the centres of the layer and boudin. The peak assemblage consists mainly of orthopyroxene (Opx_1 , 0.5–18.0 mm

Fig. 3. Outcrop photographs of sapphirine-bearing granulite enclaves in charnockite: (a) Sapphirine-bearing granulite (SprGr) layer in charnockite (Charno) shows garnet (Grt) that occurs as rounded structures and biotite (Bt) + cordierite (Crd) intergrowths at the contact between sapphirine-bearing granulite and charnockite (diameter of coin is 3.0 cm); (b) Conjugate shear bands forming pinch and swell structures in sapphirine-bearing granulite (SprGr) with inflow of charnockite (Charno) (diameter of lens cap is 6.0 cm). Rectangles on the photos indicate the sampling points and the location of the sketches presented in Fig. 4a and b.

long), sapphirine (Spr_1 , 0.3–2.5 mm long) and biotite (Bt_1 , 0.5–8.0 mm long) porphyroblasts in the layer (sample 155, Table 1; Fig. 4a) and in the boudin (sample 155B, Table 1; Fig. 4b). Spinel occurs as inclusions (Spl_{1i}) in xenomorphic sapphirine grains only in the layer (Figs. 4a, 5a). When sapphirine occurs as sub-euhedral porphyroblasts with straight contacts with orthopyroxene, sapphirine is free of spinel inclusions (Figs. 4a, 5b). Biotite also occurs as small grains (Bt_{1i}) included in spinel, sapphirine and orthopyroxene (Fig. 5a, b, c). Rare inclusions of mesoperthite (Kfs) are found in the orthopyroxene porphyroblasts that occur at the margins of the domain (Fig. 4a). Cordierite (Crd_2) is a post-peak mineral and occurs as grains and coronas (≤ 1.0 mm) (Figs. 4b, 5c) that isolate biotite, orthopyroxene and sapphirine from each other (Figs. 4a, b, 5a, b).

Domain II is the inner rim of the layer (and the boudin). It is never in direct contact with the charnockite host, but rather constitutes an intermediate area between domains I and III. The peak assemblage consists of sillimanite, orthopyroxene, sapphirine, biotite, K-feldspar and plagioclase in the layer (samples 155A, 155C and 155C4, Table 1; Fig. 4a) and in the boudin (sample 155C5, Table 1; Fig. 4b). Sillimanite occurs as either prismatic grains ($Sill_1$, 0.5–8.0 mm long) with spinel (Spl_{1i}) inclusions (Fig. 5d) or as inclusions ($Sill_{1i}$) up to 0.3 mm without spinel inclusions (Fig. 5e). Orthopyroxene (Opx_1) occurs as porphyroblasts (0.3–4.0 mm long) (Fig. 5e) and sapphirine is rare and occurs as inclusions (Spr_{1i}) in sillimanite (Fig. 5d). Biotite occurs as rare inclusions (Bt_{1i}) in perthite (Pt), and as porphyroblasts (Bt_1 , 0.3–

0.8 mm long) around sillimanite and orthopyroxene (Fig. 5d, e). Some of the biotite porphyroblasts contain rare inclusions of ilmenite (Ilm) (Fig. 5e). Mesoperthite is included in, or surrounded by biotite (Fig. 5d) while plagioclase (Pl, 0.3–0.9 mm long) is in contact with biotite orthopyroxene and sillimanite porphyroblasts (Fig. 5d, e). Cordierite (Crd₂) is the main post-peak mineral produced at the expense of the peak mineral assemblage and occurs as moat and symplectite microstructures (samples 155C4 and 155C5, Table 1). The moats are

composed of grains up to 0.7 mm long (Fig. 5d, e), that contain small inclusions (≤ 0.2 mm) of sapphirine and sillimanite (Fig. 5e). The symplectites show minor lamellae and/or globules of spinel (Spl₂) closely intergrown with magnetite grains (Mag) (Fig. 5f), and occur in contact with sillimanite and close to orthopyroxene porphyroblast (Fig. 5f). One of the symplectites contains minute crystals (≤ 0.1 mm) of corundum (Crm) and is located between biotite and sillimanite (Fig. 5f). Symplectites of Crd₂+Spl₂+Mag are also observed at the transition

Fig. 4. Representative sketches showing domains of mineral assemblages and microstructures of the sapphirine-bearing granulite. Microstructures are based on those shown in Figs. 5 and 6. (a) sketch of section across the sapphirine-bearing layer shown in Fig. 3a; (b) sketch of section across the sapphirine-bearing boudin shown in Fig. 3b.

Fig. 4 (continued).

between Domains II and III, close to the symplectites of orthopyroxene (Opx_2^*) with exsolution lamellae of magnetite (Figs. 5g, 6a).

Domain III occurs at the contact between the sapphirine-bearing granulite and the charnockite (Fig. 4a, b). The peak mineral assemblage contains garnet, orthopyroxene₁, biotite₁, K-feldspar and plagioclase in the layer (samples 155C4 and 155F, Table 1; Fig. 4a) and the boudin (samples 155C5 and 155C2, Table 1; Fig. 4b). In the outer part of this domain garnet occurs as aggregates surrounded by biotite-rich selvages (Fig. 3a). In contrast, within the domain, garnet (Grt_1) occurs as xenomorphic grains (Fig. 6a) and porphyroblasts (0.3–5.0 mm long), with biotite inclusions (Fig. 6b). Orthopyroxene appears as xenomorphic porphyroblasts (up to 2.0 mm long) with inclusions of mesoperthite (Fig. 6c). Biotite occurs as inclusions in mesoperthite (Fig. 6a) or as porphyroblasts (up to 0.6 mm long, Fig. 6b). Plagioclase, mesoperthite, perthite and antiperthite (Apt) occur in the outer rim of the domain

(Figs. 5f, g, 6a, c). The post-peak assemblage consists of cordierite moats around garnet₁ and orthopyroxene₁ (Figs. 5g, 6a, b) and cordierite-bearing symplectites that may contain orthopyroxene₂, cordierite₂ and biotite₂ or quartz in the layer (samples 155C4 and 155F, Fig. 4a) and in the boudin (samples 155C5 and 155C2, Fig. 4b). Orthopyroxene occurs either as porphyroblasts (Opx_2^*) with magnetite lamellae/globules (Figs. 5g, 6a, b) or as symplectites (Opx_2) in host cordierite surrounding garnet (Fig. 6a, b). Symplectites consisting of cordierite with minor lamellae of biotite (Bt_2) or quartz (Qtz) are developed at the expense of garnet and orthopyroxene only in the outer rim of the Domain III when they are in contact with the charnockite (Fig. 6b, c). In the same reaction sites mesoperthite is bordered by antiperthite and myrmekite (Myr) and biotite₂–quartz symplectite occurs between mesoperthite and orthopyroxene₁ (Fig. 6c). Zircon (Zrc) and monazite (Mnz) appear as small inclusions in cordierite, biotite₁ and orthopyroxene₁ (Fig. 6b, c).

Table 1

Chemical data and mineral assemblages present in sapphirine-bearing granulite and host charnockite

Sample/ rock	155	155B	155A	155C	155C4	155C5	155C2	155F	155E
	SprGr La	SprGr Bo	SprGr La	SprGr La	SprGr La	SprGr Bo	SprGr Bo	SprGr La	Charno
	D I	D I	D II	D II	D II and III	D II and III	D III	D III	
Minerals									
Opx ₁	0.67–0.69	0.69–0.70	0.66–0.74	X	0.65–0.66	0.66–0.68	0.66–0.67	X	0.70–0.72
Opx ₂					0.63–0.64	0.66–0.69	0.62–0.64	X	
Spl _i	0.39–0.69		0.44–0.53	X		0.44–0.46			
Spl ₂			0.36–0.38	X	0.36–0.39	0.36–0.39			
Grt					0.47–0.49	0.39–0.48	0.41–0.47	X	X
Sill			X	X	X	X			
Spr	0.73–0.79	0.75–0.78	0.75–0.81	X					
Crd	0.82–0.86	0.85–0.86	0.78–0.87	X	0.82–0.85	0.83–0.84	0.83–0.84	X	
Bt _{1i}	1.68–3.09	1.77–2.43	2.21–3.15	X	3.10–5.25	X	X	X	4.55–5.34
Bt ₁	5.24–5.50	5.28–5.53	X	X	5.24–5.53	X	5.28–5.55	X	4.60–5.21
Bt ₂					4.28–6.05	X	3.41–5.64	X	X
Kfs					X	X	X	X	X
Pt						X	X	X	X
Pl					X	X	X	X	X
APt					X		X	X	X
Qtz							X	X	X
Mag			X	X	X	X	X	X	X
Ilm				X					X
Crn						X			

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D I—Domain I; D II—Domain II; D III—Domain III; Charno—Charnockite; i—inclusion. All numbers refer to X_{Mg} , not corrected for Fe^{3+} , except TiO_2 (wt.%) in biotite. Zircon and monazite are present in all samples. Mineral symbols after Kretz (1983) plus Kfs for orthoclase/mesoperthite, Pt for perthite and APt for antiperthite.

4.2. Charnockite

The charnockite contains up to 12% in volume of orthopyroxene with biotite in addition to feldspar, and quartz (sample 155E). Garnet, which is restricted to the contact with the sapphirine-bearing granulite, occurs as porphyroblasts, up to 9.0 mm in diameter, that contain biotite and plagioclase inclusions (Fig. 6d). Orthopyroxene porphyroblasts are 2.0–8.0 mm long and they have biotite inclusions (Bt₁). A special kind of microstructure involving the orthopyroxene–garnet pair is observed where they are in contact with perthite and plagioclase. Garnet rims contain small orthopyroxene crystals (Fig. 6d) in a situation which resembles “dragging”-microstructures (Jessel, 1987). Biotite also appears as porphyroblasts (Bt₁), which are 2.0–8.0 mm long. Perthite and antiperthite occur as porphyroblasts up to 1.0 cm long, the latter mostly substituting mesoperthite. Quartz appears as interstitial grains or composes aggregates mantling orthopyroxene or garnet. The only symplectites present are composed of biotite (Bt₂) and quartz that occur at the margins of biotite (Bt₁) porphyroblasts in contact with mesoperthite. Zircon and monazite also occur as small inclusions in orthopyroxene, mesoperthite, antiperthite and biotite.

5. Mineral chemistry

5.1. Analytical procedure

Mineral compositions were obtained using a Cameca SX 100 electron microprobe analyser in the Electron Microprobe Laboratory at Université Blaise Pascal in Clermont Ferrand, France. Operating conditions were 15 kV, 15 nA, 5–10 μ m beam size and counting time of 10 s. Natural silicates were used as standards for most elements, except for Zn which was calibrated using synthetic sphalerite, and F using natural fluorite. Ferric iron contents in mineral structural formulae were estimated using NORM software, version 4.0 (Ulmer, 1993) where $^{VI}Fe^{3+} = ^{IV}Al^{3+} - (^{VI}Al^{3+} + Cr_{TOTAL})$. The exceptions are for

garnet ($Fe^{3+} = 4 - (Al^{VI} + Ti + Cr)$), spinel (Bohlen and Essene, 1977) and sapphirine (Higgins et al., 1979).

5.2. Orthopyroxene

Orthopyroxene shows slight chemical zoning of X_{Mg} and Al_2O_3 (Table 2). Opx₁ porphyroblasts have X_{Mg} varying from 0.67 to 0.70 in sapphirine-bearing granulite and from 0.70 to 0.72 in the charnockite. Orthopyroxene grains either with magnetite exsolution lamellae (Opx₂^{*}) or as lamellae (Opx₂) in cordierite have X_{Mg} of 0.65 and 0.63, respectively. The Al_2O_3 content of Opx₁ varies from 8.33 to 10.38 wt.% in sapphirine-bearing granulite and from 8.94 to 9.55 wt.% in charnockite while in Opx₂^{*} and Opx₂ ranges from 7.50 to 6.18 wt.%. The $y(opx)$ values (i.e. cations of Si+Al-2, with Fe^{3+} recalculation) show variations of 0.139–0.203, 0.166–0.179 and 0.123–0.130 in Opx₁ of the Domains I, II and III, respectively. For Opx₂^{*} the $y(opx)$ values vary from 0.103 to 0.119, and for Opx₂ from 0.119 to 0.122. Al and X_{Mg} zonation varies according to the mineral assemblages and rock type. The Opx₁ mantled by feldspar or biotite₂ in both rock types have X_{Mg} increasing rimward. In contrast, Opx₁ surrounded by cordierite show lower X_{Mg} at the rims. Opx₁ shows Al_2O_3 decreasing rimward (10.38 to 6.19 wt.%) in sapphirine-bearing granulite and the opposite pattern (8.94 to 9.55 wt.%) in charnockite.

5.3. Spinel

Spinel is essentially a spinel–hercynite solid solution (Table 3) with X_{Mg} varying from 0.38 (hercynite-rich solution) to 0.72 (spinel-rich solution). Hercynite component increases rimward in spinel (Spl₁) inclusions. In contrast, the spinel component increases rimward in symplectite (Spl₂). Recalculation of spinel composition according to stoichiometry (Bohlen and Essene, 1977) gives 1.53–4.30 wt.% Fe_2O_3 in Spl₁ and 1.76–3.89 wt.% Fe_2O_3 in Spl₂. ZnO contents are higher in Spl₁ (1.86 to 3.35 wt.%) and ranging from 1.15 to 1.76 wt.% in Spl₂.

Fig. 5. Photomicrographs of minerals and microstructures. (a) Sapphirine (Spr) corona around spinel (Spl_{II}) and cordierite (Crd) forming a film between sapphirine and orthopyroxene porphyroblast (Opx_1), sample 155, Domain I; (b) Sapphirine (Spr) and cordierite (Crd) either substituting orthopyroxene porphyroblast (Opx_1) or forming a rim between sapphirine or biotite (Bt_1) and orthopyroxene porphyroblast (Opx_2), sample 155, Domain I; (c) Sapphirine (Spr) partially substituted by cordierite (Crd) sample 155B, Domain I; (d) Spinel (Spl_1) and remains of sapphirine (Spr) crystals included in sillimanite (Sill) which is surrounded by biotite (Bt_1) and cordierite (Crd); (e) Sillimanite (Sill) and sapphirine (Spr) inclusions in cordierite, sample 155A, Domain II; (f) Fine cordierite–spinel–magnetite ($Crd+Spl_2+Mag$) symplectite between sillimanite (Sill) and orthopyroxene porphyroblast (Opx_1) and cordierite–spinel–magnetite–corundum ($Crd+Spl_2+Mag+Crn$) symplectite between sillimanite (Sill) and biotite porphyroblast (Bt_1), sample 155C5, Domain II; (g) Two kinds of symplectite: exsolved magnetite (Mag) on host-orthopyroxene (Opx_2) and cordierite–spinel–magnetite ($Crd+Spl_2+Mag$) between orthopyroxene (Opx_2) and sillimanite (Sill), sample 155C5, Domains II and III.

Fig. 6. Photomicrographs of minerals and microstructures. (a) Fine cordierite–orthopyroxene₂ (Crđ + Opx₂) symplectite between garnet (Grt) and orthopyroxene (Opx₁*) with exsolved magnetite (Mag), sample 155C5, Domain III; (b) Cordierite symplectites formed through garnet consuming reactions: at the garnet (Grt) border against orthopyroxene (Opx₂*), the symplectite has orthopyroxene (Opx₂) lamellae whereas at the rim against mesoperthite (Kfs) the symplectite has quartz lamellae and cordierite shows intergrowth with biotite (Bt₂), sample 155C4, Domain III; (c) Symplectites controlled by the presence of melt (now represented by mesoperthite (Kfs) crystals) that reacted with orthopyroxene (Opx₁): cordierite (Crđ)+quartz (Qtz), biotite (Bt₂)+quartz (Qtz) and cordierite (Crđ)+biotite (Bt₂), note also the presence of antiperthite (Apt) and myrmekite (Myr), sample 155C2, Domain III; (d) Garnet (Grt) forming “dragging”-microstructures (Jessel, 1987) over orthopyroxene (Opx), sample 155F, charnockite.

5.4. Sapphirine

Sapphirine shows compositional zoning depending on the coexisting phases. Grains with spinel inclusions and in contact with Opx₁ have slight X_{Mg} increasing rimward, while sapphirine inclusions in Crđ show a decreasing pattern (Table 4). Sapphirine included in cordierite is the most aluminous (Al^{Tot} : 8.43–8.57 a.p.f.u.), while those containing spinel inclusions and in contact with Opx₁ or Crđ have lower aluminium (Al^{Tot} : 8.32–8.45 a.p.f.u.). Sapphirine compositions, recalculated following Higgins et al. (1979), have Fe_2O_3 varying from 3.53 to 5.15 wt.%. Sapphirine compositions occur off the tie line joining the 2:2:1 and 7:9:3 end members (Fig. 7).

5.5. Garnet

Garnet is an almandine–pyrope solid solution with minor spessartine and grossular contents (Table 5). The pyrope component decreases from the core (39–42 mol%) to the rim (35–40 mol%) while almandine, spessartine and grossular increase rimward from 50 to 54 mol%, 4.0 to 6.0 mol% and 2.3 to 4.2 mol%, respectively. Profiles of Ca, Mg, Fe and Mn concentrations show a mirror image between Mg and Fe and enrichment at rims of Ca, Fe and Mn (Fig. 8).

5.6. Cordierite

Cordierite has only minor compositional variation whether it forms rims around sapphirine and orthopyroxene or occurs as moats and symplectites (Table 6). Grains adjacent to sapphirine are the most

magnesian (X_{Mg} : 0.86–0.87) whereas grains forming symplectites with quartz are more iron-rich (X_{Mg} : 0.83). The high wt.% totals suggest low contents of fluid species (H_2O , CO_2) in the structural channels.

5.7. Biotite

Biotite is phlogopite rich (Fig. 9a). Biotite porphyroblasts (Bt₁) in sapphirine-bearing granulite are richer in X_{Mg} (0.78–0.81) and F (1.62–2.06 wt.%) than the small inclusions (Bt_{1i} with X_{Mg} : 0.69–0.75 and F: 1.15–1.51 wt.%) and biotite in symplectites (Bt₂ with X_{Mg} : 0.67–0.68 and F: 0.54–1.39 wt.%) with quartz or cordierite (Table 7). Biotite in charnockite has X_{Mg} between 0.69 and 0.73, F from 0.30 to 0.48 wt.% and X_{Fe} between 0.27 and 0.30. Bt₂ tends to be richer in TiO_2 (0.463–0.605 Ti a.p.f.u.) than Bt_{1i} (0.337–0.580 Ti a.p.f.u.) and Bt₁ (0.223–0.257 Ti a.p.f.u.). There is also a negative correlation between X_{Mg} and Ti (Fig. 9b) which can be explained by the substitution $(Ti^{4+})^{VI} + ()^{VI} \Leftrightarrow 2(Mg^{2+})^{VI}$ (Guidotti, 1984) or $(Ti^{4+})^{IV} + ()^{VI} \Leftrightarrow (Mg^{2+})^{IV} + (Mg^{2+})^{VI}$ (White et al., 2002). Although differences in X_{Mg} between core and rim are subtle, F decreases towards the rims, while Ti increases (Table 7) which can be explained by the substitution $(Ti^{4+})^{IV} + (O^{2-})^{HD} \Leftrightarrow (Mg^{2+})^{IV} + 2(OH, F^{-})^{HD}$ (Henry and Guidotti, 2002) where HD represents the hydroxyl site.

5.8. Plagioclase

Plagioclase is an oligoclase (An_{24-27}). In general, Na increases slightly rimwards in the individual grains (Table 8). In charnockite, the anorthite content is higher (An_{27}) in antiperthite intergrowths than matrix plagioclase rims (An_{25}) (Table 8).

Table 2
Representative orthopyroxene analyses

Sample/ rock	155 SprGr	155 SprGr	155B SprGr	155B SprGr	155A SprGr	155A SprGr	155C4 SprGr	155C4 SprGr	155C5 SprGr	155C5 SprGr	155E Charno	155E Charno
	La	La	Bo	Bo	La	La	La	La	Bo	Bo		
	D I	D I	D I	D I	D II	D II	D II	D II	D III	D III		
Position	A11cP	A12rP	A16cP	A15rP	A01cP	A02rP	A34cE	A33rE	A41L	A50cP	A39cP	A40rP
SiO ₂	48.99	47.74	46.66	47.33	46.59	47.03	47.90	48.76	48.50	47.52	46.99	46.63
TiO ₂	0.01	0.05	0.03	0.02	0.12	0.08	0.14	0.12	0.05	0.08	0.10	0.22
Al ₂ O ₃	10.10	9.07	9.64	8.71	10.38	9.65	7.50	6.19	6.18	8.78	8.94	9.55
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.04	0.01	0.00	0.00
Fe ₂ O ₃	0.97	4.11	4.08	2.77	3.23	3.12	3.30	2.22	1.29	4.18	4.87	5.21
FeO	18.73	17.50	16.35	16.98	17.56	17.98	19.25	19.79	20.79	18.34	16.82	15.44
MnO	0.26	0.35	0.30	0.24	0.30	0.34	0.56	0.61	0.45	0.33	0.23	0.16
MgO	22.11	21.95	21.91	22.04	21.19	21.24	20.74	21.22	20.42	21.41	21.98	22.55
CaO	0.07	0.02	0.08	0.03	0.06	0.02	0.05	0.06	0.11	0.05	0.01	0.03
Na ₂ O	0.01	0.03	0.00	0.00	0.01	0.02	0.10	0.00	0.04	0.00	0.01	0.03
K ₂ O	0.01	0.00	0.00	0.02	0.02	0.01	0.03	0.04	0.02	0.00	0.00	0.00
Total	101.3	100.8	99.04	98.14	99.45	99.49	99.57	99.04	97.90	100.7	99.93	99.81
O	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Si	1.772	1.748	1.732	1.769	1.726	1.744	1.789	1.829	1.843	1.749	1.735	1.715
Ti	0.000	0.001	0.001	0.000	0.003	0.002	0.004	0.004	0.001	0.002	0.002	0.006
Al	0.431	0.391	0.422	0.384	0.453	0.422	0.330	0.274	0.277	0.381	0.389	0.414
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000
Fe ³⁺	0.026	0.113	0.114	0.078	0.090	0.087	0.093	0.063	0.037	0.116	0.135	0.144
Fe ²⁺	0.567	0.536	0.507	0.531	0.544	0.558	0.601	0.621	0.661	0.564	0.519	0.475
Mn	0.008	0.011	0.010	0.008	0.009	0.011	0.018	0.019	0.015	0.010	0.007	0.004
Mg	1.192	1.198	1.212	1.228	1.170	1.174	1.155	1.186	1.157	1.175	1.210	1.236
Ca	0.003	0.001	0.003	0.001	0.002	0.001	0.002	0.002	0.004	0.002	0.000	0.001
Na	0.001	0.002	0.000	0.000	0.001	0.002	0.007	0.000	0.003	0.000	0.000	0.001
K	0.001	0.000	0.000	0.001	0.001	0.000	0.001	0.002	0.001	0.000	0.000	0.000
Sum	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
X _{Mg} (Fe ₂)	0.678	0.691	0.705	0.698	0.683	0.678	0.658	0.657	0.636	0.675	0.700	0.723
y(opx)	0.203	0.139	0.154	0.153	0.179	0.166	0.119	0.103	0.120	0.130	0.124	0.129

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D I—Domain I; D II—Domain II; D III—Domain III; Charno—Charnockite; c—core; r—rim; P—Porphyroblast (Opx₁); E—Symplectite (Opx₂^{*}) with exsolved magnetite; L—Symplectite lamella (Opx₂) in cordierite; y(opx)=Si+Al-2.

5.9. K-feldspar

K-feldspar composition in mesoperthite varies from Or₇₈–Ab₂₁ to Or₈₈–Ab₁₃. The re-integrated composition is estimated at Ab_{11–20} Or_{75–88}An_{03–06}. In antiperthite or perthite intergrowths, the K-feldspar lamellae composition varies from Or₉₂–Ab₀₈ to Or₉₄–Ab₀₆ (Table 8).

6. Whole rock major and trace element chemistry

Geochemical analyses were performed on the three domains of the sapphirine-bearing granulite and the host charnockite in order to assess the role of bulk composition and mass transfer on the development of mineral assemblages in the sapphirine-bearing granulite.

The samples were analyzed at the Lakefield GEOSOL Laboratories using X-ray fluorescence and atomic absorption spectrometry for most major and trace elements. Atomic absorption spectrometry allowed the determination of low contents of Na₂O (less than 1 wt.%). H₂O⁺ was determined by the Penfield tube method, and CO₂ was determined by liberation of the gas using HCl attack with heating on an oil bath at 130 °C.

The analytical data (Table 9) show that from the center (Domain I, sample 155) to the rim (Domain III, sample 155C4) of the layer or boudin, the sapphirine-bearing granulite is enriched in SiO₂ (from 43.3 to 62.4 mol%) whereas the contents of MgO, Al₂O₃ and K₂O decrease. Domain II is the richest in Fe₂O₃. These differences in bulk chemistry are reflected mineralogically, with higher amounts of spinel, sapphirine and biotite in Domain I, of magnetite in Domain II, and of quartz in Domain III. Enrichments of Rb, F and Zr in Domain I compared to Domains II and III are related to the abundance of biotite with inclusions of zircon.

The charnockite (sample 155E) has a larger SiO₂ content than rocks of the three domains of sapphirine-bearing granulite (Table 9). Its 1.64 Alumina Saturation Index suggests peraluminous magma genesis formed by partial crustal melting (see Frost et al., 2001; Frost and Frost, 2008).

7. Interpretation of microstructures, mineral reactions and P–T evolution

The interpretation of microstructures and mineral reactions uses phase relationships that include calculated pseudosections in the KFMASH (K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O) system using Perple_X'07 software (Conolly and Petrini, 2002) with the updated version of the internally consistent thermodynamic database of Holland and Powell (2001). Activity-compositions considered in this modeling are listed in Table 10. To constrain the P–T path of the mineral reactions we performed a forward petrologic modeling using P–T pseudosections. The effects of variations in silica content related to melt infiltration on phase relationships are modeled using isobaric T–M(SiO₂) pseudosections.

Some of the mineral reactions are represented with phase relationships graphically portrayed in the FMAS (FeO–MgO–Al₂O₃–SiO₂) tetrahedron projected onto the plane (F+M)–Al–Si'. In these projections Si'=Si+Fe²⁺+Mg–(Al/2); Mg'=Mg; Fe'=Fe²⁺ and Al'=(Al+Fe³⁺+Cr³⁺)/2 (Kriegsman and Schumacher, 1999).

7.1. Microstructures and mineral reactions

Field observations show a transitional contact between sapphirine-bearing granulite and charnockite (Fig. 3a, b). It appears clearly that the development of cordierite-bearing symplectites, is controlled

Table 3
Representative spinel analyses

Sample/ rock	155 SprGr La	155 SprGr La	155A SprGr La	155A SprGr La	155C5 SprGr Bo	155A SprGr La	155A SprGr La	155C4 SprGr La	155C4 SprGr La
	D I	D I	D II	D II	D II	D II	D II	D II	D II
Position	A15cl _{spr}	A16rl _{spr}	A01cl _{sill}	A02rl _{sill}	A01cl _{sill}	A06cS	A07rS	A16cS	A15rS
SiO ₂	0.01	0.02	0.01	0.03	0.06	0.00	0.00	0.86	0.02
TiO ₂	0.01	0.02	0.07	0.02	0.00	0.01	0.00	0.00	0.01
Al ₂ O ₃	65.87	61.27	59.27	58.20	59.35	60.80	61.65	58.79	59.19
Cr ₂ O ₃	0.08	0.05	0.09	0.06	0.08	0.04	0.00	0.10	0.00
Fe ₂ O ₃	1.56	2.68	3.86	4.30	3.45	2.97	3.00	1.76	3.89
FeO	12.51	23.43	24.19	24.37	23.64	21.91	19.54	26.39	25.21
MnO	0.13	0.15	0.18	0.08	0.19	0.17	0.19	0.31	0.33
ZnO	2.08	1.86	3.35	3.23	3.27	1.27	1.25	1.76	1.15
MgO	18.35	10.75	9.18	8.83	9.44	11.77	13.43	8.98	9.51
CaO	0.01	0.03	0.00	0.00	0.00	0.02	0.03	0.00	0.01
Total	100.6	100.3	100.2	99.16	99.48	98.97	99.07	99.01	99.32
O	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Si	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.024	0.001
Ti	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000
Al	1.968	1.943	1.915	1.906	1.924	1.938	1.940	1.914	1.918
Cr	0.002	0.001	0.002	0.001	0.002	0.001	0.000	0.002	0.000
Fe ³⁺	0.030	0.054	0.080	0.090	0.071	0.061	0.060	0.037	0.081
Fe ²⁺	0.265	0.527	0.555	0.566	0.544	0.496	0.436	0.610	0.580
Mn	0.003	0.004	0.004	0.002	0.004	0.004	0.004	0.007	0.008
Zn	0.039	0.037	0.068	0.066	0.066	0.025	0.025	0.036	0.023
Mg	0.693	0.431	0.375	0.366	0.387	0.475	0.534	0.370	0.390
Ca	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.000
Sum	3.000	2.999	3.000	2.999	2.999	3.001	3.000	3.000	3.001
Spinel	0.682	0.419	0.359	0.349	0.372	0.461	0.519	0.345	0.374
Hercynite	0.261	0.512	0.531	0.539	0.523	0.481	0.423	0.576	0.556
Gahnite	0.038	0.036	0.064	0.063	0.063	0.024	0.025	0.025	0.022
Mgferrite	0.011	0.012	0.015	0.017	0.014	0.015	0.016	0.008	0.016
Franklinite	0.001	0.001	0.003	0.003	0.002	0.001	0.001	0.001	0.001
Magnetite	0.004	0.014	0.023	0.026	0.020	0.015	0.013	0.013	0.024
Galaxite	0.003	0.004	0.003	0.002	0.003	0.004	0.004	0.003	0.008
Jacobsite	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
X _{Mg} (Fe ²⁺)	0.723	0.450	0.403	0.392	0.416	0.489	0.550	0.378	0.402

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D I—Domain I; D II—Domain II; c—core; r—rim; l_{spr}—Spl₁ included in sapphirine; l_{sill}—Spl₁ included in sillimanite; S—Spl₂ symplectite in host cordierite.

by the proximity of the charnockite (Figs. 5f, 6a, c, d). This feature suggests that part of the microstructures were probably formed by interactions between the charnockite melt and the enclaves of sapphirine-bearing granulite. If this is the case, melt would have acted both as a reactant and as an appropriate medium to enhance element diffusion to grain boundaries (Kriegsman and Hensen, 1998; Brown, 2002).

In Domains I and II, the microstructural relationships suggest that orthopyroxene₁ and spinel₁ are relict minerals. The crystallization and preservation of these two minerals indicate that melting and melt loss occurred (White and Powell, 2002). Thus spinel₁ and orthopyroxene₁ are considered to be peritectic products of crustal anatexis.

In Domain I, sapphirine grains may contain spinel inclusions and have cordierite rims that isolate sapphirine from orthopyroxene (Fig. 5a, b). Sapphirine may form by fluid-assisted diffusion of silica or alumina into the spinel site (Dunkley et al., 1999). Silica diffusion probably occurred as a consequence of the establishment of chemical potential gradients for Si (μ_{Si}) between Si-rich charnockitic melt and spinel grains. Once sapphirine was formed, continued Si-diffusion would allow the growth of rims of cordierite (Fig. 5a, b) between orthopyroxene and sapphirine. FMAS projections (Fig. 10a) suggest the following continuous reactions:

This Si-diffusion processes and maybe related Al-diffusion may also explain the fact that sapphirine compositions occur off the tie line

joining the 2:2:1 and 7:9:3 end members (Fig. 7). It suggests extensive Ferri-Tschermak exchange: $^{\text{VI}}(\text{Mg}, \text{Fe})^{2+} + ^{\text{IV}}\text{Si}^{4+} \Leftrightarrow ^{\text{VI}}(\text{Al}, \text{Fe})^{3+} + ^{\text{IV}}\text{Al}^{3+}$ during sapphirine forming and consuming reactions.

Crystallization of cordierite can also be produced by changes in *P*–*T* conditions. The calculated *P*–*T* pseudosection in the KFMASH system for the Domain I (Fig. 11a) shows that the peak assemblage (Bt₁ + Opx₁ + Spr + Kfs + L) is stable in a large field at low pressure and high temperature. A decrease in temperature to ~900 °C at a pressure below 8 kbar will induce the crystallization of cordierite in equilibrium with the sub-solidus peak assemblage. The sequence of mineral assemblages produced during a cooling path is summarized below:

The lack of spinel predicted by the pseudosection highlight the fact that the effective bulk composition used here is inappropriate to model pre-sapphirine-bearing assemblage. This is consistent with the hypothesis suggesting that sapphirine-bearing assemblage was produced at the expense of Opx₁ + Spl₁ + Bt₁ by the addition of silica.

In Domain II, sillimanite occurs either as inclusions in cordierite (Fig. 5e) or with spinel₁ and sapphirine inclusions, the latter containing remnants of spinel₁ (Fig. 5d). These microstructures suggest that sillimanite was formed as a product of the destabilization of

Table 4
Representative sapphirine analyses

Sample rock	155 SprGr La D I	155 SprGr La D I	155 SprGr La D I	155 SprGr La D I	155B SprGr Bo D I	155B SprGr Bo D I	155A SprGr La D II	155A SprGr La D II
Position	A18c■	A17r□	A06c■	A07r□	A12c■	A13r□	A08c●	A07r○
SiO ₂	13.54	12.93	13.49	12.80	13.15	13.10	12.89	12.56
TiO ₂	0.00	0.00	0.10	0.03	0.05	0.06	0.04	0.01
Al ₂ O ₃	57.78	59.16	57.75	58.86	57.11	57.70	58.38	59.58
Cr ₂ O ₃	0.03	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Fe ₂ O ₃	4.27	4.88	3.89	4.59	5.15	4.64	4.34	3.93
FeO	8.6	7.27	8.76	7.65	7.86	7.90	7.08	7.39
MnO	0.15	0.10	0.01	0.06	0.19	0.12	0.11	0.14
MgO	15.16	15.43	15.06	15.21	15.16	15.20	15.55	15.13
CaO	0.03	0.06	0.02	0.05	0.03	0.00	0.01	0.04
Na ₂ O	0.00	0.04	0.01	0.01	0.01	0.02	0.00	0.00
K ₂ O	0.00	0.03	0.02	0.00	0.02	0.00	0.01	0.02
Total	99.56	99.90	99.11	99.27	98.74	98.74	98.40	98.81
O	20.000	20.000	20.000	20.000	20.000	20.000	20.000	20.000
Si	1.651	1.565	1.651	1.560	1.618	1.608	1.580	1.533
Ti	0.000	0.000	0.009	0.003	0.005	0.005	0.003	0.001
Al	8.303	8.439	8.328	8.457	8.282	8.349	8.435	8.573
Cr	0.003	0.000	0.000	0.000	0.001	0.000	0.000	0.000
Fe ³⁺	0.392	0.445	0.358	0.421	0.477	0.428	0.401	0.361
Fe ²⁺	0.877	0.736	0.897	0.780	0.808	0.811	0.726	0.754
Mn	0.015	0.011	0.001	0.006	0.020	0.012	0.012	0.015
Mg	2.755	2.783	2.747	2.764	2.780	2.781	2.841	2.754
Ca	0.003	0.007	0.002	0.006	0.003	0.000	0.001	0.006
Na	0.001	0.009	0.003	0.003	0.003	0.004	0.000	0.000
K	0.000	0.005	0.004	0.000	0.003	0.000	0.002	0.002
Sum	14.000	14.000	14.000	14.000	14.000	14.000	14.000	14.000
X _{Mg} (Fe ²⁺)	0.759	0.791	0.754	0.780	0.775	0.774	0.796	0.785

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D I—Domain I; D II—Domain II; c—core; r—rim; ■ and □—sapphirine with spinel inclusion and in contact with orthopyroxene₁; ● and ○—sapphirine included in cordierite.

sapphirine while cordierite crystallized after sillimanite. Cordierite + spinel₂ symplectites developed at the expense of sillimanite and orthopyroxene (Fig. 5f) suggest the following continuous reaction in the FMAS system (Fig. 10b).

The enrichment in Fe₂O₃ of Domain II is expressed by the crystallization of magnetite exsolution from spinel₂ grains (Fig. 5f). Ferric iron and Zn are known to stabilize spinel to lower temperatures and higher pressures (e.g. Hensen, 1986; Hensen and Harley, 1990; Das et al., 2001, 2003). According to Hensen (1986) magnetite exsolves from Fe-rich spinel on cooling and the experiments of Turnock and Eugster (1962) demonstrate that a miscibility gap between spinel and magnetite exists at $T \leq 860$ °C. The occurrence of corundum in cordierite + spinel₂ + magnetite symplectites (Fig. 5f) also suggests that alumina would be present in excess in spinel solid solution to be exsolved on cooling. Alternatively, magnetite and corundum could be products of the following reactions controlled by increasing oxygen fugacity:

(Viertel and Seifert, 1981)

In Domain III, garnet grains with biotite₁ inclusions and the residual grains of orthopyroxene₁ next to plagioclase and mesoperthite (Fig. 6b, d), suggest that orthopyroxene₁ in contact with melt was partly consumed to produce garnet following the multi-variant back-melting reaction (Kriegsman and Hensen, 1998) in the (NC) KFMASH system:

The formation of biotite-rich selvages surrounding garnet crystals (Fig. 3a) could also be explained by garnet resorption:

Garnet, orthopyroxene₁ and biotite₁ facing the charnockite are mantled by symplectites comprising cordierite, biotite₂ and quartz (Fig. 6b, c). The crystallization of cordierite–quartz or cordierite–

Fig. 7. The compositions of sapphirine in Al vs Si (a.p.f.u for 10 oxygens) diagram. 7:9:3 and 2:2:1 are ideal molecular ratios to MgO: Al₂O₃: SiO₂ in sapphirine (Higgins et al., 1979). The compositions fall away off the line joining 7:9:3 and 2:2:1 ideal molecular ratios suggesting Tschermak substitution $\text{VI}(\text{Mg}, \text{Fe})^{+2} + \text{Si}^{+4} \Leftrightarrow \text{VI}(\text{Al}, \text{Fe})^{+3}$. In general, core compositions (filled symbols) are poorer in Al than rim compositions (open symbols) with compensation by Si.

Table 5
Representative garnet analyses

Sample/ rock	155C4 SprGr La	155C4 SprGr La	155C4 SprGr La	155C4 SprGr La	155C5 SprGr Bo	155C5 SprGr Bo	155E Charno
	D III	D III	D III	D III	D III	D III	
Position	A37c	A35r	A39c	A38r	A6c	A7r	A15c
SiO ₂	39.18	38.68	38.49	38.39	38.19	38.56	38.31
TiO ₂	0.12	0.03	0.04	0.00	0.04	0.03	0.01
Al ₂ O ₃	22.39	21.87	22.28	22.41	22.34	22.29	22.14
Cr ₂ O ₃	0.00	0.00	0.00	0.02	0.00	0.03	0.00
Fe ₂ O ₃	0.54	1.37	2.77	3.14	3.14	2.23	2.87
FeO	24.94	25.43	24.00	23.95	23.93	25.44	25.69
MnO	1.98	2.15	1.37	1.51	2.25	2.17	2.11
MgO	10.64	9.78	11.05	10.60	10.20	9.46	9.23
CaO	0.75	0.82	0.70	1.14	0.83	1.13	1.20
Na ₂ O	0.02	0.03	0.02	0.01	0.05	0.03	0.00
K ₂ O	0.00	0.01	0.01	0.00	0.00	0.01	0.00
Total	100.6	100.2	100.7	101.2	100.9	101.3	101.6
O	12.000	12.000	12.000	12.000	12.000	12.000	12.000
Si	2.977	2.972	2.923	2.910	2.909	2.936	2.923
Ti	0.007	0.002	0.002	0.000	0.002	0.002	0.001
Al	2.005	1.980	1.994	2.002	2.005	2.000	1.990
Cr	0.000	0.000	0.000	0.001	0.000	0.001	0.000
Fe ³⁺	0.031	0.079	0.158	0.179	0.180	0.128	0.164
Fe ²⁺	1.584	1.634	1.524	1.518	1.524	1.620	1.638
Mn	0.128	0.140	0.088	0.097	0.145	0.140	0.136
Mg	1.205	1.120	1.250	1.198	1.158	1.071	1.049
Ca	0.061	0.068	0.057	0.093	0.068	0.093	0.099
Na	0.002	0.004	0.002	0.002	0.007	0.004	0.000
K	0.001	0.001	0.001	0.000	0.000	0.001	0.000
Sum	8.001	8.000	7.999	8.000	7.998	7.996	8.000
X _{Mg} (Fe ²⁺)	0.432	0.407	0.451	0.441	0.432	0.399	0.390
X _{Fe}	0.531	0.551	0.522	0.522	0.535	0.553	0.561
Almandine	0.529	0.538	0.505	0.505	0.507	0.538	0.541
Pyrope	0.403	0.370	0.416	0.401	0.388	0.359	0.350
Spessartine	0.045	0.050	0.039	0.044	0.060	0.055	0.054
Grossular	0.023	0.026	0.029	0.042	0.035	0.039	0.042
Andradite	0.000	0.001	0.001	0.002	0.002	0.001	0.002

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D III—Domain III; Charno—charnockite; c—core; r—rim.

biotite₂ symplectites suggests post-peak reactions involving melt (Stevens and Clemens, 1993). The topological relations of these phases (Fig. 10c, d) allow us to propose that these symplectites were formed via the following di- or multi-variant KFMASH reactions:

The calculated *P*–*T* pseudosection in the KFMASH system for the Domain III (Fig. 11b) predicts that cordierite–biotite₂–quartz symplectites are produced at the expense of orthopyroxene during cooling at temperatures lower than 860 °C. The resulting equilibrium is:

Reaction (8) and assemblage (4) suggest that the consumption of orthopyroxene₁ occurred in the presence of melt. In contrast, cordierite+orthopyroxene₂ symplectites at the expense of garnet and orthopyroxene₁ (Fig. 6a, b) could have been produced through a divariant melt-absent FMAS reaction (Fig. 10e):

The occurrence of magnetite exsolution in host orthopyroxene₂ (Opx₂^{*}), always in close association to spinel₂ + cordierite + magnetite and orthopyroxene₂ + cordierite symplectites (Fig. 6a, b) can also be related to cooling. This interpretation is supported by the fact that orthopyroxene₂^{*} is less aluminous and magnesian than orthopyroxene₁.

7.2. Role of variations in *P*–*T* conditions and SiO₂ bulk composition on the evolution of silica-undersaturated sapphirine-bearing assemblages

The estimation of maximum preserved *P*–*T* conditions using classic geothermobarometry (reverse modelling) based on cation exchange and/or net transfer reactions is subject to uncertainties since elemental equilibrium between the rock-forming minerals is rarely preserved upon cooling (Frost and Chacko, 1989; Pattison et al., 2003).

Fig. 8. Compositional variations along the profile in the garnet porphyroblast of 155C4 sapphirine-bearing granulite sample.

This limitation has been overcome somewhat by retrieval techniques that are based on the Al content of orthopyroxene (Harley and Green, 1982; Harley, 1984; Hensen and Harley, 1990) and on the re-adjustment of Fe–Mg mineral compositions to converge in P – T space with $y(\text{opx})$ (Pattison and Bégin, 1994; Fitzsimons and Harley, 1994; Pattison et al., 2003). Estimation of peak P – T conditions using calculated phase diagrams (forward modeling) reduces uncertainties since the stability field of the peak mineral assemblage is defined (Kelsey et al., 2003b). To estimate the P – T conditions and the evolution of mineral assemblages we have combined both approaches: reverse and forward modelling.

The pseudosection calculated for Domain I (Fig. 11a) show that sapphirine-bearing mineral assemblages without garnet and in the presence of melt can occur at temperatures as high as 1050 °C. The crystallization of cordierite in this assemblage limits the pressure to less than 8.0 kbar at a temperature close to 930 °C. Sub-solidus assemblages are stable at P – T conditions lower than 7.5 kbar and 930 °C.

In the Domain II, the fact that the mineral assemblage has coexisting orthopyroxene + sillimanite suggests minimum P – T conditions of 8.0–9.0 kbar and 900 °C in KFMASH system (Kelsey et al., 2003b).

The pseudosection calculated for Domain III (Fig. 11b) show that garnet–cordierite-bearing mineral assemblages without sapphirine but with quartz and melt present are stable at pressures lower than 8.5 kbar and temperatures ranging from 1050 °C to 860 °C. This pseudosection also suggests that the formation of quartz–biotite–cordierite symplectites as well as the crystallization of K-feldspar would occur at P – T conditions lower than 8.0 kbar and 860 °C.

P – T conditions estimated via reverse modeling based on the regression method of Pattison and Bégin (1994) have been possible on Domain III and the garnet-bearing portion of the charnockite. This

method retrieves close-to-peak mineral compositions from which close-to-peak pressure and temperature estimates are obtained with the Al–orthopyroxene–garnet barometer of Harley and Green (1982) and the garnet–orthopyroxene geothermometer of Harley (1984), respectively. Garnet and orthopyroxene₁ core compositions have been used for calculations of P – T conditions following the protocol of Pattison and Bégin (1994). The results obtained on the Domain III (155C5) and in the charnockite (155E) samples are similar (Table 11). In the Domain III of the sapphirine-bearing granulite the calculated P is 8.5 ± 2.0 kbar that leads to a retrieved T of 950 ± 40 – 60 °C while in charnockite P – T conditions are 8.0 ± 2.0 kbar and 945 ± 40 – 60 °C. The errors are after Harley (1984) who assumes ± 0.1 as the maximum error in the calculated K_D .

The results from the calculated pseudosections and the retrieval technique support the mineralogical evidence (i.e. opx + sill and spr + opx) for ultrahigh temperature (UHT) metamorphic conditions (Harley, 1998). Other features also indicate that UHT conditions prevailed during peak metamorphism: (1) Al_2O_3 content greater than 10.0 wt.% and TiO_2 close to 5.0 wt.% in orthopyroxene and biotite porphyroblasts, respectively (Harley, 1998; Mouri et al., 1996); and (2) low volatile content in cordierite which according to the experimental work of Carrington and Harley (1996) indicates temperatures in excess of 900 °C.

The sequence of mineral assemblages (1), (2) and (3) in Domain I and the crystallization of cordierite–quartz and cordierite–biotite₂ symplectites in Domain III are consistent with a near-isobaric retrograde path trajectory (Fig. 11a, b) with thermal peak conditions in excess of 930 °C.

P – T pseudosections for silica-undersaturated rocks in a KFMASH system is also characterized by multi-variant equilibria highly sensitive to bulk silica composition (e.g. White et al., 2002; Kelsey et al., 2003b, 2004, 2005; White et al., 2007). In order to investigate

Table 6
Representative cordierite analyses

Sample/ rock	155	155B	155A	155C4	155C5	155C4	155C4	155C5
	SprGr La	SprGr Bo	SprGr La	SprGr La	SprGr Bo	SprGr La	SprGr La	SprGr Bo
	D I	D I	D II	D II	D II	D III	D III	D III
Position	A38R _{spr}	A10R _{opx}	A33C _{spr}	A52S _{spl}	A58S _{spl}	A40S _{opx}	A21S _{qtz}	A45S _{bt}
SiO ₂	50.50	49.46	49.73	49.65	50.00	49.93	49.56	49.51
TiO ₂	0.00	0.00	0.00	0.01	0.01	0.00	0.06	0.00
Al ₂ O ₃	33.81	33.52	33.69	33.88	33.97	33.52	33.36	33.74
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.02	0.01	0.02	0.00
FeO	3.21	3.46	3.11	3.58	3.66	3.47	4.10	3.97
MnO	0.03	0.07	0.03	0.15	0.11	0.08	0.12	0.10
MgO	11.88	11.48	11.77	11.42	11.47	11.68	11.13	11.39
CaO	0.00	0.00	0.00	0.04	0.01	0.02	0.06	0.00
Na ₂ O	0.03	0.00	0.07	0.08	0.05	0.07	0.02	0.06
K ₂ O	0.03	0.00	0.01	0.04	0.02	0.00	0.00	0.00
Total	99.49	97.99	98.41	98.85	99.32	98.78	98.43	98.78
O	18.000	18.000	18.000	18.000	18.000	18.000	18.000	18.000
Si	5.016	4.994	4.994	4.980	4.989	5.005	5.001	4.976
Ti	0.000	0.000	0.000	0.001	0.001	0.000	0.004	0.000
Al	3.957	3.989	3.986	4.004	3.995	3.959	3.967	3.996
Cr	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.000
Fe ²⁺	0.266	0.292	0.261	0.300	0.305	0.291	0.346	0.333
Mn	0.002	0.006	0.002	0.013	0.009	0.007	0.010	0.009
Mg	1.759	1.728	1.762	1.707	1.706	1.745	1.674	1.706
Ca	0.000	0.000	0.000	0.004	0.001	0.002	0.006	0.000
Na	0.006	0.000	0.013	0.015	0.009	0.013	0.004	0.011
K	0.004	0.001	0.001	0.005	0.002	0.001	0.000	0.000
Sum	11.010	11.009	11.019	11.029	11.018	11.024	11.013	11.032
X _{Mg} (Fe ²⁺)	0.868	0.855	0.871	0.851	0.848	0.857	0.829	0.836
X _{Fe}	0.131	0.144	0.131	0.148	0.152	0.142	0.170	0.163

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D I—Domain I; D II—Domain II; D III—Domain III; R_{spr}—Crd as rim surrounding sapphirine; R_{opx}—Crd as rim between orthopyroxene (Opx₁) and biotite (Bt₂); G_{spr}—Crd as grain with sapphirine inclusion; S_{spl}—Crd as symplectite with spinel (Spl₂); S_{opx}—Crd as symplectite with orthopyroxene (Opx₂); S_{qtz}—Crd as symplectite with quartz; S_{bt}—Crd as symplectite with biotite (Bt₂).

Fig. 9. Compositional plots of biotite: (a) Ternary diagram $^{VI}Al+Fe^{3+}+Ti+Cr-Mg-Fe^{2+}+Mn$ (a.p.f.u for 22 oxygens) to show phlogopite component enrichment; (b) Ti vs X_{Mg} (a.p.f.u for 22 oxygens) to show negative correlation.

the effects of silica introduction into the sapphirine-bearing layer or boudin from the hosting charnockite we have calculated a $T-M(SiO_2)$ pseudosection at a fixed pressure of 8.0 kbar on the basis of the M1 bulk composition. In Fig. 11c, $M(SiO_2)$ is the mole percent amount of silica expressed as a normalized value ranging between 0 and 1. The Domain I has a $M(SiO_2)$ value of 0.24. Fig. 11c shows that for $M(SiO_2)$ lower than 0.05 and for a large interval of T (850–1050 °C), the stable assemblage consists of Bt+Spl+Opx+Kfs. This assemblage is consistent with the pre-peak assemblage defined in Domain I (i.e. Opx₁+Spl_{1i}+Bt_{1i}). An increase of SiO_2 content at constant pressure and temperature has the direct consequence of crystallizing sapphirine at the expense of spinel with production of the peak assemblage Bt₁+Opx₁+Spr+Kfs+L. This assemblage is stable over a large range of $M(SiO_2)$ (0.07 to ~0.45) at temperatures greater than 910 °C. The crystallization of late cordierite can either be produced by a continuous increase in silica content at constant $P-T$ conditions or by an isobaric and isochemical cooling down to 910 °C (Fig. 11c). Here, we favor the cooling hypothesis because the minimum amount of SiO_2

required to produce cordierite ($MSiO_2=0.7$ at 910 °C) at constant $P-T$ conditions is inconsistent with analytical data in Domain I (Table 9).

8. Geochronology of the UHT metamorphism

The U–Th–Pb electron microprobe (EMP) method of monazite dating (Montel et al., 1996) has been used to constrain the timing of the mineral assemblages. The *in-situ* nature and the high spatial resolution of the technique allow dating of grains in their petrographical context, therefore combining geochronological information with the metamorphic petrology (Kelsey et al., 2003a; Gonçalves et al., 2003; Santosh et al., 2003; Gonçalves et al., 2004; Mahan et al., 2006; Santosh et al., 2006).

Monazite compositions (Table 12) from sapphirine-bearing granulite (sample 155) and charnockite (sample 155E) were obtained on the same Cameca SX100 electron microprobe used for analysing the mineral compositions. The analytical conditions and the used standards are the same as those described by Gonçalves et al. (2004). The theoretical basis and associated statistical treatment of data follow the procedure detailed by Montel et al. (1996), Braun et al. (1998) and Gonçalves et al. (2004).

Monazite grains have diameters varying from 20 to 100 μm and can occur as inclusions in sapphirine (Fig. 12a, b), biotite (Fig. 12c, d), orthopyroxene (Fig. 12e, f), cordierite (Fig. 12g, h) and K-feldspar. Backscattered electron imaging did not reveal significant zoning but it does not preclude that some grains can be chemically zoned. Monazite is richer in P and in REE in the charnockite whereas in the sapphirine-bearing granulite monazite is richer in Si, U, Th, Pb and Ca (Table 11) and this is reflected in the higher Pb/(Th+U) ratios for monazite in the charnockite (Table 12).

Twenty-two measurements carried out mainly on monazite included in cordierite were selected for the sapphirine-bearing granulite and twenty measurements were selected for the charnockite on grains included in orthopyroxene and biotite. The calculated ages are 2057 ± 17 Ma for monazite in sapphirine-bearing granulite (Fig. 13a) and 2080 ± 26 Ma for monazite in charnockite (Fig. 13b). Taking into account the uncertainties, we suggest that these two ages represent a single event that corresponds to the emplacement of the charnockite intrusion and the UHT metamorphism and melt/rock interactions recorded by the sapphirine-bearing enclaves. These ages are in good agreement with (1) SHRIMP ages of the granulite metamorphism in plutonic rocks of the Caraíba Complex ($2072 \pm 17/22$ Ma after Silva et al., 1997, 2002) and (2) monazite *in-situ* ages for peraluminous magmatism (2080 ± 15 Ma after Leite, 2002) in the area.

9. Discussion

9.1. UHT metamorphism: regional and global implications for the assembly of Paleoproterozoic continents

The Salvador–Curaçá Belt (SCB) is recognized as a granulite terrane involved in the oblique collision of Archean blocks at c. 2.0–2.1 Ga (Ledru et al., 1994; Sabaté, 1996; Barbosa and Sabaté, 2002, 2004). The resultant crustal thickening is considered as the driving force for the metamorphism (Ledru et al., 1994; Barbosa and Sabaté, 2002, 2004). High-grade metamorphism throughout the belt is estimated at pressures up to 7.0 kbar and temperatures around 850 °C (Barbosa and Sabaté, 2002, 2004). However sapphirine-bearing granulites, with the same mineralogical features as the one described in this contribution, have been recognized in two other localities (Fujimori and Allard, 1966; Stormer, 1973; Fujimori, 1985; Ackermann et al., 1987), suggesting that UHT metamorphism might be widespread in SCB. This implies that a heat source additional to crustal thickening and accretion of radioactive material would be necessary to cause the extreme crustal perturbation (Harley, 1989). We suggest that pulses of charnockitic magma emplacement promoted the documented UHT

Table 7
Representative biotite analyses

Sample/ rock	155	155B	155B	155A	155A	155C4	155C4	155C5	155E	155E
	SprGr	SprGr	SprGr	SprGr	SprGr	SprGr	SprGr	SprGr	Charno	Charno
	La	Bo	Bo	La	La	La	La	Bo		
	D I	D I	D I	D II	D II	D II	D III	D III		
Position	A8cl	A7cP	A6rP	A8cP	A9rP	A12cl	A15cl	A09cS	A13cP	A14rP
SiO ₂	37.22	38.20	38.40	37.95	37.41	36.77	37.09	36.40	37.05	36.64
TiO ₂	3.10	2.08	2.28	2.21	2.34	5.25	5.54	4.15	4.55	4.95
Al ₂ O ₃	16.15	16.06	15.92	15.49	15.09	15.34	15.23	15.58	16.08	15.92
FeO	10.24	9.46	9.60	8.26	8.23	12.31	12.78	13.42	12.07	13.09
MnO	0.01	0.03	0.00	0.03	0.00	0.03	0.02	0.03	0.00	0.03
MgO	17.70	19.10	19.09	19.76	19.77	15.19	15.18	15.55	17.14	15.95
CaO	0.00	0.00	0.00	0.00	0.03	0.02	0.01	0.00	0.00	0.01
Na ₂ O	0.16	0.20	0.16	0.18	0.17	0.11	0.09	0.06	0.04	0.06
K ₂ O	10.40	10.30	10.10	10.38	10.33	9.93	10.03	9.95	10.32	10.33
F	1.51	2.06	1.90	2.00	1.62	1.15	1.39	0.54	0.30	0.48
Total	96.49	97.49	97.45	96.26	94.96	96.10	97.36	95.68	97.54	97.45
O	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000
Si	5.396	5.446	5.470	5.459	5.463	5.401	5.388	5.406	5.301	5.289
Ti	0.337	0.223	0.244	0.239	0.257	0.580	0.605	0.463	0.489	0.537
Al	2.759	2.697	2.672	2.626	2.595	2.655	2.607	2.727	2.710	2.709
Fe ²⁺	1.241	1.128	1.143	0.994	1.005	1.512	1.552	1.667	1.355	1.492
Mn	0.002	0.004	0.000	0.003	0.000	0.003	0.002	0.003	0.000	0.004
Mg	3.825	4.056	4.054	4.236	4.301	3.324	3.286	3.443	3.655	3.431
Ca	0.000	0.000	0.000	0.000	0.004	0.002	0.001	0.000	0.000	0.001
Na	0.043	0.055	0.044	0.052	0.047	0.032	0.024	0.018	0.011	0.016
K	1.923	1.873	1.835	1.905	1.925	1.861	1.858	1.884	1.883	1.902
F	0.689	0.929	0.858	0.910	0.746	0.536	0.640	0.255	0.137	0.217
Sum	16.215	16.411	16.319	16.424	16.343	15.906	15.963	15.866	15.541	15.598
X _{Mg} (Fe ²⁺)	0.755	0.782	0.780	0.810	0.811	0.687	0.679	0.674	0.729	0.697
X _{Fe}	0.245	0.217	0.220	0.190	0.189	0.312	0.321	0.326	0.270	0.303

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D I—Domain I; D II—Domain II; D III—Domain III; Charno—Charnockite; c—core; r—rim; l—Bt₁ included in Opx₁; P—porphyroblast (Bt₁); S—Bt₂ as symplectite with quartz or cordierite.

Table 8
Representative feldspar analyses

Sample/ rock	155A	155A	155C5	155C5	155C5	155E	155E	155E	155E
	SprGr	SprGr	SprGr	SprGr	SprGr	Charno	Charno	Charno	Charno
	La	La	Bo	Bo	Bo				
	D II	D II	D II	D II	D III				
Position	01cPl	02rPl	16hPt	15ePt	35cOrt	76hAPt	75eAPt	40cPl	39rPl
SiO ₂	62.32	62.20	64.01	62.74	63.97	61.53	63.53	59.63	61.17
TiO ₂	0.03	0.02	0.03	0.05	0.06	0.02	0.03	0.00	0.02
Al ₂ O ₃	23.26	23.39	18.45	23.41	18.53	24.35	18.54	23.24	23.76
Cr ₂ O ₃	0.00	0.03	0.00	0.02	0.03	0.07	0.00	0.00	0.01
FeO	0.06	0.10	0.00	0.00	0.09	0.08	0.00	2.36	0.06
MnO	0.02	0.00	0.04	0.00	0.01	0.00	0.02	0.25	0.01
MgO	0.02	0.00	0.02	0.00	0.00	0.01	0.00	0.88	0.00
CaO	4.91	5.43	0.10	5.08	0.10	5.80	0.01	5.21	5.37
Na ₂ O	8.45	8.53	0.83	8.60	1.22	8.33	0.63	7.77	8.73
K ₂ O	0.45	0.43	15.52	0.15	15.10	0.23	15.73	0.18	0.32
Total	99.51	100.1	99.00	100.1	99.11	100.4	98.50	99.53	99.44
O	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Si	2.781	2.756	2.981	2.784	2.970	2.722	2.976	2.681	2.723
Ti	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.000	0.001
Al	1.223	1.222	1.013	1.224	1.014	1.270	1.024	1.232	1.246
Cr	0.000	0.001	0.000	0.001	0.001	0.002	0.000	0.000	0.000
Fe ²⁺	0.002	0.003	0.000	0.000	0.003	0.003	0.000	0.080	0.002
Mn	0.001	0.000	0.002	0.000	0.000	0.000	0.001	0.010	0.000
Mg	0.001	0.000	0.002	0.000	0.000	0.001	0.000	0.059	0.000
Ca	0.235	0.258	0.005	0.241	0.005	0.275	0.001	0.251	0.260
Na	0.731	0.733	0.075	0.740	0.110	0.714	0.058	0.678	0.754
K	0.026	0.024	0.922	0.009	0.894	0.013	0.940	0.011	0.018
Sum	5.001	4.998	5.001	5.001	4.999	5.001	5.001	5.002	5.004
An	0.237	0.254	0.005	0.244	0.005	0.274	0.001	0.267	0.249
Ab	0.737	0.722	0.075	0.747	0.109	0.713	0.058	0.721	0.733
Or	0.026	0.024	0.920	0.009	0.886	0.013	0.942	0.011	0.018

SprGr—Sapphirine-bearing granulite; La—Layer; Bo—Boudin; D II—Domain II; D III—Domain III; Charno—Charnockite; c—core; r—rim; Pl—Plagioclase; Pt—Perthite where h represents host phase and e exsolution lamella; Ort—Orthoclase in mesoperthite; APt—Antiperthite where h represents host phase and e exsolution lamella.

evolution of the studied sapphirine-bearing granulite enclaves. Charnockitic magma of probable peraluminous affiliation (Table 9) could be generated by extensive anatexis of the lower continental crust. U–Pb SHRIMP ages of Paleoproterozoic mafic magmatism, related to the collision event, are reported in the northern and western part of SCB, outside the study area. They are constrained at $2085 \pm 5/9$ Ma (Oliveira et al., 2004) and are in good agreement with the ages obtained for the granulite metamorphism (Silva et al., 1997, 2002), peraluminous magmatism (Leite, 2002). The Paleoproterozoic mafic magmatism suggests that asthenospheric upwelling could provide the additional heat input to trigger mantle/lower crust anatexis and extreme crustal metamorphism (cf. Santosh et al., 2007; Santosh and Omori, 2008a,b). This could be achieved by detachment of the lithospheric thermal boundary layer after crustal thickening by orogenic collapse (cf. Harley, 1998) or slab break-off during collision (Davies and von Blanckenburg, 1995; von Blanckenburg and Davies, 1995).

The possible assembly of the 2.1–1.8 Ga Columbia supercontinent (Rogers and Santosh, 2002; Zhao et al., 2002, 2004; Hou et al., in press) has been correlated to orogenic belts with granulites that reached ultrahigh-metamorphic conditions (Brown, 2006, 2007; Santosh et al., 2007; Santosh and Omori, 2008a,b). These Paleoproterozoic granulites have been reported in North China Craton (Santosh et al., 2007), Taltson magmatic zone, northwestern Canada (Farquhar et al., 1996) and South Harris, Lewisian Complex, Scotland (Baba, 1999a,b; Hollis et al., 2006). This correlation implies a relationship between continent assembly and high geothermal gradients (Kelsey, 2008). Teixeira et al. (2007) proposed that the São Francisco Craton was one of the landmass that composed the Atlantica paleocontinent part (Rogers, 1996) of the Columbia supercontinent and Barbosa et al. (2006) demonstrated the presence of a UHT metamorphic occurrence in the Itabuna Belt (the southern part of the major Paleoproterozoic Itabuna–Salvador–Curaçá Belt). Thus if there is a relationship between supercontinent assembly and UHT metamorphism, our work supports the hypothesis that the Salvador–Curaçá Belt would represent one of the orogens that contributed to the amalgamation of the Columbia supercontinent.

Table 9

Chemical analysis of major (wt.%) and trace elements (ppm) for sapphirine-bearing granulite and charnockite

Sample/rock	155	155A	155C4	155E
	SprGr La	SprGr La	SprGr La	Charno
	D I	D II	D III	
SiO ₂	43.30	55.10	62.40	68.10
TiO ₂	0.93	0.44	0.96	0.80
Al ₂ O ₃	21.70	16.60	16.30	14.10
Fe ₂ O ₃	1.70	3.10	2.00	0.79
FeO	8.50	6.50	5.10	6.00
MnO	0.10	0.12	0.19	0.13
MgO	14.50	10.20	5.40	3.00
CaO	0.23	1.10	1.30	2.00
Na ₂ O	0.24	2.60	2.00	2.00
K ₂ O	6.70	3.10	2.95	1.50
P ₂ O ₅	0.02	0.06	0.06	0.08
H ₂ O ⁺	1.00	0.56	0.65	0.51
CO ₂	0.59	0.72	0.85	1.30
Total	99.51	100.20	100.16	100.31
Ba	1103	1195	728	501
Rb	224	83	103	53
Sr	53	147	235	127
Zr	240	198	172	167
F	8500	1550	880	780
X _{Mg} (Fe ²⁺)	0.75	0.74	0.65	0.47

SprGr—Sapphirine-bearing granulite; La—Layer; D I—Domain I; D II—Domain II; Domain III; Charno—Charnockite; X_{Mg} = (MgO/MgO + FeO)_{Molar}

Table 10

Solution models and end members used for pseudosections

Solution model	Independent end members	Reference
Spr(KWP)	spr4, fspr	Kelsey et al. (2004)
Spl(HP)	spl, herc	Holland and Powell (1998)
Bt(HP)	ann, phl, sdph, east	Holland and Powell (1998)
Grt(HP)	py, alm, gross	Holland and Powell (1998)
Opx(HP)	en, fs, mgts	Holland and Powell (1998)
hCrd	crd, fcrd, hcrd	Holland and Powell (1998)
Melt(HP)	qtz8L, kspL, sill8L, fo8L, fa8L, H ₂ OL	White et al. (2001)

See PerpleX07 documentation (www.perplex.ethz.ch) for solution models reference.

9.2. UHT metamorphism and the development of compositional domains

The presence of compositional domains and spatial disposition of the microstructures with respect to the margin of the sapphirine-bearing granulite (Fig. 4a, b) suggests that reactions were driven by the infiltration of silicate melt from the charnockite, which induced an increase of the bulk silica content resulting in the transformation of spinel into sapphirine and ultimately into cordierite (Fig. 11c). The crystallization of spinel–cordierite symplectites in sillimanite-rich and garnet-rich domains is related to cooling and decompression during orogeny evolution (cf. Harley, 1989; White et al., 2002, 2007). The formation of Opx₂ + Crd symplectites at the expense of Al-rich Opx₁ + Grt porphyroblasts (reaction 9) is also favoured by decompression (Hensen, 1988). Thus the significance of compositional domains in the sapphirine-bearing granulite would be the result of melt–rock interactions and the establishment of Si–chemical potential gradients between the charnockite and the silica-undersaturated granulite combined with *P–T* changes.

10. Conclusions

The studied silica-undersaturated sapphirine-bearing granulite enclaves in charnockite outcrop indicate that UHT metamorphic conditions were locally achieved in the Salvador–Curaçá Belt at *P–T* conditions of 7.0–8.0 kbar and 900–950 °C. The *in-situ* EMP monazite ages indicate that UHT metamorphism occurred during the 2.08–2.05 Ga (Rhyacian) Paleoproterozoic orogeny.

The enclaves show a strong chemical and mineralogical zoning from core to rim with the following features: Spr + Spl₁ in the core, relicts of Sill porphyroblasts and Crd–Spl₂–Mag symplectites between core and margin, and relicts of Grt porphyroblasts breakdown into Crd–Opx₂ symplectites and Qtz–Crd + Qtz–Bt₂ + Qtz–Bt₂ symplectites at margin. This organisation reflects an increase of bulk SiO₂ content from the core to the margins due to silica diffusion as a response of the establishment of chemical potential gradients in Si between proto-enclave minerals and charnockite magma intrusion. The growth of sapphirine, spinel–cordierite and orthopyroxene–cordierite symplectites were favoured in the lowest Si domains furthest from the charnockite contact. In contrast, more silica-rich minerals such as garnet and quartz-bearing cordierite and biotite symplectites developed at or close to the contact with the charnockite. The calculated pseudosections also suggest that cordierite–host symplectites were formed during cooling and decompression of the orogenic evolution. This Paleoproterozoic UHT metamorphism represents one of the main processes of São Francisco Craton amalgamation and can be related to other UHT metamorphic events that occurred during Columbia supercontinent assembly.

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Fig. 10. Projections from sillimanite to ternary planar sections within a FeO–MgO–Al₂O₃–SiO₂ tetrahedron (Kriegsman and Schumacher, 1999). Si' = Si + Fe⁺² + Mg – (Al/2); Mg' = Mg; Fe' = Fe⁺² and Al' = (Al + Fe⁺³ + Cr⁺³)/2, all of them in a.p.f.u., in FMAS (a, b, e) and KFMASH (c) systems. The diagrams show inferred reactions from the observed microstructures.

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Fig. 11. Pseudosections in the KFMASH system for the sapphirine-bearing granulite: *P*–*T* diagrams with retrograde paths depicted by mineral assemblages in Domain I (a) and Domain III (b); and (c) *T*–*M*(SiO₂) at 8.0 kbar for Domain I depicting the influence of increasing SiO₂ for sapphirine and cordierite crystallizations.

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Table 11

Core compositions of garnet and orthopyroxene₁ used for *P* and *T* calculations for samples 155C5 (Domain III of sapphirine-bearing granulite) and 155E (charnockite) using Grt–Opx thermometer Harley (1984) and Grt–Opx barometer of Harley and Green (1982), following the method of Pattison and Bégin (1994)

Samples	155C5	155E
Garnet	$X_{\text{mg}}(\text{Fe}^{2+})=0.451$	$X_{\text{mg}}(\text{Fe}^{2+})=0.481$
Orthopyroxene ₁	$X_{\text{mg}}(\text{Fe}^{2+})=0.665$ $y(\text{opx})=0.132$	$X_{\text{mg}}(\text{Fe}^{2+})=0.723$ $y(\text{opx})=0.129$
<i>T</i> (°C) (±40–60)	950	945
<i>P</i> (kbar) (±2.0)	8.5	8.0

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Table 12

Representative monazite analyses (oxides in wt.%) in sapphirine-bearing granulite (155) and charnockite (155E)

Sample/ position	155-2	155-22	155-1	155-11	155E-9	155E-12	155E-13	155E-1
UO ₂	0.54	0.77	0.95	1.18	0.54	0.88	0.67	0.11
PbO	0.99	0.85	1.32	1.26	0.52	0.63	0.51	0.45
ThO ₂	8.63	6.46	10.67	9.06	3.50	3.05	2.68	4.50
CaO	1.93	1.96	1.99	2.58	1.33	1.35	1.26	1.76
P ₂ O ₅	27.01	29.16	25.76	29.12	29.95	30.32	30.23	29.54
Y ₂ O ₃	1.94	2.66	1.16	3.21	2.44	1.59	1.45	0.54
SiO ₂	1.43	0.65	2.05	0.51	0.22	0.09	0.13	0.42
La ₂ O ₃	14.94	15.29	13.21	13.63	15.34	16.13	16.29	15.44
Ce ₂ O ₃	27.51	27.34	27.31	24.45	29.52	30.03	30.68	30.20
Pr ₂ O ₃	2.46	2.24	2.54	2.06	2.66	2.71	2.74	2.89
Nd ₂ O ₃	8.91	8.37	8.99	7.92	10.44	9.76	10.23	11.17
Sm ₂ O ₃	1.14	1.22	1.28	1.18	1.62	1.34	1.41	1.48
Gd ₂ O ₃	1.02	1.23	1.04	1.21	1.12	0.99	0.90	0.96
Total	98.45	98.20	98.27	97.37	99.20	98.87	99.18	99.43
P	3.764	3.897	3.656	3.919	3.966	3.986	3.980	3.934
Si	0.236	0.103	0.344	0.081	0.034	0.014	0.020	0.066
La	0.907	0.890	0.817	0.799	0.885	0.924	0.934	0.896
Ce	1.658	1.580	1.676	1.423	1.690	1.707	1.747	1.739
Pr	0.148	0.129	0.155	0.119	0.152	0.153	0.155	0.165
Nd	0.524	0.472	0.538	0.450	0.583	0.541	0.568	0.628
Sm	0.065	0.066	0.074	0.065	0.087	0.072	0.076	0.080
Gd	0.056	0.064	0.058	0.064	0.058	0.051	0.046	0.050
Y	0.170	0.223	0.103	0.272	0.203	0.131	0.120	0.045
ΣREE	3.527	3.425	3.422	3.191	3.658	3.580	3.646	3.603
U	0.020	0.027	0.035	0.042	0.019	0.030	0.023	0.004
Th	0.323	0.232	0.407	0.328	0.125	0.108	0.095	0.161
Pb	0.044	0.036	0.059	0.054	0.022	0.026	0.021	0.019
Pb/(Th + U)	0.128	0.139	0.133	0.146	0.153	0.188	0.178	0.115
Ca	0.340	0.332	0.357	0.439	0.223	0.225	0.210	0.297

Structural formulae (a.p.f.u.) based on eight cations assuming P + Si = 4 (Montel et al., 1996).

Fig. 12. Backscattered electron images (BSE) of monazite inclusions (the crosses mark the analyzed spots): (a, b) in sapphirine grains; (c, d) in biotite grains; (e, f) in orthopyroxene grains; (g, h) in cordierite grains.

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Fig. 13. Weighted histogram representations of monazite data for (a) sapphirine-bearing granulite and (b) charnockite. Each measurement is represented by its probability density function (bell-shaped curve). Each thick curve is the sum of all individual ages (bell curves). The dashed curves are the statistically derived age populations. There is no unit for the vertical scale.

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