

Calc-Alkaline Magmatism at the Archean–Proterozoic Transition: the Caicó Complex Basement (NE Brazil)

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The Paleoproterozoic metaplutonic rocks of the Caicó Complex Basement (Seridó region, NE Brazil) provide important and crucial insights into the petrogenetic processes governing crustal growth and may potentially be a proxy for understanding the Archean–Proterozoic transition. These rocks consist of high-K calc-alkaline diorite to granite, with Rb–Sr, U–Pb, Pb–Pb and Sm–Nd ages of c. 2.25–2.15 Ga. They are metaluminous, with high Yb_N , K_2O/Na_2O and Rb/Sr, low I_S , ratios, and are large ion lithophile elements (LILE) enriched. Petrographic and geochemical data demonstrate that they belong to differentiated series that evolved by low-pressure fractionation, thus resulting in granodioritic liquids. We propose a model in which the petrogenesis of the Caicó Complex orthogneisses begins with partial melting of a metasomatically enriched spinel- to garnet-bearing lherzolite (with high-silica adakite melt as the metasomatic agent), generating a basic magma that subsequently evolved at depth through fractional crystallization of olivine, followed by low-pressure intracrustal fractionation. A subduction zone setting is proposed for this magmatism, to account for both negative anomalies in high field strength elements (HFSE) and LILE enrichment. Mantle-derived juvenile magmatism with the same age is also known in the São Francisco and West Africa cratons, as well as in French Guyana, and thus the Archean–Proterozoic transition marks a very important continental accretion event. It also represents a transition from slab-dominated (in the Archean) to wedge-dominated post-Archean magmatism.

KEY WORDS: calc-alkaline; magmatism; NE Brazil; Paleoproterozoic; petrogenesis

INTRODUCTION

In Earth history, the Archean represents the most important period of continental crustal growth. It was characterized by much higher heat production than today and, as a consequence, higher geothermal gradients, which resulted in the genesis of unique lithologies such as komatiites and massive volumes of tonalite–trondhjemite–granodiorite (TTG) magmas (Condie, 1981; Taylor & McLennan, 1985; Martin, 1986, 1987; Nisbet, 1987). TTGs have strongly fractionated rare earth element (REE) patterns, with low heavy REE (HREE) contents ($Yb_N \leq 8$) and are devoid of significant Eu anomalies. Their K_2O/Na_2O is low such that, in contrast to classical calc-alkaline basalt–andesite–dacite–rhyolite (BADR) suites, their differentiation results in a Na_2O enrichment defining trondhjemitic differentiation trends.

Based on petrological and experimental studies, as well as on geochemical modelling, the genesis of Archean TTG has been explained by partial melting of an Archean tholeiite transformed into garnet-bearing amphibolite or eclogite (Barker & Arth, 1976; Martin, 1986, 1987, 1993, 1994;

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Rapp *et al.*, 1991, 2003; Rapp & Watson, 1995; Martin *et al.*, 1997, 2005; Foley *et al.*, 2002; Martin & Moyen, 2002). Although there is consensus about the tholeiitic nature of the source of Archean TTGs, the tectonic setting in which they were generated is still a subject of controversy. It has been interpreted as either slab melting in a subduction zone (Condie, 1981; Tarney *et al.*, 1982; Martin, 1986, 1987; Rapp *et al.*, 1991, 2003; Rapp & Watson, 1995; Foley *et al.*, 2002; Martin & Moyen, 2002; Martin *et al.*, 2005) or hotspot-related melting of underplated basaltic crust (Atherton & Petford, 1993; Wolde *et al.*, 1996).

Most Archean K₂O-rich granites with the isotopic signature of a mantle-derived source were emplaced at the end of the Archean (2.8–2.5 Ga), and intruded both greenstone belts and TTGs. They are also referred to as ‘sanukitoids’ (Stern, 1989; Stern & Hanson, 1991; Smithies & Champion, 1999) or ‘Closepet-type’ granites (Moyen *et al.*, 2001, 2003). However, they display geochemical characteristics intermediate between Archean TTG (strongly fractionated REE patterns and low Yb_N contents) and modern juvenile continental crust [K and more generally large ion lithophile element (LILE) enrichment] and their petrogenesis is still under debate. Nevertheless, they generally appear to have been derived through variable extents of interactions between mantle peridotite and TTG magmas (Jayananda *et al.*, 1995; Moyen *et al.*, 1997; Smithies & Champion, 1999, 2000; Martin *et al.*, 2005).

When compared with TTGs, post-Archean granitoids are richer in K; their compositions range from granodiorite to granite, with high Yb_N (>10) and negative Eu anomalies. A number of them with trace element and isotopic compositions of mantle-derived magmas are considered as having been generated in a subduction zone environment by partial melting of a fluid metasomatized mantle wedge. The dehydration of the subducted oceanic crust produces LILE-enriched fluids that interact with the overlying mantle wedge and initiate its melting, resulting in potassic calc-alkaline magmatism (e.g. Wyllie, 1983; Tatsumi, 1989; Hawkesworth *et al.*, 1993; Keppler, 1996; Kogiso *et al.*, 1997; Bureau & Keppler, 1999; Kessel *et al.*, 2005).

In modern subduction zones, Archean TTG-like magmas can be generated when high geothermal gradients are achieved along the Benioff plane; for instance, during subduction of an actively spreading mid-ocean ridge. These magmas, referred to as adakites, are richer in Mg, Ni and Cr than Paleoarchean and Mesoarchean (>3 Ga) TTG but are very similar to Neoarchean (<3.0 Ga) TTG (Martin, 1999; Smithies, 2000; Martin *et al.*, 2005). These differences are explained by assuming that the adakitic magma, once generated by partial melting of the subducted oceanic crust, interacts with the overlying mantle wedge and/or

lowermost arc crust (Defant & Drummond, 1990; Drummond & Defant, 1990; Sen & Dunn, 1994a, 1994b; Rapp & Watson, 1995; Schiano *et al.*, 1995; Maury *et al.*, 1996; Stern & Kilian, 1996; Sigmarsson *et al.*, 1998; Martin, 1999; Martin *et al.*, 2005).

The Archean–Proterozoic boundary is marked by changes from a generalized high geothermal gradient and subsequent production of about two-thirds to three-quarters of the continental crust by accretion of juvenile magmas in the Archean, to a regime of lower and more diversified geothermal gradients, with predominance of crustal recycling during the Proterozoic (Taylor & McLennan, 1985; Martin, 1986, 1993, 1994; Sylvester, 1994). Although at the world scale it is possible to find evidence for a progressive change in TTG composition throughout Archean times (Martin & Moyen, 2002), the transition at 2.5 Ga was not sharp. On the contrary, it was progressive, such that some TTG are still known in Early Proterozoic terrains. In this context the orthogneisses of the 2.2 Ga Caicó Complex in NE Brazil provide an attractive opportunity to study calc-alkaline magmatism at this period of important petrogenetic changes. In addition, the Early Proterozoic is also characterized by a very significant accretion event, leading to the production of huge volumes of new juvenile continental crust; for example, in the São Francisco (Conceição, 1997; Teixeira *et al.*, 2000) and West Africa (Boher *et al.*, 1992; Toteu *et al.*, 2001) cratons, and in French Guyana (Gruau *et al.*, 1985; Delor *et al.*, 2003). It also marks the formation of voluminous juvenile crust after a period of ~300 Myr (2.5–2.2 Ga), characterized by negligible magmatic activity and even lack of magmatism in several areas (Martin, 1993). In this context, the purpose of this paper is: (1) to describe all magmatic components of this juvenile transitional crust from NE Brazil; (2) to constrain its petrogenesis; (3) to discuss, in the light of these data, the Archean–Proterozoic transition and the subsequent Paleoproterozoic evolution.

GEOLOGICAL SETTING

Tectonic framework

Almeida *et al.* (1981) defined the Borborema Province in northeastern Brazil (Fig. 1), which consists of tectonic units stabilized during the Brasiliano orogeny (0.60 ± 0.05 Ga). This province developed after the convergence of the West Africa–São Luís and São Francisco–Congo cratons during the assembly of Western Gondwana at c. 600 Ma. In a pre-drift reconstruction, it extends from central and SE Brazil (Brasília–Ribeira mobile belt) to West Africa through the Trans-Sahara belt composed of the Cameroon, Nigeria and Hoggar shields (Caby, 1989).

This area has been studied for many years and several contrasting geodynamic reconstructions have been proposed (Almeida *et al.*, 1981; Caby, 1989; Bertrand & Jardim de Sá, 1990; Caby *et al.*, 1991; Jardim de Sá, 1994;

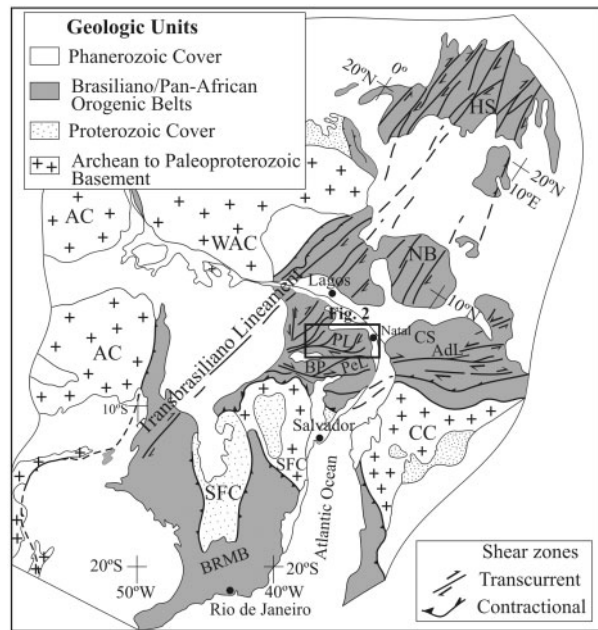


Fig. 1. Pre-drift reconstruction for West Africa and eastern South America (after Jardim de Sá, 1994). Rectangle outlines approximate area of Fig. 2. WAC, West Africa craton; AC, Amazonian craton; SFC, São Francisco craton; CC, Congo craton; BRMB, Brasília and Ribeira mobile belts; BP, Borborema Province; CS, Cameroon Shield; NB, Nigerian Belt; HS, Hoggar Shield; PL, Pato lineament; PeL, Pernambuco lineament; AdL, Adamaoua lineament.

Van Schmus *et al.*, 1995, 2003). Briefly, the Borborema Province consists of several supracrustal sequences deposited over an Archean to Paleoproterozoic gneissic basement that has been intruded by large amounts of Brasiliano-age granitoids. Jardim de Sá (1994) interpreted it as being made up of a number of allochthonous terrains that amalgamated just before and/or during the Brasiliano orogeny, and Santos (1996) noted that tectonic collages occurred in both the Cariris Velho–Kibaran (1.1–0.95 Ga) and Brasiliano–Pan-African orogenies in the so-called Transversal Zone.

A notable feature of this province is the complex system of crustal-scale high-temperature shear zones (Corsini *et al.*, 1991; Jardim de Sá, 1994) that separate domains of variably strained massifs and supracrustal sequences. These were developed (and/or activated) during and after the collision between the West Africa, Congo and São Francisco cratons, and are closely associated with the emplacement of the Brasiliano granitoids (Caby *et al.*, 1981; Bertrand & Jardim de Sá, 1990; Archanjo & Bouchez, 1991; Corsini *et al.*, 1991; Jardim de Sá, 1994). The Pato and Picuí–João Câmara dextral shear zones are believed to accommodate the displacement of the Rio Piranhas massif toward the São José de Campestre massif, which resulted in transpression of the Seridó belt.

In this context, the Seridó domain (Fig. 2), situated to the north of the Pato lineament, comprises: (1) the Caicó Complex Basement; (2) supracrustal sequences of indeterminate age belonging to the Seridó Group [late Paleoproterozoic according to Jardim de Sá (1994) and Jardim de Sá *et al.* (1995), or Neoproterozoic following Hackspacher & Dantas (1997) and Van Schmus *et al.* (2003)]; (3) granitoids of both late Paleoproterozoic (the so-called G₂ orthogneisses) and late Neoproterozoic ages and interpreted as having been derived from melting of an enriched lithospheric mantle or the lower continental crust, with variable crustal contamination and mixing (Leterrier *et al.*, 1990, 1994; Jardim de Sá, 1994; Hollanda *et al.*, 2003).

The Caicó Complex Basement

Field relationships

In the regional literature, the Caicó Complex corresponds to the high-grade basement of the Seridó Group, which forms an area of ~60% (~35 000 km²) of the exposed Precambrian units in the region studied (Fig. 2). It consists mainly of Paleoproterozoic meta-plutonic rocks, intruded and/or interlayered with older and subordinate meta-supracrustal rocks (Jardim de Sá, 1984, 1994; Hackspacher *et al.*, 1990; de Souza *et al.*, 1993). This association occurs in both the Rio Piranhas and São José de Campestre massifs; in the latter, Archean protoliths have also been identified (Dantas *et al.*, 2004). The present paper essentially deals with the Paleoproterozoic orthogneisses, which are hereafter simply referred to as the Caicó Complex.

The older tectonic fabric in these orthogneisses is a high-grade banding (D₁) associated with isoclinal to intrafolial folds and strong transposition, followed by an event of tangential kinematics (D₂). D₁ and D₂ are usually interpreted as temporally distinct events (e.g. Jardim de Sá, 1984, 1994); the deposition of the Seridó Group and intrusion of the G₂ orthogneisses occurred between D₁ and D₂. The age of the D₂ event is also controversial; the *c.* 1.8 Ga age proposed by Jardim de Sá (1994), Jardim de Sá *et al.* (1995) and others has been challenged by the younger (Neoproterozoic) U–Pb detrital zircon and Sm–Nd model dates of the Seridó belt supracrustal sequences (Van Schmus *et al.*, 2003). Recently, Hollanda *et al.* (2007) reported precise U–Pb sensitive high-resolution ion microprobe (SHRIMP) zircon ages of 2.20 ± 0.03 Ga for G₂ orthogneisses in the Seridó region, and thus constrained the timing of the D₂ event. The last tectonometamorphic event (D₃) is marked by transcurrent to oblique shear zones and emplacement of the late Neoproterozoic (Brasiliano) granitoids. The associated metamorphism ranges from upper amphibolite to granulite facies near plutonic intrusions and crustal-scale shear zones to greenschist facies in other places.

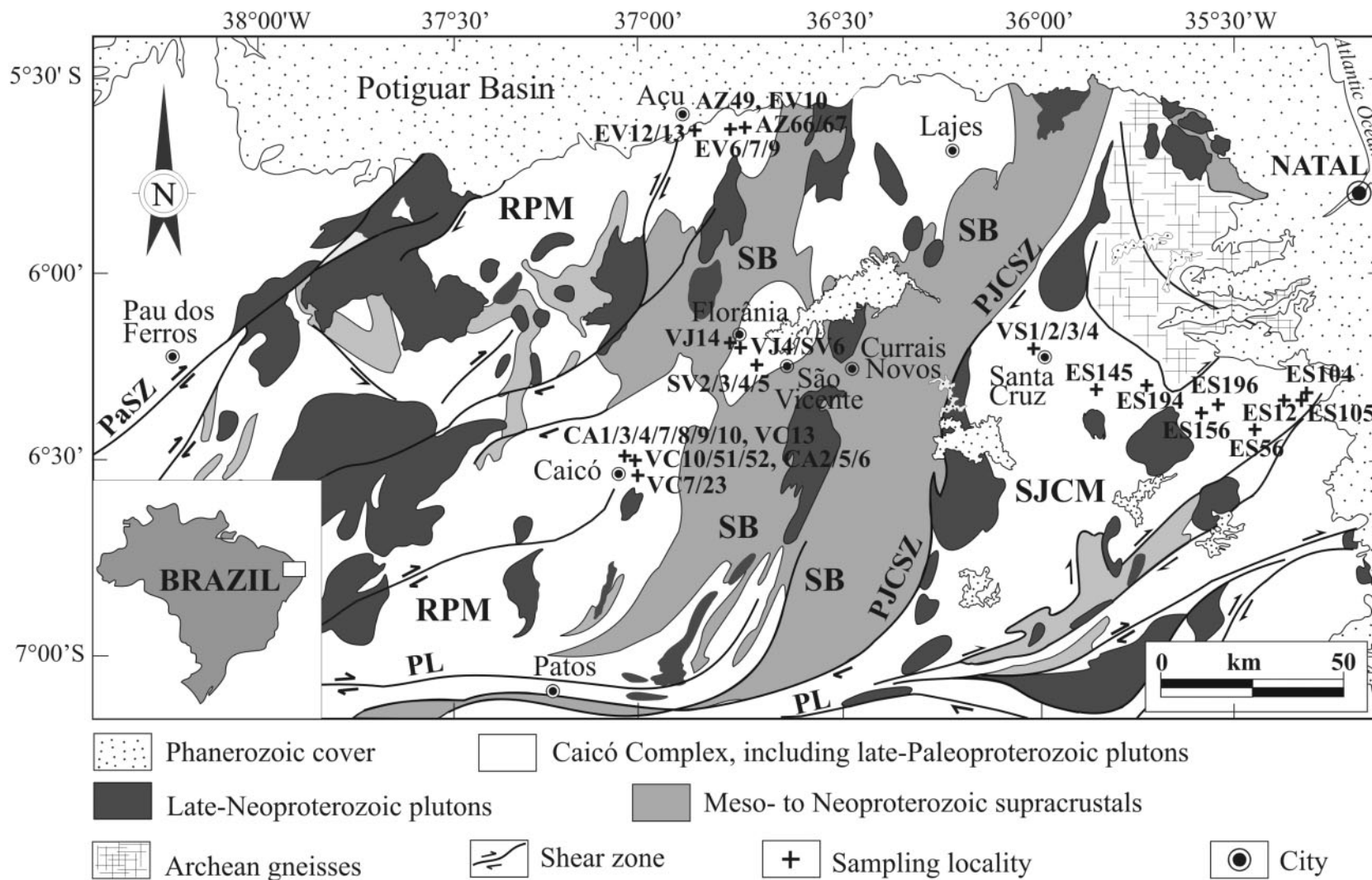


Fig. 2. Geological framework of the Seridó Domain, north of the Patos lineament, NE Brazil (modified after Jardim de Sá, 1994; Dantas *et al.*, 2004). RPM, Rio Piranhas Massif; SJCM, São José de Campestre Massif; SB, Seridó belt; PL, Patos lineament; PJCSZ, Picuí-João Câmara Shear Zone; PaSZ, Portalegre Shear Zone.

Geochronology and geochemistry

Hackspacher *et al.* (1990) and Van Schmus *et al.* (1995) published U–Pb data on zircons for gneisses and metagabbros from the São Vicente–Florânia region (Fig. 2), which gave ages in the range 2.16–2.13 Ga. For granodiorites of the Caicó area, Legrand *et al.* (1991) reported a whole-rock Rb–Sr isochron of 2.12 ± 0.08 Ma and a U–Pb zircon age of 2.24 ± 0.01 Ma. Available Sm–Nd data for metagabbros indicate T_{DM} values of 2.76–2.62 Ga (Hackspacher *et al.*, 1990; Dantas, 1992; Van Schmus *et al.*, 1995). Whole-rock Rb–Sr isochrons of granitic gneisses and porphyritic granodioritic gneisses in both the São Vicente–Florânia and Açu areas give ages in the range 2.2–2.0 Ga, and I_{Sr} of 0.7041–0.7028 (Macedo *et al.*, 1984; Jardim de Sá *et al.*, 1987; Legrand *et al.*, 1991; Dantas, 1992).

U–Pb zircon data from the Caicó Complex in the Santa Cruz region, to the east of the Seridó belt, yield an age of 2.18 ± 0.02 Ga (Dantas, 1996). In the São José de Campestre massif, Paleoproterozoic terrains surrounding the Archean domains and correlated to the Caicó Complex orthogneisses yield the following conventional and SHRIMP U–Pb zircon and Nd model ages (Dantas, 1996; Dantas *et al.*, 2004): (1) 3.5 Ga tonalitic gneiss with T_{DM} of 4.0–3.8 Ga; (2) 3.3 Ga grey monzogranitic gneiss with T_{DM} of 3.7–3.1 Ga; (3) 2.7 Ga alkaline clinopyroxene-bearing syenogranitic gneiss with T_{DM} of 3.5–3.2 Ga. However, no Archean terrain has been recognized to the west in the Rio Piranhas massif.

Geochemical studies of the Caicó Complex led to two groups of genetic interpretation: (1) the orthogneisses consist of Archean-like TTG suites formed by several pulses of magmatism and associated processes of magma mixing and mingling (Dantas, 1992; Petta, 1995), and significant contamination by crustal material accounts for their negative ϵ_{Nd} values (Dantas, 1996); (2) the parental magmas were derived by partial melting of an enriched mantle; these melts then evolved by fractional crystallization with little or no interaction with the continental crust (Martin *et al.*, 1990; de Souza, 1991; de Souza *et al.*, 1993).

ANALYTICAL PROCEDURES

In this paper, the modal composition has been established from an average counting of 1300 points for each individual thin section. Microprobe analyses were carried out at the Universidade de Brasília with a Cameca SX50 electron microprobe, operating at 15 kV accelerating voltage, 25 nA beam current, and 10 s counting time, using synthetic and natural minerals as standards. The analytical errors are within ± 0.5 –2% for SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , MnO , CaO and TiO_2 , and 4.5–5.6% for Na_2O and K_2O .

Concentrations of major and trace elements for 61 samples were determined by X-ray fluorescence (XRF) at the Université de Rennes I with a Philips PW

1404 spectrometer, and seven other samples were analysed for trace elements by inductively coupled plasma mass spectrometry (ICP-MS) at the Université de Lyon. Analytical precision for major elements is within 2%, but may reach 10% for elements of low abundance (MnO , P_2O_5). Total iron is reported as Fe_2O_3 . For trace elements, precision is better than 5%, except for elements present at concentrations <30 ppm, where the uncertainties are within 10%. The REE contents of nine samples were determined by ICP-MS at the Université de Nancy ($n=3$) and the Université Blaise Pascal ($n=6$). Concentrations of REE, Ta, U, Th, Hf and Sc in nine samples were measured by instrumental neutron activation analysis (INAA) at the Pierre Sue laboratory (CEN, Saclay). Details of the analytical methods have been given elsewhere (Govindaraju *et al.*, 1976; Martin, 1987). Chondrite normalization values used for the REE are from Sun & McDonough (1989).

Rb contents were measured by isotope dilution with a Cameca THN-206 mass spectrometer at the Université de Rennes I. A Finnigan Mat 262 multicollector mass spectrometer was used to determine Sr content as well as isotopic ratios. Total blanks were as follows: 0.1 ng for Rb, 1 ng for Sr, and measurements of NBS standard 987 gave an $^{87}Sr/^{86}Sr$ value of 0.71025 ± 0.00001 . Uncertainties of $^{87}Rb/^{86}Sr$ are within 2%, and $^{87}Sr/^{86}Sr$ ratios are quoted at 2σ . Sr and Nd isotopic compositions measured at Clermont-Ferrand were determined by mass spectrometry with a Cameca THN-206 [analytical methods have been described by Pin & Paquette (1997)]. $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$ (Faure, 1986), and $^{143}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$. Single zircon analyses were performed at the Université de Rennes I using a Cameca THN-206 mass spectrometer and steps at 2.6, 2.8 and 3.2 A, following the procedure of Köber (1986). Decay constants and isotopic abundance ratios for all methods are those of Steiger & Jäger (1977). The ages, MSWD and errors were calculated using the Excel-based version 3 of Isoplot (Ludwig, 2003). All isotopic ratios and age calculations in this paper, as well as previously published data, were (re)calculated to a 2σ error.

STRATIGRAPHY AND STRUCTURAL PATTERNS

The Caicó Complex is composed of two units, a meta-volcano-sedimentary unit and a volumetrically dominant, meta-plutonic one. In the region investigated, the supra-crustal sequences represent <6% of outcropping area; they mainly consist of garnet-bearing paragneisses and fine-grained amphibolites (meta-basalts and meta-andesites) together with intermediate to felsic gneisses (meta-rhyolites and meta-greywackes). Subordinate amounts of banded

iron formations (BIFs), quartzites, marbles and calc-silicate gneisses are also found. The meta-supracrustal rocks may form 20–150 cm xenoliths included in the intrusive meta-plutonic rocks. The meta-plutonic rocks consist of (an estimation of the exposed area is indicated as a percentage of the total area of basement rocks): (1) quartz diorites and subordinate meta-gabbro and meta-ultramafic (hornblendites, serpentinites, steatites) bodies (~3%); (2) fine- to medium-grained tonalitic (~28%) and granitic (~11%) gneisses; (3) medium- to coarse-grained porphyritic granodioritic and granitic gneisses (~52%).

Basic to intermediate rocks, which are volumetrically subordinate, may form 100–500 m diameter stocks or, more commonly, occur as 10–200 cm enclaves within the granitoids, and as 1–5 m thick sheets in the meta-supracrustal rocks. Quartz diorites, which are volumetrically more abundant than gabbros, diorites and meta-ultramafic rocks, may contain small elliptical dioritic microgranular enclaves, and euhedral to rounded millimetre-sized plagioclase phenocrysts. Field relationships indicate that the tonalitic gneisses are intruded by augen gneisses, which are in turn intruded by granitic gneisses. In low-strain regions, dioritic, quartz dioritic, granodioritic, granitic and tonalitic gneisses have gradational, interlobate, or wedge-shaped contacts, the first two lithotypes corresponding to the less differentiated petrographic facies. All features and intrusive relationships described above indicate that the meta-plutonic rocks of the Caicó Complex are coeval intrusions, spatially related to each other and probably with a common, less evolved, basic to intermediate parental magma.

The most penetrative fabric (D_2) is a metamorphic banding that overprints earlier magmatic fabrics (contacts between enclaves and more differentiated granitoid hosts; alignment of feldspar and amphibole phenocrysts). The D_2 fabric is also marked on G_2 granitoid sheets intruded into the interface between the Caicó basement and supracrustal rocks of the Seridó Group. The metamorphism associated with D_2 is generally in upper amphibolite facies and of low to medium pressure, as indicated by paragenesis including cordierite $\pm$ sillimanite $\pm$ kyanite $\pm$ rutile in garnet-bearing paragneisses. Jardim de Sá (1994) and Jardim de Sá *et al.* (1995) ascribed the D_2 event to a late Paleoproterozoic stage, based on the assumption of a syn-tectonic (syn- D_2) emplacement of the G_2 orthogneisses and meta-pegmatites, dated at 1.9–1.8 Ga according to U–Pb zircon and Rb–Sr isochron ages (Jardim de Sá *et al.*, 1995); a U–Pb titanite age of 1.97 ± 0.02 Ga from a Caicó Complex orthogneiss (Hackspacher *et al.*, 1995) may be an indication of basement overprint during the D_2 thermotectonic event. The D_2 tangential fabrics are overprinted by NE–SW Brasiliano-age transcurrent (in the Rio Piranhas massif) and extensional (in the São José de Campestre massif) shear zones (D_3). Near and inside the shear zones,

amphibole, biotite and feldspar are dynamically retrogressed into epidote, carbonate, chlorite, actinolite and titanite.

PETROGRAPHY AND TEXTURES

General characteristics

Table 1 shows the average modal compositions of 128 meta-plutonic rocks of the Caicó Complex from both the Rio Piranhas and São José de Campestre massifs. All samples were plotted in the Q–A–P (quartz–alkali feldspar–plagioclase) triangle (Fig. 3; Lameyre & Bowden, 1982). The modal compositions of basic to intermediate rocks are gabbro and quartz diorite, respectively, which all follow a tholeiitic differentiation trend. Tonalitic gneisses plot along a low-K calc-alkaline (trondhjemitic) trend akin to the most evolved members of the Paleoproterozoic low-K gabbro–diorite–tonalite–trondhjemite series of SW Finland (Arth *et al.*, 1978). Augen gneisses vary from granodiorite to syenogranite, with a few samples having monzodioritic and monzonitic compositions. In fact, both augen and granitic gneisses do not define real trends but rather plot on the medium-K to high-K calc-alkaline trends. Consequently, they are clearly different from typical Archean TTG, which have low-K affinity (Martin, 1987, 1994). On the other hand, they are very similar to Neoproterozoic K_2O -enriched calc-alkaline granitoids as exemplified by rocks of the Armorican Massif (Graviou & Auvray, 1985; Graviou *et al.*, 1988).

One outstanding feature of the Caicó meta-plutonic rocks is the abundance of ferromagnesian minerals, mainly clino-amphibole and biotite, which distinguishes them from the amphibole-poor typical Archean TTG (Martin, 1987, 1994). In tonalitic, augen and granitic gneisses the less evolved facies are richer in amphibole and poorer in biotite than the more differentiated members; this feature emphasizes the role played by the fractionation of these phases at the beginning of differentiation. The regular variation of mafic and felsic minerals together with preserved igneous textures (clinopyroxene, amphibole, feldspar, titanite and apatite phenocrysts), absence of metasomatic replacement of K-feldspar by Na-plagioclase (Drummond *et al.*, 1986) and conservation of magmatic geochemical trends (see below) all suggest that the mineral assemblage observed at present is the same as in the magmatic protoliths.

Basic to intermediate rocks (BIR)

According to their degree of recrystallization the basic to intermediate rocks of the Caicó Complex display granoblastic, nematoblastic, pokilitic and laminated textures. Based on modal composition, three main petrographic facies can be distinguished: (1) hornblende > biotite, the most widespread facies; (2) biotite > hornblende;

Table 1: Average modal composition of meta-plutonic rocks of the Caicó Complex, Borborema Province, NE Brazil

	Basic to intermediate rocks (n = 29)			Augen gneisses (n = 55)			Granitic gneisses (n = 21)			Tonalitic gneisses (n = 23)		
Facies:	Dio + Hb	Hb > Bio	Bio > Hb	Hb > Bi	Bio > Hb	Bio	Hb > Bio	Bio > Hb	Bio	Hb > Bio	Bio > Hb	Bio
n:	8	13	8	12	26	17	3	3	15	4	13	6
Qz (%)	2.80	6.7	10.5	18.4	24.9	29.3	27.6	29.4	32.7	24.7	31.6	36.8
AF	0.01	0.2	0.0	14.5	16.8	27.5	30.7	19.8	31.9	3.4	2.6	5.2
Pl	20.1	37.7	52.1	38.3	36.6	32.7	31.1	35.7	26.9	39.2	42.7	44.3
Bio	2.8	14.9	21.7	10.3	13.5	7.4	1.4	6.4	6.1	6.8	15.4	11.3
Hb	56.6	37.1	10.8	14.5	4.2	0.0	6.2	2.1	0.0	19.0	3.8	0.1
Dio	13.4	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0
Tit	2.0	1.5	1.6	1.6	1.4	1.0	0.8	1.0	0.3	1.6	1.1	0.2
Op	0.4	0.2	0.2	0.3	0.5	0.7	0.2	1.1	0.6	0.1	0.5	0.4
Ep	1.3	0.7	2.6	0.9	1.4	0.3	0.8	3.2	0.3	4.6	1.5	0.8
Apt	0.1	0.2	0.2	0.5	0.5	0.3	0.4	0.4	0.2	0.4	0.6	0.5
Zrn	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	0.1	0.1
Others	0.4	0.8	0.3	0.7	0.2	0.8	0.1	0.9	1.0	0.2	0.1	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
ΣM	75.6	55.3	35.8	28.1	21.5	9.7	10.5	14.3	7.6	32.4	23.0	13.3
AF/Pl	0.0	0.0	0.0	0.4	0.5	0.8	1.0	0.6	1.2	0.1	0.1	0.1

Qz, quartz; AF, alkali-feldspar; Pl, plagioclase; Bio, biotite; Hb, hornblende; Dio, diopside; Tit, titanite; Op, opaque minerals; Ep, epidote; Apt, apatite; Zrn, zircon; Others, chlorite ± carbonate ± muscovite; ΣM, total of mafic phases; tr, trace.

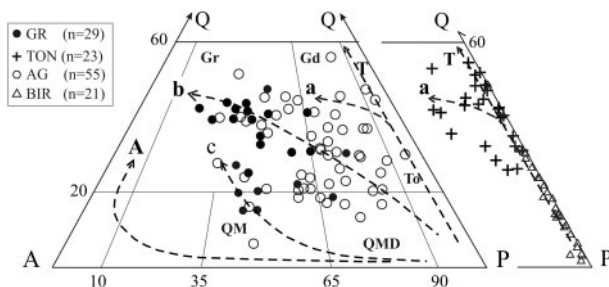


Fig. 3. Modal composition of orthogneisses of the Caicó Complex reported in the Q-A-P triangle (Streckeisen, 1976). T, tonalite; Gd, granodiorite; Gr, granite; QM, quartz monzonite; QMD, quartz monzodiorite. The arrows correspond to typical differentiation trends (Lameyre & Bowden, 1982): T, tholeiitic; A, alkaline. Calc-alkaline trends: a, low-K; b, intermediate-K; c, high-K. BIR, basic to intermediate rock; TON, tonalitic gneiss; AG, augen gneiss; GR, granitic gneiss.

(3) clinopyroxene + hornblende and rare biotite, subordinate to (1) and (2).

Clinopyroxene is a colourless or pale green diopside up to 2–5 mm long that is sometimes transformed into green amphibole or brown biotite. Amphibole often occurs as euhedral to subhedral polygonal aggregates; it is strongly pleochroic (*X* pale yellow, *Z* deep green to blue) and its length ranges from 0.5 to 4 mm. Its optical properties are

those of common green hornblende, but chemical variation from Mg-hornblende to actinolite and X_{Mg} of 0.7–0.4 were reported by Petta (1995) in the São Vicente–Florânia region. Plagioclase (An_{25-40}) appears as millimetre-sized phenocrysts with sharp contacts or rounded margins, commonly forming recrystallized polygonal mosaics.

Accessory minerals are: (1) grey to brown lozenge-shaped titanite phenocrysts (with quartz, amphibole, apatite, and biotite inclusions), intergranular crystals or small grains also following the cleavage of biotite, amphibole or clinopyroxene; (2) small light yellow prisms and irregular crystals of epidote, with frequent metamictic allanite core; (3) opaque minerals that occur as lamellae and quadratic or poikilitic grains associated to biotite and titanite; (4) apatite and zircon inclusions in clinopyroxene, amphibole and plagioclase. Plagioclase and biotite alteration occasionally and locally gives rise to carbonate and chlorite, respectively.

Augen gneisses (AG)

The augen gneisses are derived from porphyritic plutonic protoliths and have granoblastic to granonematoblastic textures. The most important feature is millimetre- to centimetre-sized (0.1–20 mm) augens of perthitic K-feldspar (microcline $Or_{93}Ab_7$, Table 2) and slightly zoned plagioclase (An_{22-30} , Table 2). K-feldspar augens often contain

inclusions of plagioclase, biotite, amphibole, titanite and zircon. Both types of augen can be deformed, recrystallized, and wrapped by quartz ribbons and new feldspar grains. Myrmekite and replacement of plagioclase by microcline is common between recrystallized aggregates as well as in pressure shadows near feldspar augens. Accessory minerals are: titanite (poikilitic or interstitial grains); pistacite-rich epidote ($P_{ss}=37$; Table 2) forming anhedral rims around metamictic allanite core, anhedral grains in reaction contacts with biotite and amphibole, or associated with saussuritization of plagioclase; oxides (usually bordered by epidote and titanite); and apatite and zircon included in other mineral phases.

Amphibole and biotite mark the main planar fabric (S_2). The former occurs as anhedral to subhedral prismatic and strongly pleochroic grains (x yellowish green, z deep green), 0.1–2 mm in size. It consists of Ca-rich amphibole (Table 2) with $(Na + K)_A = 0.7$, $(Ca + Na)_B = 1.8$, $Ti = 0.1$ p.f.u., $Fe^{3+} > Al^{VI}$ and $X_{Mg} = 0.4$, and can be classified as magnesian–hastingsitic hornblende according to the classification of Leake (1978). Some crystals contain inclusions of plagioclase, quartz, titanite, biotite and apatite. Biotite appears as isolated flakes, locally as inclusions

or in reaction contact with amphibole, in this case associated with epidote and titanite. It has variable size (0.1–4 mm), strong pleochroism (X light yellow, Z deep yellow), with low Ti contents and X_{Mg} of 0.5 (Table 2), and can be classified as Fe-biotite.

Granitic gneisses (GR)

Granitic gneisses are mineralogically similar to augen gneisses, except that they contain smaller amounts of dark minerals (Table 1). Texturally, they are equigranular (1–2 mm) or slightly inequigranular, and microporphyritic. Plagioclase (An_{20-25}) is slightly zoned or optically homogeneous. Biotite is brown and relatively rare, and colourless clinopyroxene (diopside) has also been scarcely observed in the less differentiated samples. Amphibole is green to blue with optical properties of common green hornblende. Epidote, opaque minerals, apatite and zircon are frequent accessory phases.

Tonalitic gneiss (TON)

Tonalitic gneisses are compositionally and texturally similar to granitic and augen gneisses except that they have little or no K-feldspar and are richer in mafic minerals.

Table 2: Mineral chemistry of selected samples of tonalitic gneiss and augen gneiss from the Açú region

	Tonalitic gneiss (sample AZ49C)			Augen gneiss (sample AZ66C)				
	Amphibole	Biotite	Plagioclase	Amphibole	Biotite	Plagioclase	K-Feldspar	Epidote
<i>n</i> :	15	3	4	6	7	5	1	1
SiO ₂ (wt %)	39.51	35.39	64.83	41.05	35.46	63.40	64.79	37.42
TiO ₂	0.86	2.23	–	0.67	1.84	–	–	0.07
Cr ₂ O ₃	0.02	0.02	–	0.05	0.02	–	–	–
Al ₂ O ₃	11.64	14.67	22.16	11.14	14.84	23.60	18.66	22.8
FeOt	23.62	24.14	0.06	21.38	20.23	0.08	0.03	–
Fe ₂ O _{3t}	–	–	–	–	–	–	–	14.0
MnO	1.51	1.0	–	0.4	0.29	–	–	0.09
MgO	5.62	8.34	–	7.75	10.39	–	–	0.02
CaO	11.03	0.03	3.22	11.51	0.06	4.93	–	23.31
Na ₂ O	1.38	0.06	9.81	1.36	0.06	9.17	0.73	–
K ₂ O	1.50	9.30	0.21	1.43	9.28	0.11	15.63	–
Total	96.69	95.18	100.29	96.74	92.47	101.29	99.84	97.71
	$X_{Mg} = 0.30$	$X_{Mg} = 0.38$	An = 15.1	$X_{Mg} = 0.39$	$X_{Mg} = 0.48$	An = 22.7	An = 0.0	$P_{ss} = 37.0$
	P^1 7.4		Ab = 83.6			Ab = 76.6	Ab = 6.7	
	T^2 705		Or = 1.1			Or = 0.6	Or = 93.3	

¹ P (± 0.6 kbar) (Schmidt, 1992).

² T ($\pm 75^\circ\text{C}$) (Blundy & Holland, 1990).

$X_{Mg} = Mg/(Mg + Fe^{2+})$; $P_{ss} = Fe^{3+}/(Fe^{3+} + Al)$; An = $Ca/(Ca + Na + K)$; Ab = $Na/(Ca + Na + K)$; Or = $K/(Ca + Na + K)$. Amphiboles were normalized to 23 O²⁻ atoms, 1 OH⁻ group; biotite to 22 O²⁻ atoms, 2 OH⁻ group; epidote to 12 O²⁻ atoms, 1 OH⁻ group; feldspar to 8 O²⁻ atoms. Fe^{3+} of amphibole were calculated assuming a fixed ratio $Fe^{3+}/Fe_t = 0.27$ (Hammarstrom & Zen, 1986), and the remaining Fe was assumed to be Fe^{2+} . In epidote, FeO (wt %) was transformed into Fe₂O₃ assuming an Fe₂O₃/FeO ratio of 1.1114.

Plagioclase (An_{12-18}) is slightly less calcic than in the augen and granitic gneisses (Table 2). Amphibole is strongly pleochroic ranging from brown to deep green, with other optical properties similar to amphiboles of the augen gneisses. Chemically, they have $(\text{Na} + \text{K})_{\text{A}} = 0.7$, $(\text{Ca} + \text{Na})_{\text{B}} = 1.7$, $\text{Ti} = 0.1$ p.f.u., $\text{Fe}^{3+} > \text{Al}^{\text{VI}}$ and $X_{\text{Mg}} = 0.3$, they are slightly Si- and Mg-impoverished when compared with amphibole from the augen gneisses, and they can be classified as hastingsitic hornblende (Leake, 1978). Biotite is slightly Ti-rich and Mg-poorer than in the augen gneisses.

***P-T* conditions of both emplacement and recrystallization**

The Caicó Complex has been variably deformed and recrystallized under amphibolite-facies conditions. Despite this, mineral shapes and inclusion relationships allow us to distinguish between relicts of igneous textures and metamorphic features. The former are represented by plagioclase and K-feldspar, as well as amphibole and titanite phenocrysts. Generally, plagioclase, K-feldspar and amphibole are texturally strongly similar to feldspar and amphibole phenocrysts described in quartz diorite and granodiorites from well-preserved calc-alkaline granitoids (Graviou & Auvray, 1985; Graviou *et al.*, 1988). Taking into account these points, we selected the less deformed and/or metamorphically recrystallized samples for microprobe study.

The Al-in amphibole geobarometer (Schmidt, 1992) and the plagioclase-hornblende geothermometer (Blundy & Holland, 1990) were used to constrain the *P-T* conditions of re-equilibration of amphibole (data from Table 2). Based on the experimental errors of the method

(± 0.6 kbar and $\pm 75^\circ\text{C}$), the calculated *P-T* values are in the range 7.4–6.8 kbar and 732–705°C; they are the same for amphibole of both tonalitic and augen gneisses. This corresponds to the transition between the upper amphibolite to granulite facies, in the field of partial melting of water-saturated granitic systems. These values are consistent with both recrystallization of feldspar phenocrysts in meta-plutonic rocks and migmatization of the meta-pelitic components of the Caicó Complex. On the other hand, as coexisting amphibole and biotite have different X_{Mg} , overall chemical equilibrium was not achieved (Vynhal *et al.*, 1991). It is proposed that the syntectonic emplacement and cooling of the meta-plutonic rocks occurred between 7.4 and 6.8 kbar and 732 and 705°C, which is consistent with all other field data, textural observations, and the mineralogical sequence described above. This corresponds to an average geothermal gradient of $\sim 30^\circ\text{C}/\text{km}$ near the pluton contacts.

GEOCHRONOLOGY AND ISOTOPIC DATA

Five samples of tonalitic gneisses from Caicó and Agu were analysed for Rb–Sr isotopic composition (Table 3). They yielded an age of 2229 ± 64 Ma with $\text{MSWD} = 1.9$ and initial $^{87}\text{Sr}/^{86}\text{Sr}$ (I_{Sr}) of 0.7023 ± 0.0005 (Fig. 4a). Single zircon from sample EV10A gave a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2181 ± 10 Ma (Table 4, Fig. 4a), which is within the error limits of the whole-rock Rb–Sr age. The zircon grains are idiomorphic, dark (metamictic?) to light brown, and may contain minute inclusions of apatite and fluid.

Table 3: Rb–Sr isotope data for meta-plutonic rocks of the Caicó Complex basement in the Rio Piranhas massif

Lithology	Facies	Sample	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$ ($\pm 2\%$)	$^{87}\text{Sr}/^{86}\text{Sr}_m$ ($\pm 0.001\%$)
Tonalitic gneiss	Bio + Hb	EV10A	57	503	0.32 ± 0.01	0.712612 ± 08
Tonalitic gneiss	Bio + Hb	EV10B	59	431	0.40 ± 0.01	0.715147 ± 09
Tonalitic gneiss	Bio + Hb	VC13C	108	487	0.64 ± 0.01	0.722722 ± 13
Tonalitic gneiss	Bio + Hb	EV7B	113	493	0.66 ± 0.01	0.723314 ± 09
Tonalitic gneiss	Bio	VC13D	98	417	0.68 ± 0.01	0.724450 ± 13
Augen gneiss	Bio + Hb	EV12C	123	857	0.42 ± 0.02	0.716119 ± 12
Augen gneiss	Bio + Hb	EV13E	100	467	0.61 ± 0.01	0.721942 ± 11
Augen gneiss	Bio	EV12F	100	688	0.42 ± 0.01	0.716226 ± 10
Augen gneiss	Bio	EV12E	119	544	0.63 ± 0.01	0.721890 ± 10
Augen gneiss	Bio	EV13B	94	233	1.16 ± 0.02	0.739604 ± 12
Augen gneiss	Bio	EV13C	125	170	2.13 ± 0.04	0.770845 ± 15
Augen gneiss	Bio	EV13D	123	135	2.63 ± 0.05	0.784864 ± 10
Granitic gneiss	Bio	EV7A	114	299	1.10 ± 0.02	0.737658 ± 09

Bio, biotite; Hb, hornblende. The NBS 987 standard gave $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710248 ± 0.000009 . m, measured.

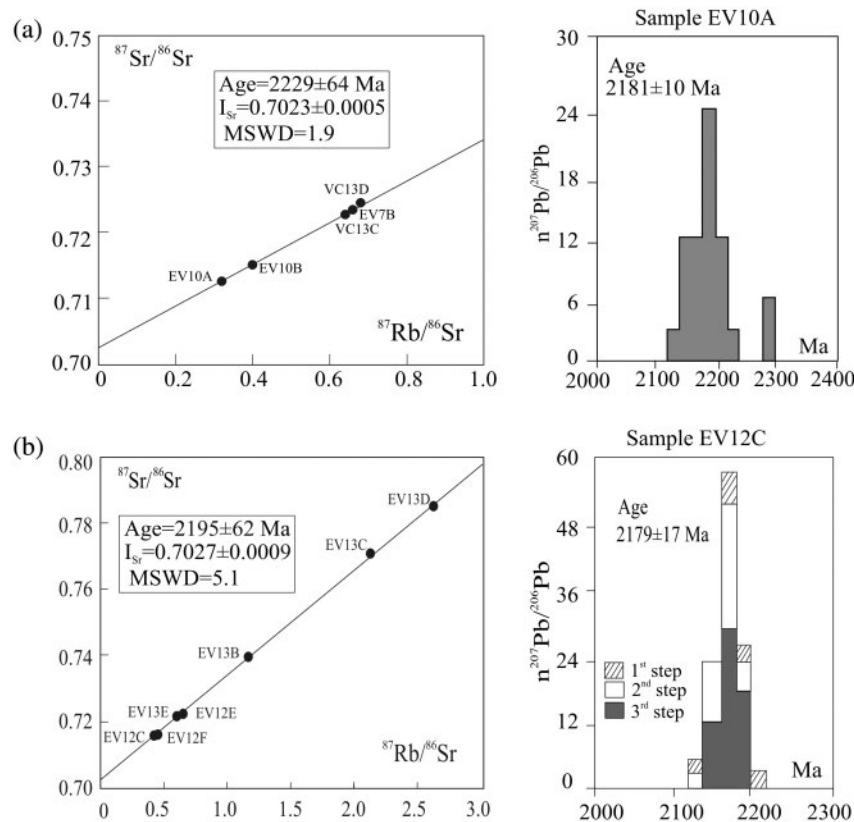


Fig. 4. Rb–Sr whole-rock isochron and single zircon $^{207}\text{Pb}/^{206}\text{Pb}$ age for tonalitic gneisses (a) and augen gneisses (b) of the Caicó Complex from the Rio Piranhas massif.

Table 4: Single zircon Pb isotopic data for samples EV10A and EV12C

Lithology	Sample	Current (A)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$ corrected	Error (2 σ)	$^{207}\text{Pb}/^{206}\text{Pb}$ age (Ma)	Error (2 σ)
Tonalitic gneiss	EV10A	2.6	20000	0.1363	0.0008	2181	10
Augen gneiss	EV12C	2.6	5806	0.1356	0.0002	2172	5
		2.8		0.1350	0.0005	2164	5
		3.2		0.1362	0.0030	2178	17

Seven samples of augen gneisses from Açú were analysed for the Rb–Sr whole-rock composition (Table 3). They define an isochron with an age of 2195 ± 62 Ma and I_{Sr} of 0.7027 ± 0.0009 , with $\text{MSWD} = 5.1$ (Fig. 4b). Three-step heating of single zircon from sample EV12C gives similar results (Table 4, Fig. 4b), with an average $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2179 ± 17 Ma, which is similar to the Rb–Sr age. The zircon grains are idiomorphic, usually concentrically zoned, colourless or light brown, with many apatite inclusions.

In the Santa Cruz region (Fig. 2), in the São José de Campestre massif, seven samples of the Caicó Complex were analysed for Sr and Nd isotopes (Table 5). For these samples, an Rb–Sr isochron yielded an age of 2144 ± 70 Ma, with I_{Sr} of 0.7025 ± 0.0005 and MSWD of 24 (Fig. 5a). The whole-rock Sm–Nd isochron with all points resulted in an extremely elevated error on age and MSWD (2253 ± 450 Ma and 189, respectively). The best fit is produced when samples ES56A, ES145 and ES196

Table 5: Rb–Sr and Sm–Nd isotopic data for meta-plutonic rocks of the Caicó Complex in the São José de Campestre massif

Lithology	Facies	Sample	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}^*$ ($\pm 2\%$)	$^{87}\text{Sr}/^{86}\text{Sr}_m$ ($\pm 0.002\%$)	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$ ($\pm 0.001\%$)	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 0.15\%$)	ε_{Nd} (2.2 Ga)	T_{DM} (Ga)
BIR	Dio + Hb	ES12	34.2	673.4	0.147 ± 0.003	0.706607 ± 11	4.33	22.55	0.11612 ± 17	0.511420 ± 07	−0.99	2.69
TON	Bio + Hb	ES56B	59.0	692.5	0.247 ± 0.005	0.710678 ± 11	5.70	34.33	0.10039 ± 15	0.511197 ± 10	−0.89	2.61
TON	Bio + Hb	ES105Z	39.7	767.7	0.150 ± 0.003	0.706673 ± 16	4.61	33.47	0.08328 ± 12	0.510938 ± 12	−1.10	2.57
TON	Bio + Hb	ES196	86.9	411.3	0.612 ± 0.012	0.721279 ± 13	6.61	40.11	0.09968 ± 15	0.511247 ± 07	0.29	2.53
TON	Bio	ES104A	37.9	684.6	0.160 ± 0.003	0.707349 ± 16	3.00	20.39	0.08906 ± 13	0.511034 ± 07	−0.86	2.57
AG	Bio + Hb	ES145	99.3	690.4	0.416 ± 0.008	0.715791 ± 12	8.86	51.22	0.10454 ± 16	0.511207 ± 07	−1.87	2.70
GR	Bio + Hb	ES56A	66.4	767.1	0.250 ± 0.005	0.709937 ± 17	5.76	32.60	0.10677 ± 16	0.511336 ± 08	0.02	2.57
GR	Bio + Hb	ES156	85.2	137.6	1.800 ± 0.036	0.757734 ± 10	12.32	87.50	0.08511 ± 13	0.510969 ± 06	−1.02	2.57

*Calculated values.

BIR, basic to intermediate rocks; TON, tonalitic gneiss; AG, augen gneiss; GR, granitic gneiss; Bio, biotite; Hb, hornblende; Dio, diopside. The NBS 987 standard gave $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710248 ± 0.000009 . Nd model ages (T_{DM}) were calculated relative to a depleted mantle with $^{147}\text{Sm}/^{144}\text{Nd} = 0.2137$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.5135$. $\varepsilon_{\text{Nd}}(2.2 \text{ Ga})$ represents the deviation of initial $^{143}\text{Nd}/^{144}\text{Nd}$ relative to CHUR and is equal to $(\text{measured } ^{143}\text{Nd}/^{144}\text{Nd} / 0.512638 - 1) \times 10\,000$ (DePaolo, 1988). m, measured.

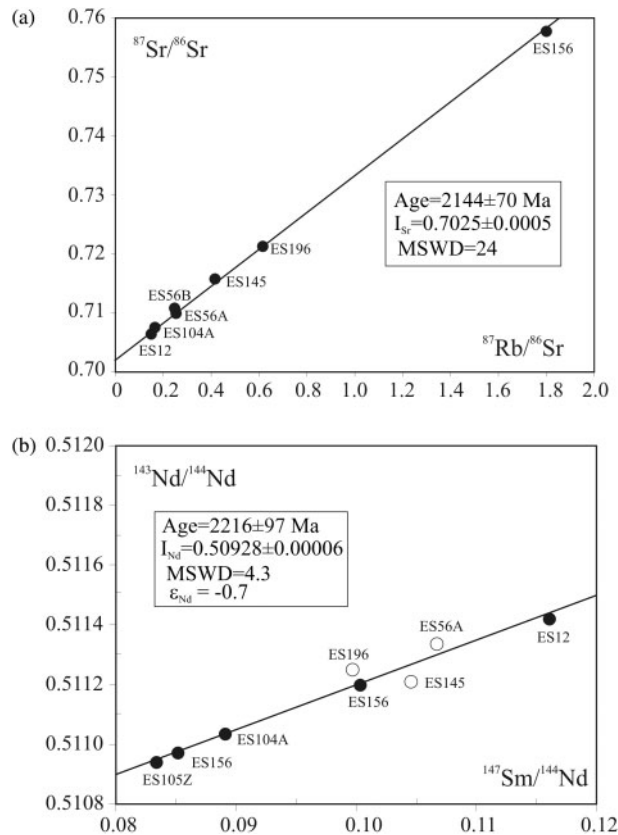


Fig. 5. Rb–Sr (a) and Sm–Nd (b) whole-rock isochrons of the Caicó Complex from the São José de Campestre massif. White circles represent samples not used for age calculation.

are discarded. In this case, the Sm–Nd whole-rock isochron gave an age of $2216 \pm 97 \text{ Ma}$, with I_{Nd} of 0.50928 ± 0.00006 , MSWD of 4.3 and ε_{Nd} of -0.7 (Fig. 5b). The T_{DM} ages vary from 2.69 to 2.53 Ga, and the $\varepsilon_{\text{Nd}}(t = 2.2 \text{ Ga})$ ranges from -1.87 to $+0.02$ (Table 5). Samples ES56A and ES145 have the highest titanite (2.2–3.1%) and apatite (1.0–1.2%) modal contents; sample ES196 has very low titanite (0.1%) and the highest zircon ($\sim 0.6\%$). The reason for dispersion of the samples on the Sm–Nd isochron could be the cumulative nature of titanite, apatite and zircon. Indeed, these minerals have high distribution coefficients (>5) for Sm and Nd (e.g. Rollinson, 1993); consequently, addition of small amounts of them into the magma would significantly modify the initial Sm/Nd ratio, resulting in an erroneous estimation of T_{DM} and ε_{Nd} . Another reason for the dispersion of samples ES56A, ES145 and ES196 could be a slight difference in age and/or source.

Within the range of analytical errors, the whole-rock Rb–Sr isochron and U/Pb ages, and I_{Sr} ratios of the orthogneisses studied are similar. This reveals a comparable isotopic history, with parental magmas possibly derived from a common source. This conclusion is in agreement with the presence of rounded and elliptical enclaves of diorite within tonalitic gneisses, as well as the rounded or interlobate contacts between tonalitic, granitic and augen gneisses. These features typically indicate the prevalence of low viscosity contrast between enclaves and host magma and lead to the conclusion that they were comagmatic at the time of intrusion. The ages are then

interpreted as emplacement ages at about 2.2 Ga for the plutonic protoliths of these orthogneisses.

PETROGENESIS

Sixty-nine samples were analysed: nine basic to intermediate rocks (BIR), 13 tonalites (TON), 16 granites (GR) and 31 augen gneisses (AG), as well as one basic dyke (now transformed into orthoamphibolite) and two meta-volcanic rocks (one meta-andesite and one meta-basalt). The complete whole-rock analysis dataset is given as an Electronic Appendix (which may be downloaded from <http://www.petrology.oxfordjournals.org>), and summarized in Table 6. They are displayed according to increasing SiO_2 content, the iron being expressed as $\text{Fe}_2\text{O}_3\text{t}$. Because of the low contents of water, all analyses were recalculated to a volatile-free basis, the loss on ignition being reported.

Geochemical characteristics

The main geochemical features of the rocks studied are presented in Fig. 6. In the A–F–M diagram (Fig. 6a), all groups plot within the calc-alkaline field defined by Kuno (1968), and scatter around the reference trondhjemitic trend delineated by Paleoproterozoic granitoids from SW Finland (Barker & Arth, 1976). The calc-alkaline affinity is also shown in the $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ vs SiO_2 diagram (Fig. 6b); there all samples plot in the upper part of the sub-alkaline field (Rickwood, 1989), which also corresponds to the calc-alkaline field (MacDonald & Katsura, 1964). However, four augen gneisses (samples EV12E, EV12F, CA8, ES145) are alkali-enriched, such that they plot in the alkaline field. The K–Na–Ca triangle (Fig. 6c) discriminates the behaviour of Na_2O and K_2O . In this diagram, all samples define a trend that evolves from Ca-rich magmas towards the K apex. This classical calc-alkaline evolution is in strong contrast to typical Archean TTG, which evolves towards the Na apex following a trondhjemitic trend (Martin, 1993, 1994). This conclusion is corroborated by the normative An–Ab–Or triangle, where the whole series evolve toward the orthoclase (Or) apex, whereas Archean TTG is Na-rich and generally plots in the trondhjemitic and tonalitic fields (Fig. 6d). In the same figure, most GR and AG samples overlap the field of late Archean calc-alkaline granites (Sylvester, 1994; Jayananda *et al.* 1995; Moyen *et al.*, 2003).

When all the meta-plutonic rocks of the Caicó Complex are plotted together in Harker diagrams for both major and trace elements (Fig. 7a and b), they show gentle differentiation trends, where most major (Al_2O_3 , $\text{Fe}_2\text{O}_3\text{t}$, MgO , CaO , TiO_2 , and P_2O_5) and trace (Sr, Co, V, and Ni) elements are negatively correlated with SiO_2 ; only K_2O and Rb, despite some scatter, are positively correlated with SiO_2 . Some elements

Table 6: Summary of the major (wt %) and trace element (ppm) compositions of the Caicó Complex rocks

	Basic to intermediate rocks				Tonalitic gneisses	
	Subset I		Subset II			
	Average (<i>n</i> = 5) ¹	SD	Average (<i>n</i> = 4) ²	SD	Average (<i>n</i> = 13) ³	SD
wt %						
SiO_2	56.52	5.28	58.77	1.54	66.42	3.28
TiO_2	0.79	0.17	0.84	0.13	0.56	0.16
Al_2O_3	18.0	0.56	15.65	1.46	16.03	0.64
$\text{Fe}_2\text{O}_3\text{t}$	8.11	2.58	7.74	2.04	4.71	1.26
MnO	0.12	0.04	0.13	0.04	0.06	0.03
MgO	3.52	0.95	4.52	1.09	1.71	0.78
CaO	6.65	1.46	6.12	1.01	4.01	0.94
Na_2O	3.71	0.21	3.38	0.53	4.04	0.53
K_2O	2.31	0.86	2.61	0.70	2.28	0.71
P_2O_5	0.26	0.05	0.26	0.02	0.18	0.06
Total	100.0	–	100.0	–	100.0	–
LOI	0.74	0.28	0.67	0.08	0.29	0.14
Mg-no.	47.0	3.0	54.0	4.0	40.0	6.0
ppm						
Ba	908.0	482.0	968.0	487.0	985.0	329.0
Co	28.0	9.0	30.0	8.0	14.0	5.0
Cr	130.0	34.0	237.0	51.0	137.0	87.0
Hf			4.0		4.5	1.3
Nb	9.0	2.0	11.0	2.0	9.0	2.0
Ni	22.0	9.0	63.0	34.0	19.0	17.0
Rb	75.0	25.0	89.0	4.0	70.0	28.0
Sc	13.0		18.0		9.0	4.0
Sr	692.0	22.0	539.0	137.0	520.0	161.0
Ta			0.9		0.7	0.3
Th			6.5		8.3	5.3
U			1.9		1.9	1.2
V	140.0	56.0	134.0	39.0	70.0	27.0
Y	26.0	11.0	23.0	7.0	19.0	10.0
Zr	133.0	16.0	147.0	22.0	182.0	85.0
La	19.8		40.17		41.12	14.75
Ce	43.8		75.73		78.67	20.90
Nd	20.7				29.13	7.4
Sm	4.17		6.80		4.9	1.3
Eu	1.31		1.91		1.27	0.28
Gd	3.41		5.33		3.48	1.22
Tb			0.77		0.50	0.24
Dy	2.68				2.57	1.15
Er	1.41				1.37	0.71
Yb	1.4		2.38		1.60	0.81
Lu	0.23		0.75		0.30	0.16

(continued)

Table 6: *Continued*

	Granitic gneisses		Augen gneisses		Meta-basalt	Meta-andesite
	Average	SD	Average	SD	EV9C	EV6E
	(<i>n</i> = 16) ⁴		(<i>n</i> = 31) ⁵		(<i>n</i> = 1)	(<i>n</i> = 1)
<i>wt %</i>						
SiO ₂	71.38	4.49	66.15	5.66	50.95	61.27
TiO ₂	0.28	0.15	0.56	0.26	1.01	1.22
Al ₂ O ₃	14.82	2.26	15.90	1.67	13.61	14.32
Fe ₂ O _{3t}	2.71	1.14	4.32	1.92	12.28	8.71
MnO	0.04	0.02	0.06	0.03	0.20	0.12
MgO	0.56	0.41	1.53	1.09	7.97	3.15
CaO	2.28	1.28	3.44	1.57	9.48	6.19
Na ₂ O	3.42	0.51	3.67	0.45	2.98	3.58
K ₂ O	4.45	0.93	4.16	1.25	1.22	1.28
P ₂ O ₅	0.07	0.05	0.20	0.10	0.30	0.16
Total	100.0	–	100.0	–	100.0	100.0
LOI	0.41	0.20	0.51	0.29	0.79	0.50
Mg-no.	28.0	10.0	38.0	8.0	56.0	42.0
<i>ppm</i>						
Ba	1153.0	437.0	1285.0	569.0	385.0	413.0
Co	4.0	3.0	12.0	7.0	43.0	30.0
Cr	84.0	83.0	92.0	64.0	406.0	196.0
Hf			9.5	0.6	2.0	3.4
Nb	9.0	3.0	13.0	8.0	7.0	8.0
Ni	6.0	3.0	13.0	9.0	104.0	55.0
Rb	125.0	51.0	118.0	33.0	38.0	48.0
Sc	8.0	3.0	12.0	4.0	28.0	14.0
Sr	339.0	193.0	470.0	179.0	446.0	344.0
Ta			1.4	0.7	0.3	0.5
Th			10.0	2.3	4.9	3.2
U			1.7	0.4	1.2	1.3
V	24.0	19.0	62.0	31.0	198.0	118.0
Y	20.0	13.0	24.0	11.0	24.0	53.0
Zr	220.0	97.0	216.0	106.0	79.0	112.0
La	73.76	41.76	90.2	35.46	45.16	20.61
Ce	145.24	89.27	160.2	44.15	81.93	44.07
Nd	49.75	27.92	40.01	7.35		
Sm	8.14	3.69	9.61	3.64	7.46	4.24
Eu	1.19	0.43	2.42	0.61	2.30	1.39
Gd	5.31	1.15	6.26	1.92	5.01	3.23
Tb			0.91	0.2	0.67	0.46
Dy	3.68	0.52	3.43	2.18		
Er	1.87	0.16	1.82	1.1		
Yb	1.89	0.16	2.23	0.81	1.83	1.7
Lu	0.28	0.04	0.41	0.2	0.48	0.42

The entire dataset is available as an Electronic Appendix, which may be downloaded from <http://www.petrology.oxfordjournals.org>. Mg-number = $100 \times \text{mol MgO} / (\text{MgO} + \text{FeO}^{2+})$. LOI, loss on ignition. ¹*n* = 1 for REE. ²*n* = 1 for REE, Sc, Ta, Th and U. ³*n* = 3 for Sc, Ta, Th and U, and *n* = 9 for REE. ⁴*n* = 3 for REE. ⁵*n* = 5 for REE, and *n* = 2 for Sc, Ta, Th and U.

(Na₂O, Zr and possibly Ba) define broken lines where positive correlation for SiO₂ < ~65% turns into negative correlation for SiO₂ > ~65%. Such broken lines are not consistent with mixing processes; these trends in the Harker diagrams cannot result from mixing between two magmas or from assimilation of older rocks by the magma, but are produced by magmatic differentiation (partial melting or fractional crystallization; Wilson, 1989). In this case, the break is due to changes in the fractionating mineral assemblage in the course of differentiation; for instance, a change from the fractionation of Al- and Na-poor phases (e.g. pyroxenes) towards Al- and Ca-rich phases (Ca-plagioclase, hornblende).

The basic to intermediate rocks (BIR) define two subsets with contrasting compositions. The subset I (VS1A, VS2A, VS1B, CA9, ES12) plots on the less differentiated portions of the general trend. The subset II (EV6D, VC52B, CA7, VC51D) deviates from the general trend by lower Al₂O₃, Na₂O and Sr contents and higher MgO, TiO₂, V, Co, and Cr contents; this deviation is not yet clearly understood.

As already pointed out in Fig. 6b, a group of augen gneisses clearly plot out of the general trend; they are characterized by higher contents of K₂O, TiO₂, P₂O₅, Nb and Ba and lower contents of MgO, CaO and Co. As their modal composition indicates that, compared with other augen gneisses, they are richer in alkali feldspar, titanite, apatite, and magnetite, it can be tentatively proposed that this enrichment results from the accumulation of minerals during magma differentiation. In this case these rocks would not represent pure magmatic liquids but rather magmatic liquid together with imperfectly extracted cumulate.

Figure 8a shows the REE patterns of diorites EV6D and ES12, as well as the associated meta-andesite EV6E and meta-basalt EV9C. All samples are light REE (LREE)-enriched (La_N = 62–143) with Yb_N of 8–14; this results in moderately fractionated patterns [(La/Yb)_N = 9–18] with no significant Eu anomaly (Eu/Eu* = 1.1–0.9). Because of their high LREE contents, BIRs are more fractionated than the average of Enriched Archean Tholeiite [EAT; (La/Yb)_N = 4.2; Condie, 1981].

Compared with the BIR, tonalitic gneisses are slightly LREE-richer (La_N = 71–199). However, because of generally lower Yb contents (Yb_N = 3.7–14), this results in more fractionated patterns [(La/Yb)_N = 7.5–40]. In addition, tonalitic gneisses systematically display a slightly negative Eu anomaly (Eu/Eu* = 0.9) and a concave-shaped HREE end.

Granitic gneisses are LREE-rich (La_N = 116–380), with moderately high HREE (Yb_N = 8.2–9.6), with a systematic important negative Eu anomaly (Eu/Eu* = 0.4). These REE patterns are intermediate between those of Late Archean and modern juvenile granites (Fig. 8c).

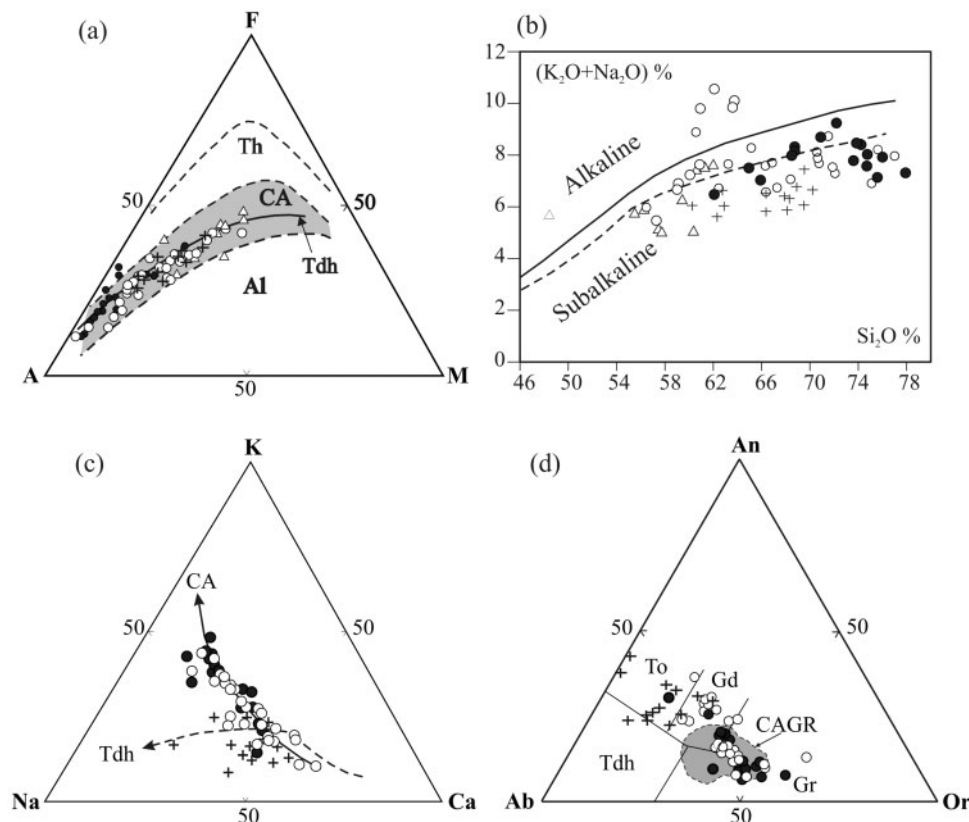


Fig. 6. Geochemical characteristics of the Caicó Complex orthogneisses. (a) A–F–M (where A = $K_2O + Na_2O$, F = $0.9 Fe_2O_3t$, M = MgO) diagram, with the alkaline (Al), calc-alkaline (CA) and tholeiite (Th) fields after Kuno (1968) and the trondhjemitic trend (Tdh) from Barker & Arth (1976). (b) $(K_2O + Na_2O)$ vs SiO_2 diagram (Rickwood, 1989), showing the subalkaline character of the Caicó Complex. The lower dotted line is from Kuno (1966) and the upper limit from Irvine & Baragar (1971). (c) Cationic Ca–Na–K diagram showing that the Caicó Complex rocks follow a classical calc-alkaline differentiation trend (CA; Nockolds & Allen, 1953) and have no affinity with the trondhjemitic (Tdh) trend (Barker & Arth, 1976). (d) Normative An–Ab–Or triangle (O'Connor, 1965) with fields of trondhjemitites (Tdh), tonalites (To), granodiorites (Gd) and granites (Gr) from Barker (1979) and calc-alkaline Archean granites (CAGR) from Sylvester (1994). Other symbols are as in Fig. 3.

Among augen gneisses, four samples (EV12C, EV12F, EV13E, ES145) have both high LREE contents ($La_N = 168\text{--}464$) and high HREE contents ($Yb_N = 9.1\text{--}14.4$); consequently, the general shape of the REE patterns is similar to that of granitic gneisses, but with a systematic negative Eu anomaly. One sample (EV13B) differs by its low Yb content ($Yb_N = 4.7$), resulting in $(La/Yb)_N = 46.7$, similar to the average Late Archean calc-alkaline granites (Fig. 8d).

The REE overall patterns of the Caicó gneisses are intermediate between those of average Archean TTG and modern calc-alkaline granitoids (Martin, 1994); their average composition is very similar to that of late Archean granites (Fig. 8b; Sylvester, 1994). Sample ES104A has very low HREE contents ($Yb_N = 1.1$), which are lower than those of average TTG but are similar to those of HREE-depleted TTG (Martin, 1987). This could indicate the contribution of an older Archean crustal component in its genesis.

Mechanism of differentiation

Procedures

All the meta-plutonic rocks of the Caicó Complex have several similarities; the same geographical occurrence, similar ages of emplacement, analogous petrographic, geochemical and isotopic compositions, and, more particularly, the same Nd model ages. Consequently, they can be assumed to be contemporaneous and cogenetic; therefore, the main trend defined in Harker plots will be considered as being due to differentiation from a generally similar source protolith. As discussed above (Fig. 7a and b), some elements such as Na_2O , Zr and possibly Ba define broken or curved trends, a characteristic that allows us to discard their derivation by mixing–mingling mechanisms, and instead indicates that they result from magmatic differentiation (partial melting or fractional crystallization), with a change of composition of the solid cumulate or residue with time.

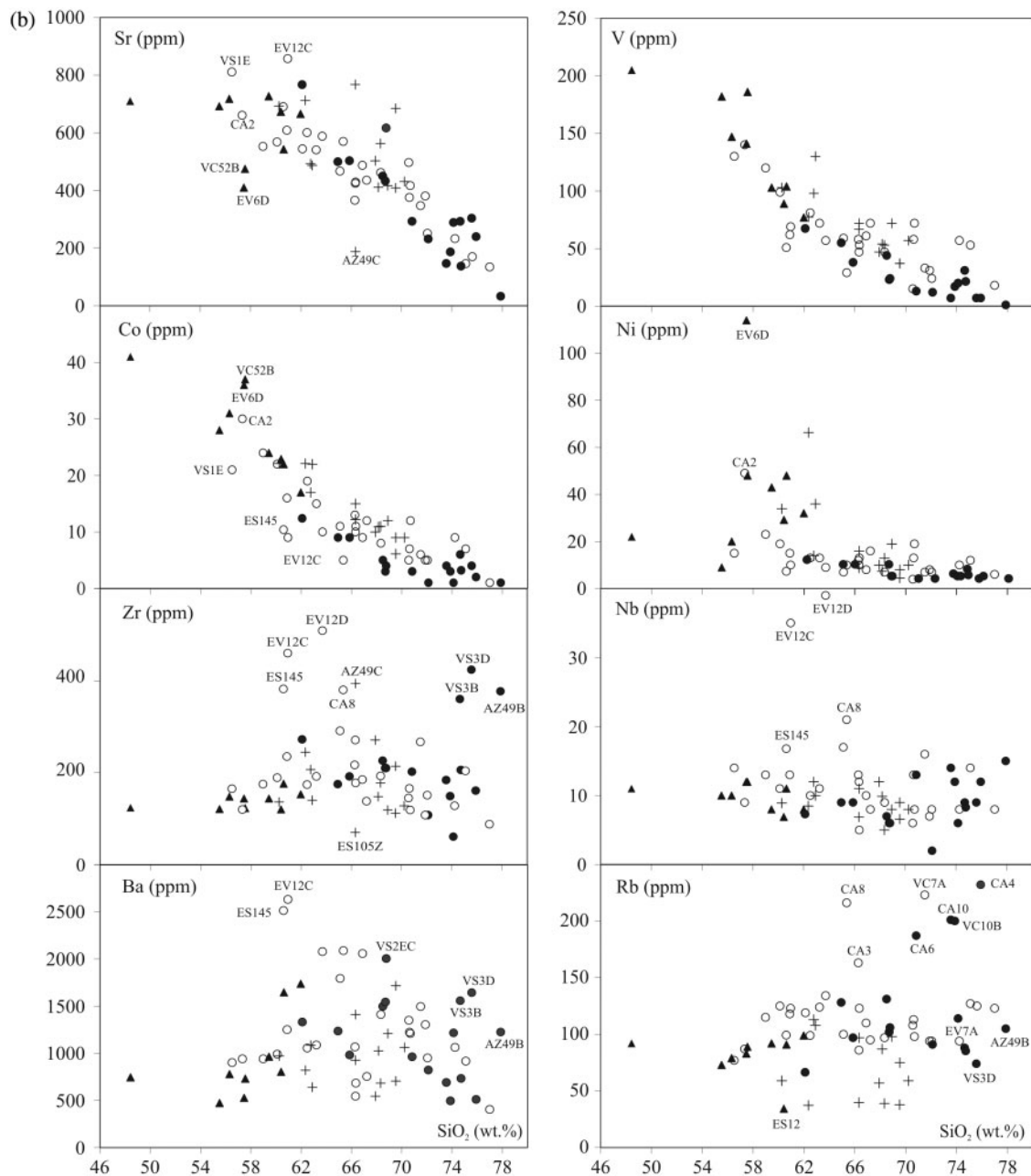


Fig. 7. Continued

modelling was computed assuming the differentiation of a parental magma (C_O) into a differentiated liquid (C_L). The accuracy of the adjustment of the theoretical model to the data is expressed by $\sum r^2 [= \sum (m_i - c_i)^2]$, where m_i is the measured concentration and c_i is the calculated concentration of oxide i . The mineral compositions used in the calculations were those analysed in this study (biotite, amphibole, plagioclase, K-feldspar); the other phase compositions were taken from Deer *et al.* (1983).

The second step consisted of reintroducing the computed modal compositions (X_i) of the cumulate and the degree of crystallization in trace element modelling. The equation chosen for fractional crystallization is that of Rayleigh (1896): $C_L = C_O F^{(D-1)}$, where C_L is the concentration of a trace element in the differentiated liquid, C_O is the concentration of a trace element in the parental magma, $F = (1 - FC)$ (FC is the degree of crystallization, with $0 < FC < 1$) and D is the bulk distribution coefficient.

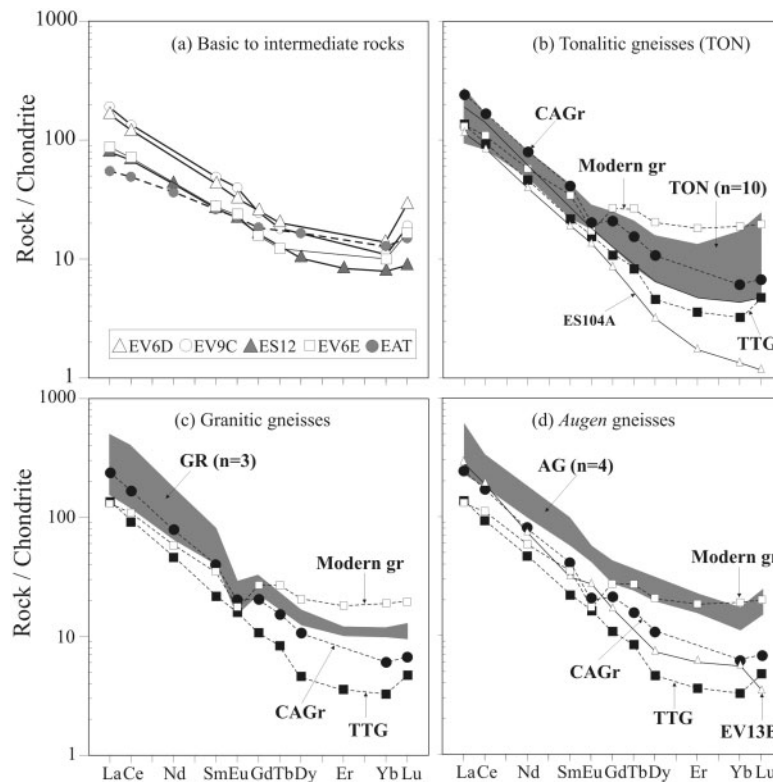


Fig. 8. Chondrite-normalized (Sun & McDonough, 1989) rare earth element patterns. (a) Diorites EV6D and ES12, together with one metabasalt (EV9C) and one meta-andesite (EV6E). (b) Tonalitic gneisses. (c) Granitic gneisses. (d) Augen gneisses. For comparison, we also plotted an Enriched Archean Tholeiite (EAT; Condie, 1981) in (a) and modern juvenile granitoids (Modern gr; Martin, 1994), average Archean trondhjemite-tonalite-granodiorite (TTG; Martin, 1994) and late Archean calc-alkaline granite (CAGr; Sylvester, 1994) in (b)–(d).

The partition coefficients (Kd_i) used for D calculation [$D = \sum (X_i \cdot Kd_i)$], were those compiled by Martin (1985, 1987), Rollinson (1993) and Nielsen (2007).

Quantification of fractional crystallization

Table 7 shows the results for both major and trace element modelling. To model the behaviour of the subset II of basic to intermediate rock (BIR), sample VC52B was chosen as C_O and VC51D as C_L , whereas for subset I C_O and C_L were VS1A and CA9, respectively. The best fit of computed model to analytical data is obtained for the crystallization of a mineral assemblage of hornblende and clinopyroxene for BIR subset I, and of hornblende, plagioclase and magnetite for BIR subset II; the degree of fractional crystallization (FC) is 80% and 30%, respectively. In BIR subset II the behaviour of trace elements and especially of Zr is accounted for only when small amounts (0.015%) of zircon are added to the cumulate.

Tonalitic gneiss crystallization was modelled assuming C_O = ES56B and C_L = EV10B (Table 7). The best statistical result ($\sum r^2 = 0.6$) was obtained for 45% fractional crystallization of a cumulate composed of hornblende, plagioclase (An_{40}), magnetite, and traces of zircon. A good agreement

between model and analytical data is observed for all other trace elements, except Ba and Cr. The addition of 0.025% zircon to the cumulate is needed to account for Zr behaviour.

In Fig. 7a and b, augen gneisses display broken or curved trends for Na_2O , Zr and Ba; this indicates that the composition of the cumulate changed over the course of differentiation, and consequently the evolution of augen gneisses has been divided into two stages: stage (1) considers differentiation from SiO_2 57% to 67%; in this case C_O = VS1E and C_L = CA3; stage (2) models liquid behaviour from SiO_2 67% to 77%; from C_O = CA3 to C_L = EV13D. The results of modelling are given in Table 7. For both stages the computed cumulate is made up of the same major minerals (hornblende + plagioclase + magnetite). These cumulates differ only in their relative modal proportions, with more hornblende and less plagioclase in stage (1); the degree of fractional crystallization is also different: FC = 55% for stage (1) and 40% for stage (2). In stage (2), less than 0.4% of apatite and 0.07% of zircon are required to account for the behaviour of P_2O_5 and Zr, respectively. In both cases, the calculated liquid compositions fit the analytical data, except for Cr and Rb in stage (2).

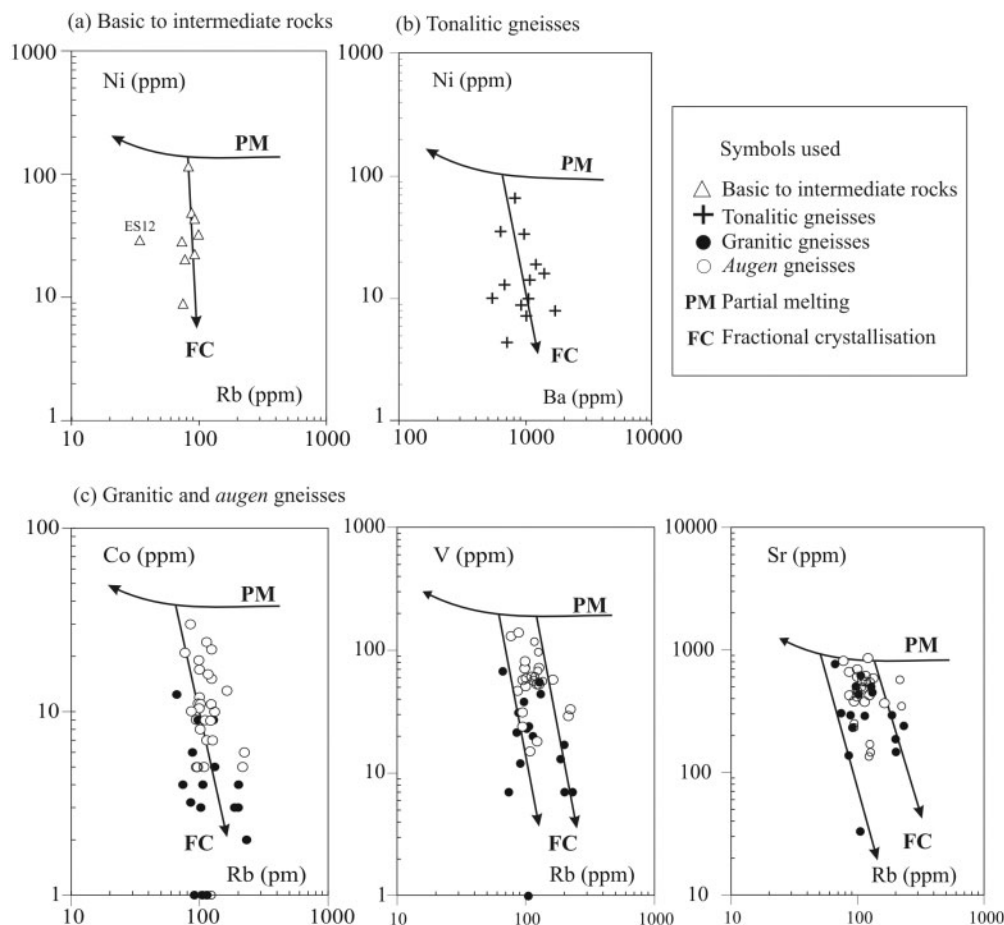


Fig. 9. Compatible (Ni, Co, V, Sr) vs incompatible (Rb, Ba) behaviour of some elements of basic to intermediate rocks (a), tonalitic gneisses (b) and augen and granitic gneisses (c). Bi-log diagrams indicate an evolution by fractional crystallization (FC), rather than by partial melting (PM).

The granitic gneisses have the same behaviour as the augen gneisses but as they do not have SiO_2 contents as low as those of the less differentiated augen gneisses, the broken or curved trends are not so well marked. Their behaviour resembles the second stage of crystallization of augen gneisses. Samples ES56A and CA4 were chosen as representative of C_O and C_L . The modelling (Table 7) shows that granitic gneisses evolved by extraction of a cumulate similar to that of both tonalitic gneisses and augen gneisses (hornblende + plagioclase + magnetite) but with less hornblende and more plagioclase and magnetite. Here too, fractionation of 0.04% zircon is needed to account for Zr behaviour. All the calculated element concentrations fit the analytical data well, except Rb.

Role of assimilation and fractional crystallization (AFC)

Figure 10a (Rb/Sr vs Sr) and 10 (Sr/Y vs Y) shows the results of fractional crystallization modelling for the subgroups presented above. When some granitic and augen gneisses are excluded the analysed rocks perfectly fall on

the computed fractional crystallization curves, which corroborates the results discussed above and presented in Table 7. However, many granitic and augen gneisses with $\text{SiO}_2 > 72\%$ deviate from the calculated trends (Fig. 10a) which indicates that other processes took place in addition to 'pure' fractional crystallization. Indeed, some of these rocks have slightly negative $\epsilon_{\text{Nd}}(t = 2.2 \text{ Ga})$ values that could reflect some kind of contamination of the parental magma with older crustal components. Indeed, Hildreth & Moorbath (1988) considered that melting of host rock, assimilation, storage, and homogenization (MASH) are expected in the lower crust or at the mantle–crust transition beneath a large magmatic centre. In this region, the basic magmas that ascent from the mantle wedge become neutrally buoyant, induce local partial melting of surrounding rocks, assimilate and mix extensively, and either crystallize completely or fractionate to the degree necessary to re-establish buoyant ascent, and then constitute starting points for subsequent fractionation and contamination. Crustal assimilation and concurrent fractional

Table 7: Major (wt %) and trace element (ppm) modelling of the Caicó Complex orthogneisses

Sample:	Basic to intermediate rocks (BIR)						Tonalitic gneiss (TON)			Granitic gneiss (GR)		
	Subset I			Subset II								
	$\Sigma r^2 = 2.9$			$\Sigma r^2 = 2.5$			$\Sigma r^2 = 0.6$			$\Sigma r^2 = 1.3$		
	C_O	C_L	$C_{L'}$	C_O	C_L	$C_{L'}$	C_O	C_L	$C_{L'}$	C_O	C_L	$C_{L'}$
	VS1A	CA9	$FC=80$	VC52B	VC51D	$FC=30$	ES56B	EV10B	$FC=45$	ES56A	CA4	$FC=60$
SiO ₂	48.52	62.03	61.62	57.65	60.68	61.70	60.33	70.25	70.16	62.15	75.92	76.07
TiO ₂	1.01	0.56	-0.29	0.85	0.77	0.60	0.76	0.39	0.22	0.69	0.12	-0.44
Al ₂ O ₃	18.94	17.40	17.77	14.06	17.17	16.48	16.97	14.92	15.04	18.52	13.22	13.79
Fe ₂ O _{3t}	11.70	4.82	4.80	9.44	5.92	6.78	6.77	3.54	3.52	5.61	1.05	1.52
MgO	5.08	2.52	2.79	5.67	3.08	2.79	2.92	0.99	1.05	1.59	0.36	0.37
CaO	8.70	4.80	4.25	6.97	4.68	4.87	5.93	3.14	2.89	4.70	1.39	1.13
Na ₂ O	3.46	3.85	3.85	2.74	4.03	3.36	3.87	4.38	4.03	4.38	2.82	2.29
K ₂ O	2.26	3.79	4.83	2.34	3.40	3.12	2.18	2.28	2.85	2.12	5.10	5.07
P ₂ O ₅	0.33	0.23	0.39	0.28	0.27	0.29	0.27	0.11	0.25	0.24	0.02	0.21
Ba	746	1737	1058	732	1647	1015	972	1062	1503	1332	510	335
Co	41	17	16	37	22	26	22	9	16	12	2	2
Cr	115	98	111	297	230	251	29	174	29	193	13	24
Nb	11	8	6	12	11	12	9	8	11	7	12	13
Ni	22	32	3	48	48	14	34	10	17	12	5	3
Rb	92	99	178	89	91	111	59	59	75	66	232	160
Sr	710	666	671	475	543	576	693	431	371	767	240	192
V	205	77	14	186	104	74	103	57	36	67	7	13
Y	39	16	21	26	18	21	19	14	16	20	18	13
Zr	124	153	144	123	176	151	137	128	122	272	161	153
Cumulate (%)												
Hornblende			81.4			51.10			51.10			22.50
Clinopyroxene			18.6									
Plagioclase				An ₅₀		42.50		An ₄₀	46.20		An ₃₀	71.70
Magnetite						6.30			2.60			5.70
Zircon						0.02			0.03			0.04
Apatite												

(continued)

crystallization (AFC) is now widely considered as an important mechanism of evolution of mantle-derived magmas interacting with the lower and upper crust (DePaolo, 1981; Huppert & Sparks, 1985; Wilson, 1989; Stern & Kilian, 1996; Moyen *et al.*, 1997, 2001). Below, we describe the modelling of AFC for the Caicó orthogneisses.

Mixing equations for trace elements and isotopic ratios were originally presented by Langmuir *et al.* (1978) and subsequently by DePaolo & Wasserburg (1979) and DePaolo (1981), with reviews by Faure (1986) and Wilson (1989). For any trace element $C_L = C_L^\circ f + [r/(r-1+D)]C^*[1-f]$, where C_L° is the concentration of the trace element in the original magma, C_L is the concentration of the trace element in the contaminated magma,

C^* is the concentration of the trace element in the contaminant, r is the ratio of the rate of assimilation to the rate of fractional crystallization, D is the bulk distribution coefficient for the fractionating assemblage, $f = F^{-(r-1+D)/(r-1)}$, and F is the fraction of magma remaining. For any radiogenic isotope $\varepsilon_L = \varepsilon_L^\circ + (\varepsilon^* - \varepsilon_L^\circ)[1 - (C_L^\circ/C_L)f]$, where ε_L , ε_L° and ε^* are isotopic ratios whose subscripts are defined above. AFC has been modelled using the same C_L° as for perfect fractional crystallization calculations (BIR subset I: $C_L^\circ = \text{VS1A}$; BIR subset II: $C_L^\circ = \text{VC52B}$; TON: $C_L^\circ = \text{ES56B}$; GR: $C_L^\circ = \text{ES56A}$; AG (1): $C_L^\circ = \text{VS1E}$; AG (2): $C_L^\circ = \text{CA3}$; Table 7). The lower continental crust has been assumed to be the potential contaminant, the composition proposed by

Table 7: Continued

	Augen gneiss (AG)					
	First stage			Second stage		
	C_O	C_L	$C_{L'}$	C_O	C_L	$C_{L'}$
Sample:	VS1E	CA3	FC = 55	CA3	EV13D	FC = 40
SiO ₂	56.59	66.34	66.48	66.34	77.01	76.75
TiO ₂	0.74	0.49	0.07	0.49	0.15	-0.09
Al ₂ O ₃	18.09	15.78	15.91	15.78	12.41	12.60
Fe ₂ O _{3t}	8.00	4.13	4.47	4.13	1.19	1.06
MgO	3.40	1.77	1.74	1.77	0.17	0.36
CaO	6.94	3.76	3.63	3.76	1.08	0.64
Na ₂ O	3.94	3.29	3.44	3.29	3.04	2.71
K ₂ O	2.05	4.30	4.01	4.30	4.92	5.86
P ₂ O ₅	0.25	0.14	0.25	0.14	0.03	0.11
Ba	901	1068	1015	1068	405	601
Co	21	13	13	13	1	3
Cr	47	57	9	57	159	60
Nb	14	13	12	13	8	13
Ni	15	12	7	12	6	2
Rb	77	163	168	163	123	192
Sr	811	366	383	366	135	162
V	130	58	37	58	18	12
Y	33	29	29	29	5	14
Zr	165	217	228	217	88	85
Cumulate (%)						
Hornblende			46.47			37.50
Clinopyroxene						
Plagioclase		An ₄₀	50.18		An ₄₀	58.60
Magnetite			3.27			3.80
Zircon			0.01			0.07
Apatite			0.07			

C_O and C_L , less evolved and more evolved samples, respectively; $C_{L'}$, calculated liquid composition after extraction of cumulate; $\sum r^2$, statistical error (accuracy of the adjustment of the theoretical model), FC , per cent of fractional crystallization.

Rudnick & Fountain (1995) was taken for trace elements and that of Faure (1986) for Sr and Nd isotopic ratios, whereas the partition coefficients used for D calculation are those compiled by Martin (1987), Rollinson (1993) and Nielsen (2007). The computed models (Fig. 10) clearly indicate that some of the silica-rich granitic and augen gneisses compositions can be accounted for by assimilation of lower continental crust concomitant with fractional crystallization of mainly hornblende + plagioclase. This is well exemplified in the Rb/Sr vs Sr plot (Fig. 10a) where about 10 granitic and augen gneisses samples plot above the curves

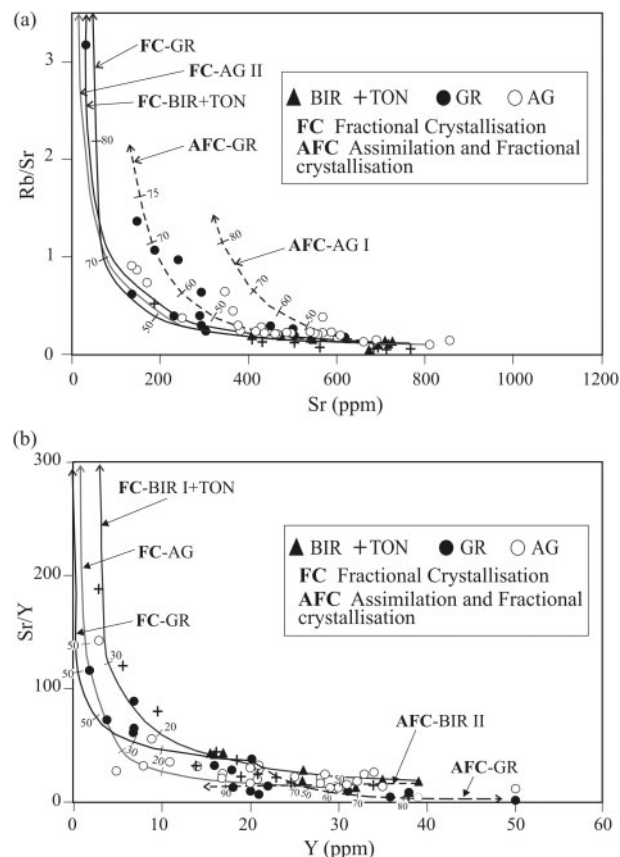


Fig. 10. Plots of Rb/Sr vs Sr (a) and Sr/Y vs Y (b) for the Caicó Complex orthogneisses. Continuous and dashed curves show pure fractional crystallization (FC) and assimilation and concurrent fractional crystallization (AFC). The cumulate compositions for each group are those computed in Table 7. Curve for AFC was calculated following DePaolo (1981) with a mass-assimilation/fractionation ratio (r) = 0.1, with fractionated phases after Table 7. Labelled tick marks indicate per cent FC.

of 'pure' fractional crystallization. The effect of continental crust assimilation results in an efficient increase of the Rb/Sr ratio of magma, which accounts for the 'deviant' behaviour.

Source

Possible sources

Didier *et al.* (1982) proposed a classification of granitoids based on their source: M granitoids originate from a mantle source whereas C granitoids are continental crust derived. Following the earlier S- and I-type classification of Chappell & White (1974), Didier *et al.* subdivided the C-type into CI (crustal igneous source) and CS (crustal sedimentary source). In fact, as reviewed by Pearce (1996), the source of granitoids is a combination between two extreme end-members: the mantle and the continental crust. The mantle may be either asthenospheric or

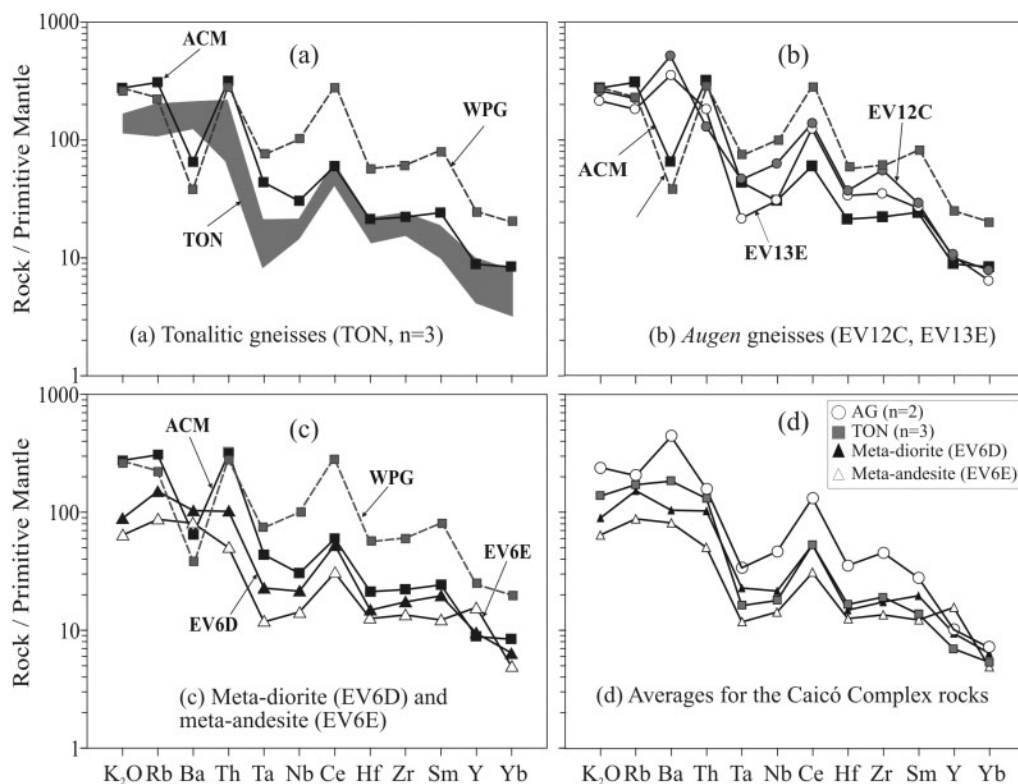


Fig. 11. Primitive mantle (Taylor & McLennan, 1985) normalized multi-elemental ratios for magmatic rocks of the Caicó Complex. (a) Tonalitic gneisses (samples EV7B, EV10B and VCI3C). (b) Augen gneisses EV12C and EV13E. (c) Diorite EV6D and meta-andesite EV6E. (d) Comparison between all samples of the Caicó Complex. In (a), (b) and (c) the average of Andean continental margin magmas (ACM) and within-plate granites (WPG) from Pearce *et al.* (1984) are also represented.

lithospheric, whereas the continental crustal sources may consist of igneous or sedimentary protoliths. In addition, for each source, the degree, temperature and depth of partial melting, as well as diverse kinds of interaction between mantle and crust, are highly variable, thus accounting for the great chemical variability of most granitoid magmas.

The mineralogical and chemical compositions of the Caicó Complex orthogneisses show that they all belong to the M-type granitoids: (1) their composition varies gradually from basic (gabbro or diorite, quartz diorite) to acidic facies (leucotonalites, granites); (2) hornblende is common, with sometimes relicts of clinopyroxene; (3) muscovite and aluminous silicates (cordierite, garnet, sillimanite) are totally absent; (4) microgranular mafic (hornblende-rich) enclaves are abundant; (5) normative corundum is <1.1%; (6) they mostly are metaluminous, with Shand's A/NCK ratios <1.1 and A/NK ratios >1.2; (7) they contain normative diopside or <1% of normative corundum; (8) they have low, mantle-like initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7022–0.7027).

The geochemical characteristics outlined above are consistent with island arc and continental arc granitoid magmas (Maniar & Piccoli, 1989); they are similar to

those of the classical calc-alkaline basalt–andesite–dacite–rhyolite (BADR) suites. In a multi-element diagram (Fig. 11a and b), it appears that although the compositions of tonalitic and augen gneisses show roughly parallel patterns, they are poorer in almost all elements when compared with the average Andean continental margin granitoids of Pearce *et al.* (1984). The dioritic gneiss EV6D and a meta-andesite EV6E also have patterns parallel to the Andean continental margin (ACM) granitoids although they are slightly LILE-poorer than the other gneisses (Fig. 11c). The Caicó gneisses are very distinct with respect to the average of within-plate granites, which are richer in all elements from Th to Yb (Fig. 11a–c). When plotted together, the Caicó Complex rocks show strong similarities, with parallel patterns (Fig. 11d), the dioritic gneiss and the meta-andesite being the LILE-poorer and the augen gneisses the LILE-richer.

In conclusion, and by analogy with Andean continental margin granitoids, a subduction-related tectonic setting could be proposed for the Caicó Complex meta-plutonic rocks. These orthogneisses are regarded as synorogenic intrusions and a magmatic arc setting is proposed for their generation and emplacement. Both experimental

and theoretical arguments have led to consideration of the genesis of juvenile calc-alkaline magmas in modern subduction zones as a function of heat distribution between the subducted oceanic lithosphere and the overlying mantle wedge (Wyllie, 1979, 1983; Martin, 1986, 1993, 1994, 1999; Peacock, 1990, 1993; Maury *et al.*, 1996). The place where calc-alkaline magmas are generated is controlled by the interplay between dehydration and partial melting processes in the subducted slab, which in turn depends on its age and on the geothermal gradients. High geothermal gradients along Benioff planes (assumed to be the common Archean situation) would favour the partial melting of the subducted lithosphere at comparatively shallower depths (Stern & Futa, 1982; Martin, 1986, 1999; Defant & Drummond, 1990; Drummond & Defant, 1990; Rapp *et al.*, 1991, 1999; Peacock *et al.*, 1994; Morris, 1995; Maury *et al.*, 1996; Prouteau *et al.*, 1996; Stern & Kilian, 1996; Sigmarsson *et al.*, 1998; Bourdon *et al.*, 2002; Samaniego *et al.*, 2002; Martin *et al.*, 2005; Samsonov *et al.*, 2005); whereas low geothermal gradients (as today) favour the partial melting of the mantle wedge metasomatized by fluids released by the dehydration of the subducted lithosphere (Wyllie & Sekine, 1982; Tatsumi, 1989; Schmidt & Poli, 1998; Bureau & Keppler, 1999; Manning, 2004; Schmidt *et al.*, 2004; Bindeman *et al.*, 2005; Kessel *et al.*, 2005). To try to account for the mineralogy and geochemistry of the Caicó Complex orthogneisses, these two possible sources (oceanic crust basalt and mantle lherzolite) will be discussed.

Basalt (oceanic crust) melting

In the last 30 years, many basalt and amphibolite melting experiments have been performed (Helz, 1976; Beard & Lofgren, 1989, 1991; Rapp *et al.*, 1991, 1995, 2003; Rushmer, 1991; Winther & Newton, 1991; Sen & Dunn, 1994a, 1994b; Wolf & Wyllie, 1994; Patiño Douce & Beard, 1995; Rapp & Watson, 1995; Zamora, 2000). Partial melting of low-K tholeiite under both water-saturated and water-undersaturated (dehydration melting) conditions leaves a residue made up of amphibole $\pm$ plagioclase $\pm$ pyroxenes $\pm$ magnetite $\pm$ ilmenite for pressures lower than 8 kbar, with garnet appearing at pressures greater than 10 kbar, and amphibole disappearing above 16 kbar (Beard & Lofgren, 1991; Rapp *et al.*, 1991; Peacock *et al.*, 1994; Sen & Dunn, 1994a; Rapp & Watson, 1995). In all these experiments, 825–1000°C is the common temperature range for 10–60% partial melting. The liquids formed are peraluminous (corundum >1.3 , $1 < A/CNK < 1.3$) and vary from diorite to tonalite–trondhjemite and granodiorite. Dacitic or rhyolitic liquids coexist with amphibole, clinopyroxene, plagioclase and magnetite in the temperature range of 800–900°C, whereas andesitic to dacitic liquids coexist with amphibole, clinopyroxene and magnetite up to the thermal stability limit of amphibole at 1000–1050°C (Rapp *et al.*, 1991; Rapp & Watson, 1995).

The hypothesis of genesis of the parental magma of the Caicó Complex orthogneisses by partial melting of tholeiites has been tested. The approach is the same as for crystallization modelling: first major element behaviour has been modelled using mass-balance equations and the Störmer & Nicholls (1978) algorithm, whereas the equilibrium melting equation $C_L = C_O/[D + F(1 - D)]$ of Shaw (1970) has been used for trace elements. As shown above, the trends in Harker diagrams result from the differentiation of a parental magma by fractional crystallization and AFC processes. Consequently, the melting modelling will not attempt to account for differentiation trends but only for the composition of the less differentiated parental magmas (i.e. with <63 wt % SiO_2). The melting of two different sources has been computed: (1) a low-K EAT ($\text{SiO}_2 = 50.2$ wt %, Mg-number = 53, $\text{K}_2\text{O}/\text{Na}_2\text{O} = 0.2$, $\text{La}_N = 55$, $\text{Yb}_N = 13$, reported by Condie, 1981); (2) the enriched tholeiite sample EV9C ($\text{SiO}_2 = 51.0$ wt %, Mg-number = 56, $\text{K}_2\text{O}/\text{Na}_2\text{O} = 0.4$, $\text{La}_N = 191$, $\text{Yb}_N = 11$). The modelling leads to residues composed of hornblende $\pm$ clinopyroxene $\pm$ garnet $\pm$ magnetite and to degrees of partial melting ranging from 40 to 55%. However, augen gneiss sample VSIE requires a higher degree of partial melting ($\sim 65\%$) and a different residue (clinopyroxene + orthopyroxene + magnetite). Because, in andesitic to dacitic liquids, $Kd_{\text{Yb}}^{\text{Hbl/liq}} > 1$ and $Kd_{\text{Yb}}^{\text{Grt/liq}} \gg 1$, the magma must be impoverished in Y and Yb with respect to the solid source, which also results in too high $(\text{La}/\text{Yb})_N$ and Sr/Y in magma. All the computed models, with or without residual garnet, predict Yb and Y impoverishment in magma whereas Yb and Y enrichment is required for the Caicó Complex orthogneisses (Figs 12a and b), and consequently, unlike Archean TTGs and modern adakites, melting of a hydrous tholeiite does not appear to be a realistic source for the Caicó Complex magmas. In addition, the high Yb and Y contents preclude garnet as a significant residual phase. It must also be noted that the less evolved Caicó Complex samples may not be exactly the parental magmas but that they could also have undergone small degrees of fractional crystallization. As shown above (Fig. 10), the crystallization of an assemblage made up of hornblende and plagioclase would result in a decrease of the Y and Yb content in the magma. Consequently, the parental magmas were probably Y- and Yb-richer than the less evolved samples of the Caicó Complex, thus making even more unrealistic their origin by melting of a basalt tholeiitic source.

Lherzolite (mantle) melting

Earlier experimental melting of lherzolite generated liquids that varied in composition from basalt to dacite. Some researchers considered that silicic liquids would be primary magmas (Kushiro *et al.*, 1972; Kushiro, 1974; Mysen & Boettcher, 1975; Tatsumi, 1981), whereas others (Nicholls & Ringwood, 1972; Green, 1973) believed that

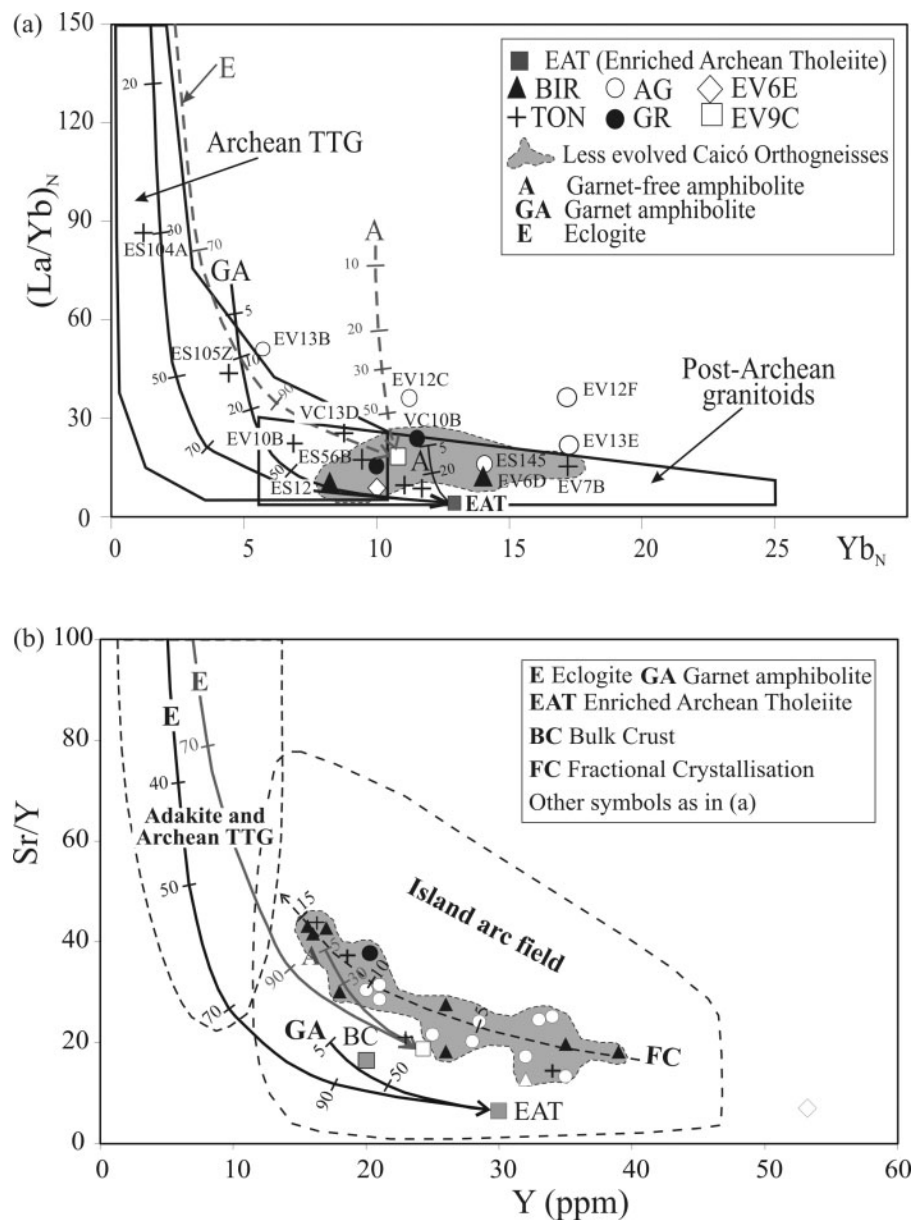


Fig. 12. (a) Plot of $(La/Yb)_N$ vs Yb_N normalized to chondritic values (Sun & McDonough, 1989) considering a tholeiite crust the source of the parental magmas of the Caicó Complex. Archean TTG (trondhjemite-tonalite-granodiorite) and post-Archean granitoid fields are from Martin (1986). Partial melting (PM) curves were calculated using the batch melting equation of Shaw (1970) and the partition coefficients compiled by Martin (1987), Rollinson (1993) and Nielsen (2007). (b) Plot of Sr/Y vs Y for the same datasets and model curves. The adakite, Archean TTG and island arc fields are from Defant *et al.* (1991); the fractional crystallization curve is the same as in Fig. 10b. For (a) and (b), the residues of melting are garnet-free amphibolite (A), garnet (10%) amphibolite (GA) and eclogite (E). Labelled tick marks indicate per cent PM of A, GA and E model curves in (a) and (b), and FC in (b).

andesitic and dacitic magmas could not be produced by direct melting of mantle peridotite, the most likely explanation being that they formed from a parental basic magma that evolved by fractional crystallization of olivine at depth. Experimental silicic liquids were generated under hydrous conditions for 1025–1150°C and 10–26 kbar with about 20–30% partial melting (Kushiro *et al.*, 1972; Nicholls & Ringwood, 1972; Green, 1973; Kushiro, 1974;

Mysen & Boettcher, 1975) or under water-undersaturated conditions for a similar P – T range (Tatsumi, 1982).

In the last 15 years, improvement in experimental techniques has allowed researchers to circumvent quenching problems and analyse liquids formed by small-degree (<5%) of melting (Baker & Stolper, 1994; Baker *et al.*, 1995; Hirose, 1997; Robinson *et al.*, 1998; Wasylenki *et al.*, 2003). Experimental melting (Baker *et al.*, 1995)

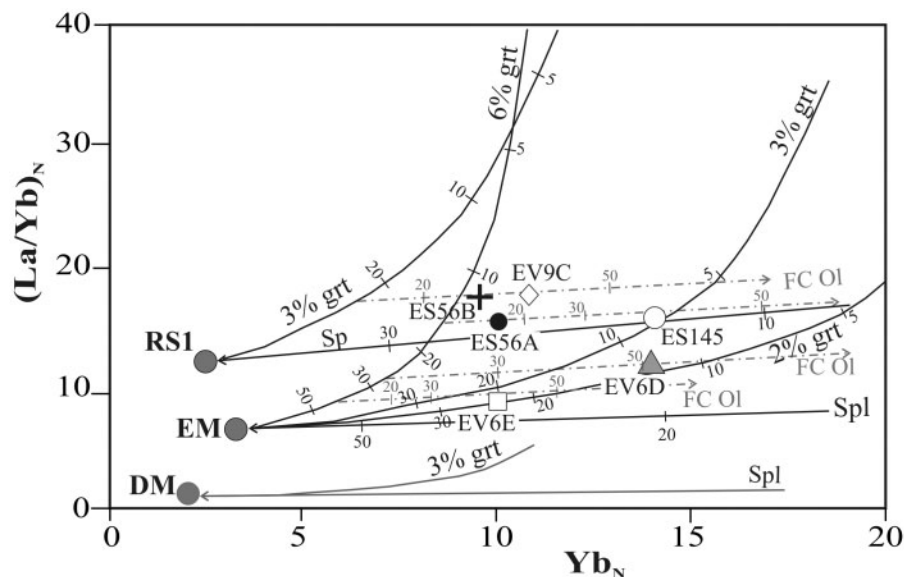


Fig. 13. Chondrite-normalized (Sun & McDonough, 1989) $(\text{La}/\text{Yb})_N$ vs Yb_N considering the upper mantle the source of the parental magmas of the Caicó Complex. Curves for melting of spinel-bearing (Spl) and garnet-bearing (2, 3 and 6% grt) lherzolite were plotted; the dashed curves represent 5, 10 and 20% partial melting. DM, Depleted Mantle ($\text{La}_N = 2$, $\text{Yb}_N = 2$), EM, Enriched Mantle ($\text{La}_N = 22$, $\text{Yb}_N = 3$); RS1, metasomatized peridotite (pargasite–phlogopite lherzolite), with $\text{La}_N = 29$ and $\text{Yb}_N = 2.4$. DM and EM after Graviou & Auvray (1985) and Martin (1985), RS1 after Menzies *et al.* (1987). FC, fractional crystallization of olivine at depth. Residue composition: olivine 58%, orthopyroxene 25–23%, clinopyroxene 12–10%, phlogopite 2%, pargasite 2%, garnet 6–0%, spinel 0–5%. Labelled tick marks indicate per cent partial melting of spinel and garnet-bearing model curves and fractional crystallization of olivine (FC Ol).

of fertile peridotite at low pressure (<15 kbar) gives silica-rich (>55 wt % SiO_2) near-solidus melts that are also alkali-rich. Experimental melting of the fertile peridotite KLB-1 (Hirose, 1997) for both water-undersaturated and water-saturated conditions generated high-silica (54–60 wt % SiO_2) and high-magnesian ($\text{MgO} = 5.6\text{--}6.8$ wt %) liquids for temperatures of 1000–1050°C. For $T > 1100^\circ\text{C}$, the liquids formed are basaltic in composition. On the other hand, melting of depleted peridotite generated low-silica and low-alkali basaltic liquids (Robinson *et al.*, 1998; Wasylenko *et al.*, 2003).

The genesis of the parental magma of the Caicó Complex orthogneisses by partial melting of the mantle has been modelled and the results are presented in a $(\text{La}/\text{Yb})_N$ vs Yb_N plot (Fig. 13). Three mantle compositions were tested: (1) DM (depleted mantle), with $(\text{La}/\text{Yb})_N = 1$ and $\text{Yb}_N = 2$ (Martin, 1985); (2) EM [slightly enriched (fluid metasomatized) mantle], with $(\text{La}/\text{Yb})_N = 6.6$ and $\text{Yb}_N = 3.4$ (Martin, 1985; Graviou *et al.*, 1988; Graviou & Auvray, 1990); (3) RS1, a phlogopite- and pargasite-bearing lherzolite representing the lithospheric mantle, with $(\text{La}/\text{Yb})_N = 12.2$ and $\text{Yb}_N = 2.4$ [sample RS1 of Menzies *et al.* (1987)]. In each group of gneisses, the sample analysed for REE and having the lowest SiO_2 and the highest MgO contents has been chosen as representative of the parental liquid EV6D (diorite), ES56B (tonalitic gneiss), ES145 (augen gneiss), and ES56A (granitic gneiss). One meta-basalt (EV9C) and one meta-andesite (EV6E) of

the supracrustal component of the Caicó basement were also plotted.

Figure 13 shows the curves for partial melting of spinel-bearing lherzolite (5% spinel) and garnet-bearing lherzolite (2, 3 and 6% garnet). It appears that partial melting of a depleted mantle, whatever the residual mineral assemblage, cannot generate magmas with La/Yb as high as in the Caicó Complex; consequently, the more likely source seems to be an enriched mantle. The genesis of the parental magma of diorite (EV6D), tonalite (ES56B), granite (ES56A) and meta-basalt (EV9C) is achieved for ~10% partial melting of the enriched lherzolite EM leaving 2–3% garnet as residual phase; the augen gneiss (ES145) and the meta-andesite (EV6E) would require ~8 and 20% partial melting, respectively. However, primary magmas derived directly from partial melting of lherzolite are believed to be basaltic, having high Mg-number (>70), Ni (>400 ppm) and Cr (>1000 ppm) with $\text{SiO}_2 < 50$ wt % (Wilson, 1989), or Mg-andesites (references above), which is not the case of the Caicó orthogneisses. Consequently, we admit that a basic magma, once formed by melting of the enriched mantle, evolves by fractionation of olivine at mantle depth or during ascent to the lower continental crust to form the parental magmas of the Caicó orthogneisses. Fractionation of olivine does not modify the La/Yb ratio but would impoverish the liquid in magnesium, thus providing a better fit of the model to the analysed samples. The parental magmas of augen (ES145) and

granitic (ES56A) gneisses, as well as the meta-basalt (EV9C), have higher La/Yb, which would require either more garnet in the residue or a lower degree of melting of the same source, or a more enriched mantle source with chemical characteristics similar to those of RS1.

Assuming present-day $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios of 0.7045 and 0.031 for the Bulk Silicate Earth (BSE; Workman & Hart, 2005), the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would be 0.702 at 2.2 Ga. The I_{Sr} values of the gneisses of the Caicó Complex range from 0.702 to 0.703, which are very close to the mantle value at 2.2 Ga. This clearly precludes an origin of the parental magma of the Caicó Complex by direct recycling of an older (Archean) continental crust, and consequently this also precludes large-scale crustal contamination. This is corroborated by the ϵ_{Nd} vs $^{87}\text{Sr}/^{86}\text{Sr}$ at $t=2.2$ Ga plot (Fig. 14). In this diagram, we calculated mixing curves between a mantle (MORB-like) derived magma and the upper continental crust (UCC), the lower continental crust (LCC), and silica-rich 2.7 Ga (Arch1) and 3.3 Ga (Arch2) gneisses of the São José de Campestre massif [U/Pb zircon data after Dantas *et al.* (2004)]. For modelling we used the mixing equations of Langmuir *et al.* (1978) and DePaolo (1981), with MORB, UCC and LCC trace element and isotopic compositions from Faure (1986) and Rollinson (1993); for Arch1 and Arch2 contaminants we used our unpublished data. It is not possible that the UCC could be a contaminant. If mixing or contamination occurred it would involve less than 3% of LCC (see detail in Fig. 14b). In addition, the ϵ_{Nd} ($t=2.2$ Ga) values of +0.3 to −1.9 of the Caicó Complex are significantly different from and greater than those of the Archean gneisses of the São José de Campestre massif [in the range −10 to −17 at 2.2 Ga; data from Dantas *et al.* (2004)], thus corroborating that older continental crust did not play any significant role in the genesis of the Caicó Complex. Moreover, 3.3–2.7 Ga gneisses of the São José de Campestre massif are (our unpublished data) silica-rich (70–75 wt % SiO_2) and Mg-poor ($\text{MgO}=0.1\text{--}0.2$ wt %) and obviously could not be the source of diorites, quartz diorites, tonalites and granodiorites of the Caicó Complex.

Discarding any significant contribution of an older Archean oceanic or continental crust leads to the conclusion that the LILE- and LREE-rich nature of the Caicó Complex orthogneisses is a characteristic of the mantle source. To accommodate their arc signature, the LILE and LREE enrichment, variable ϵ_{Nd} (in the range +0.3 to −1.9 at 2.2 Ga; Table 5), and an enriched mantle source (Fig. 13) we considered the possibility of slab-modified peridotite as the source of the Caicó magmas.

This mechanism has already been proposed to account for the genesis of Archean sanukitoids (e.g. Rapp *et al.*, 1999; Martin *et al.*, 2005). Although admitted as generated by direct partial melting of an LILE- and LREE-enriched peridotite because of their trace element contents, the Nd

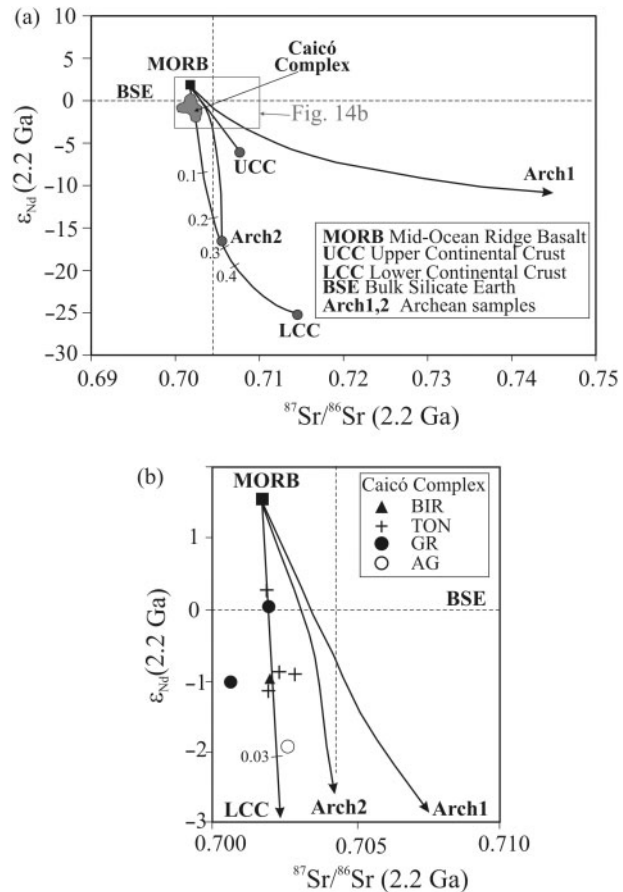


Fig. 14. (a) Initial ϵ_{Nd} vs I_{Sr} at 2.2 Ga for the Caicó Complex orthogneisses. Mixing of MORB with lower continental crust (LCC) and upper continental crust (UCC) is also displayed. For mixing computation, we used the equations deduced by DePaolo (1981; reviewed by Faure, 1986; Wilson, 1989). The ticks on the MORB–LCC curve mark the ratio of MORB to LCC. (b) Expanded field of (a).

isotope composition of sanukitoids requires a depleted mantle source (Stern *et al.*, 1989; Stern & Hanson, 1991; Stevenson *et al.*, 1999; see also reviews by Martin *et al.*, 2005; Rollinson, 2006). In an experimental study at 4 GPa, Rapp *et al.* (1999) allowed the infiltration of an adakitic melt into an overlying peridotite layer, simulating melt–rock interaction at the subducted slab–mantle interface. The hybridization of slab-derived melts by reaction with mantle peridotite produced high-Mg adakitic liquids. Figure 15 shows Mg-number vs SiO_2 and Sr/Y vs Mg-number diagrams in which the experimental results of Rapp *et al.* (1999) are reported. In addition, the composition of liquids produced by experimental melting of both depleted and enriched mantle peridotite (Takahashi *et al.*, 1993; Baker & Stolper, 1994; Hirose, 1997; Hirschmann *et al.*, 1998; Robinson *et al.*, 1998; Wasylenki *et al.*, 2003) as well as the average of Archean sanukitoids (Martin *et al.*, 2005) are also shown. Obviously, the hybridized melts have

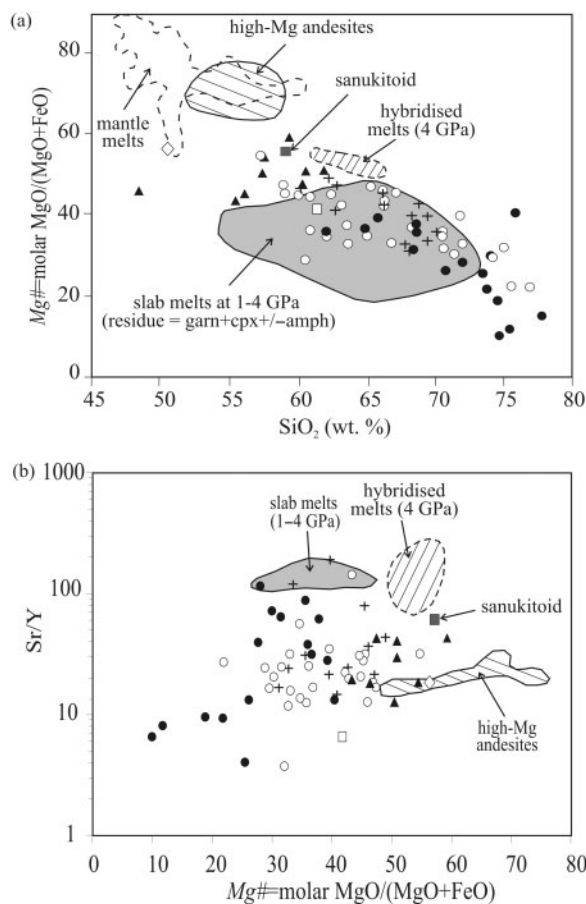


Fig. 15. Magnesium number (Mg-number) vs SiO_2 (a) and Sr/Y (b) for the Caicó Complex rocks compared with experimentally produced high-pressure upper mantle (Takahashi *et al.*, 1993; Baker & Stolper, 1994; Hirose, 1997; Hirschmann *et al.*, 1998; Robinson *et al.*, 1998; Wasylenko *et al.*, 2003) and garnet amphibolites and eclogites (compilation by Rapp *et al.*, 1999) melts. The experimental hybridized melts and the high-Mg andesite fields are from Rapp *et al.* (1999). Other symbols are as in Fig. 12a.

Mg-number and Sr/Y ratio significantly higher than in the gneisses of the Caicó Complex. As discussed above (e.g. see Fig. 12), the field of experimental slab melts does not fit the composition of the gneisses of the Caicó Complex, especially when the Sr/Y ratio is considered.

Taking into account the discussion above, we calculated the composition of a depleted mantle (Workman & Hart, 2005) metasomatized by slab melts having the composition of the high-silica adakite (HSA) of Martin *et al.* (2005). The best results are obtained for a metasomatized mantle (MM) formed by mixing 93% DM and 7% HSA (0.93DM:0.07HSA). Figure 16 shows that all of the Caicó Complex samples have patterns generally parallel to MM, thus providing an additional argument in favour of this common source. Modelling has been performed, assuming a two-stage evolution: (1) partial melting of a MM;

(2) fractional crystallization of olivine in the generated magma. The input partition coefficients are those compiled by Rollinson (1993) and Nielsen (2007); the source is assumed to have phlogopite (2%), amphibole (2%), garnet (0–5%) and spinel (5–0%) as accessory phases. The best fit is obtained for 10% melting of peridotite with up to 3% garnet, followed by 50–80% of olivine fractionation. The predicted curves are well adjusted for tonalitic (Fig. 16a), granitic (Fig. 16c) and quartz dioritic gneisses (Fig. 16d). Only augen gneisses show slightly different patterns, which have Rb to Ce and Zr to Sm normalized values greater than the expected ones (Fig. 16b). If we assume that the distribution coefficients used are correct, this could reflect either a lesser degree of melting of MM or a greater amount of olivine fractionation.

Figure 17 summarizes the petrogenetic model for the Caicó Complex. Four stages are considered: in the first stage, a depleted mantle lherzolite is metasomatized by a slab-derived melt with high-silica adakite chemistry and possibly generated during an earlier (Late Archean?) subduction episode, giving rise to an enriched mantle (MM); in the second stage, 10–15% partial melting of this MM generates a basic magma that, in the third stage, after 40–80% fractional crystallization of olivine at depth produces the less evolved samples of the Caicó Complex, which, in the fourth stage, evolve by low-pressure intracrustal fractionation of variable proportions of hornblende, plagioclase and magnetite, with eventual AFC for some silica-rich augen and granitic gneisses samples.

In conclusion, the geochemical modelling shows that the parental magmas of the Caicó Complex orthogneisses could have been generated by partial melting of LREE- and LILE-enriched lherzolite with minor amounts of, or no, residual garnet, followed by olivine fractionation at depth. This petrogenetic model is very similar to that proposed for late Archean sanukitoids and Closepet-type granites: remelting of a peridotite previously metasomatized by reaction with slab melts (Shirey & Hanson, 1984; Stern, 1989; Stern & Hanson, 1991; Rapp *et al.*, 1999; Smithies & Champion, 1999, 2000; Moya *et al.*, 2001, 2003; Halla, 2005; Lobach-Zuchenko *et al.*, 2005; Martin *et al.*, 2005). In this case, melting of LREE-enriched peridotite is assumed to generate diorites, monzodiorites and syenodiorites with high Mg-number, Ni, Cr, Sr, Ba, P_2O_5 and LREE (Stern *et al.*, 1989; Stern & Hanson, 1991). Subsequent differentiation of these melts would yield granodiorite with the following characteristics (at 65 wt % SiO_2): (1) abundant hornblende, titanite and apatite; (2) Mg-number ~50, $\text{MgO} > 3$ wt %; (3) Sr and Ba ~1000–2000 ppm, Cr ~130–50 ppm, Ni ~70–30 ppm; (4) Rb/Sr < 0.1; (5) fractionated REE patterns with only minor Eu anomaly. These are characteristics shared by most of the Caicó Complex orthogneisses, except for their

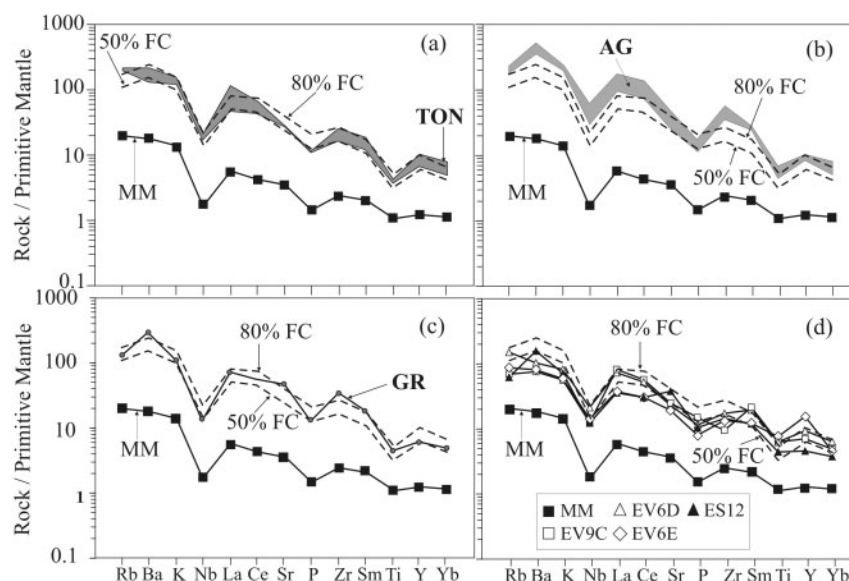


Fig. 16. Primitive mantle normalized (Taylor & McLennan, 1985) multi-elemental diagrams for the less evolved (<65 wt % SiO₂) Caicó Complex rocks and the metasomatized mantle (MM). The MM is assumed as mixing of depleted MORB mantle (Workman & Hart, 2005) and slab-derived melt with high-silica adakite composition (Martin *et al.*, 2005). (a) Tonalitic gneisses (field TON for two samples: EV7B, VC13C). (b) Augen gneisses (field AG for three samples: ES145, EV12C, EV13E). (c) Granitic gneiss (GR) sample ES56A. (d) Two diorites (ES12, EV6D), meta-andesite EV6E and meta-basalt EV9C.

slightly lower Mg-number, MgO, Ni and Sr, and higher Rb/Sr and Cr.

One important point to emphasize is that not only do the parental magmas of felsic orthogneisses appear to have had an enriched mantle source, but so also do the associated less silicic samples of unambiguous mantle origin (Table 6), such as (1) coarse-grained younger amphibolite SV3 (Mg-number = 69, Ni = 284 ppm, Cr = 783 ppm), and (2) meta-basalt (fine-grained amphibolite) EV9C (Mg-number = 56, Ni = 104 ppm, Cr = 406 ppm). Amphibolite SV3 is a dyke crosscutting granodioritic augen gneisses in the São Vicente–Florânia region and it seems to be affected by the same deformational history as the other Caicó Complex units. Meta-basalt EV9C forms metre-thick intercalations within meta-andesites, meta-rhyolites and garnet-bearing paragneisses in the Açú region (Fig. 2). It follows that the production of LILE- and LREE-enriched mantle-derived magmas was a recurrent phenomenon during Paleoproterozoic times, as found in earlier meta-basalt EV9C and late amphibolite SV3, which pre- and post-date the emplacement of the meta-plutonic rocks.

DISCUSSION

The processes and timing of formation of continental crust have been controversial, and a number of mechanisms have been proposed, such as addition of new material from the mantle, re-addition of crustal material that has

been cycled through the mantle, and redistribution of crustal rocks as a result of sedimentary and tectonic processes (see reviews by Condie, 1989; Rudnick, 1995; Kemp & Hawkesworth, 2003). It appears that collision of arcs and aggregation of microcontinents are the major mechanisms by which continents have grown (Condie, 1989; Drummond & Defant, 1990; Davidson & Arculus, 2006). However, alternative models, such as delamination of continental lithospheric mantle (Rudnick, 1995), underplating of basaltic magma at the base of the continental crust (McCulloch, 1987; Rudnick & Fountain, 1995), intralithospheric differentiation (Taylor & McLennan, 1985; Neves *et al.*, 2000; McLennan *et al.*, 2006), and mantle plumes (Abbott, 1996; Condie, 2001), have also been proposed.

Much debate also concerns the steady or episodic nature of the continental growth. The episodic growth of juvenile crust has been recognized during the last 15 years, with major events of rapid crustal growth at 3.6, 2.7 and 1.8 Ga according to McCulloch & Bennett (1994), or at 2.7, 1.9 and 1.2 Ga according to Condie (1998, 2000). The episodic pattern of continent formation led Albarède (1998) to postulate mantle plume periodicity in addition to continuum of subduction zone activity. The close temporal links between mafic volcanic rocks, supposed to represent products of mantle plumes, pre-dating silica-rich syn-tectonic plutons, in Paleoproterozoic terrains of French Guyana (Vanderhaeghe *et al.*, 1998; Delor *et al.*, 2003) and West Africa (Abouchami *et al.*, 1990; Boher *et al.*, 1992; Béziat *et al.*, 2000), has led researchers to admit mantle

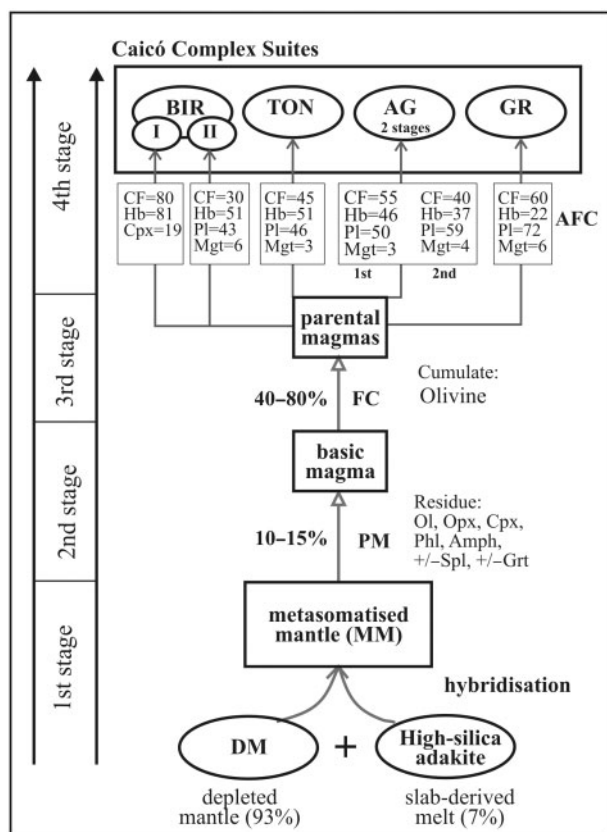


Fig. 17. Schematic diagram showing the successive petrogenetic processes that gave rise to the Caicó Complex magmatic suites. BIRs I and II, TON, GR and AG correspond to basic to intermediate rocks (subsets I and II), tonalitic gneiss, granitic gneiss and augen gneiss. Other symbols: MM, Metasomatized Mantle; DM, Depleted Mantle; FC, fractional crystallization; PM, partial melting; AFC, assimilation and fractional crystallization; Hb, hornblende; Cpx, clinopyroxene; Pl, plagioclase; Mgt, magnetite; Zrn, zircon.

plume activity associated with subduction processes. In both regions, the major event of juvenile crust formation was completed in less than 50 Myr. Regardless of the crustal growth process, there is a consensus that the Archean–Proterozoic boundary corresponds to a major change in terrestrial geodynamic conditions (rapid crustal growth, which may or may not be related to falling geotherms in the Late Archean) that also resulted in changes in continental petrogenesis (Taylor & McLennan, 1985; Condie, 1989; McLennan *et al.*, 2006).

In the model presented here, the parental magma of the Caicó Complex orthogneisses is interpreted as subduction-related. Major and trace element, and Nd isotope contents all agree with a metasomatized mantle as the source. The metasomatic agent was modelled as high-silica (TTG-like) slab-derived melt that hybridized with the depleted mantle. Of course, adakitic melt requires a previous episode of subduction (Moyen *et al.*, 2001; Martin *et al.*, 2005). The timing of the subduction should be somewhere

between 2.7–2.5 Ga (T_{DM} values for the Caicó Complex) and the emplacement age of plutonic rocks at ~2.2 Ga (U–Pb and Pb–Pb zircon, and whole-rock Rb–Sr ages). However, assuming the enriched nature of the Caicó source, it is possible to estimate model age using, instead of depleted mantle, a chondritic mantle (e.g. CHUR, $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$; Jacobsen & Wasserburg, 1980). The calculated T_{CHUR} ranges from 2.4 to 2.2 Ga, thus indicating that the subduction-related enrichment of the mantle peridotite took place 100–200 Myr before the emplacement of the parental magmas of the Caicó Complex. When tentatively correlated with the West Africa craton (Abouchami *et al.*, 1990; Boher *et al.*, 1992) and French Guyana shield (Delor *et al.*, 2003), this subduction would have followed an earlier episode of plume-related oceanic plateau magmatism (interpreted for juvenile mafic magmatism in both regions). Nevertheless, until today, no evidence of this plume event has been found in north-eastern Brazil.

Table 8 summarizes the general features of the Caicó Complex orthogneisses compared with Archean TTG, calc-alkaline granites, adakites and sanukitoids, as well as with modern juvenile granitoids. Most petrographic and chemical characteristics of the plutonic series of the Caicó Complex are clearly distinct from Archean TTG, particularly in their cogenetic association with basic and intermediate rocks, their wide compositional range in SiO_2 , higher Yb_N , Rb/Sr , Cr/Ni and $\text{K}_2\text{O}/\text{Na}_2\text{O}$, and lower Mg -number (but basic to intermediate rocks), A/CNK , $(\text{La}/\text{Yb})_N$ and Zr/Sc . The sources envisaged are also distinct: the Archean TTGs were derived by garnet-bearing amphibolite or eclogite melting, whereas the Caicó orthogneisses were derived from metasomatized lherzolite with little or no residual garnet (<5%). The Caicó orthogneisses are different from typical Archean sanukitoids by having higher $\text{K}_2\text{O}/\text{Na}_2\text{O}$, Rb/Sr and Cr/Ni ratios and less fractionated REE patterns. On the other hand, Archean calc-alkaline granites have lower Yb_N and Cr/Ni and higher $(\text{La}/\text{Yb})_N$.

Major and trace element modelling points to a four-stage evolution. After a first stage of assimilation–reaction of a depleted mantle with a slab-derived adakitic melt, this hybridized spinel- or garnet-bearing source is melted, generating a basic magma (second stage), which subsequently evolves by fractional crystallization of olivine to form the parental magmas to the Caicó Complex (third stage). Subsequently, fractional crystallization at low pressure (lower crust) of different proportions of amphibole + plagioclase + magnetite $\pm$ clinopyroxene gives rise to the differentiated Caicó Complex suites. According to this model, melting should have taken place at the spinel lherzolite–garnet lherzolite transition at pressure <20–25 kbar or equivalent depths of ~66–83 km (Takahashi & Kushiro, 1983; Green & Falloon, 1998). All these characteristics are widespread in magmas generated from partial melting of

Table 8: Selected average element ratios of the Caicó Complex orthogneisses compared with Archean and modern juvenile granitoids

	Archean				Averages of the Caicó Complex orthogneisses ⁴				Modern gr gr ¹
	TTG ¹	Sanuk ²	CAGR ³	Adakites ²	BIR	TON	AG	GR	
SiO ₂ (wt %)	64.9–74.7	55.9–61.7	69.5–72.3	52.9–67.3	48.4–62.0	60.3–79.2	57.3–77.0	62.1–77.9	61.9–74.3
K ₂ O/Na ₂ O	0.4	0.7	0.9	0.5	0.7	0.6	1.2	1.5	0.9
Mg-no.	43.0	57.0	34.0	55.0	50.0	40.0	38.0	26.0	41.0
Rb/Sr	0.1	0.0	0.3	0.1	0.1	0.2	0.3	0.8	0.4
A/CNK	1.0	0.8	1.0	0.8	0.8	1.0	1.0	1.0	1.0
(La/Yb) _N	41.7	32.6	39.3	28.0	11.1	27.3	29.1	33.3	7.0
Yb _N	1.5–5.0	3.7–11.9	3.0–9.1	4.0–6.7	11.1	9.4	13.1	11.7	15.9–21.8
Eu/Eu*	1.3	1.4	0.7	0.9	1.0	0.9	0.9	0.4	0.8
Cr/Ni	2.1	1.8	4.1	1.8	5.7	12.3	8.8	12.4	2.2
Zr/Sc	32.3	19.9	3.3	–	8.7	20.0	32.1	38.2	12.9

¹Martin (1994); ²Martin *et al.* (2005), and Stern & Hanson (1991) for Zr/Sc; ³Sylvester (1994); ⁴data from Electronic Appendix.

TTG, trondhjemite-tonalite-granodiorite; Sanuk, sanukitoid; BIR, basic to intermediate rocks; TON, tonalitic gneiss; AG, augen gneiss; GR, granitic gneiss; Modern gr, modern juvenile granitoids.

enriched shallow mantle in continental arc settings and involving the sub-continental lithosphere (Pearce & Parkinson, 1993).

As indicated by our modelling, the lherzolitic source of the Caicó Complex was already LILE-enriched and had Ta–Nb, Sc, Ti and Yb negative anomalies. Ta, Nb and Ti anomalies are generally considered as typical features of magmas generated in subduction-like tectonic setting (see reviews by Pearce, 1982; Wilson, 1989). Several explanations have been proposed to account for these anomalies: (1) interaction between a fertile arc derived fluid and a depleted peridotite (Kelemen *et al.*, 1990; Schiano *et al.*, 1995); (2) infiltration of a rutile-saturated, slab-derived melt or vapour through a depleted peridotite produced by a previous episode of MORB extraction (Ryerson & Watson, 1987; Thirlwall *et al.*, 1994); (3) presence of residual Ti-bearing minerals with high- $K_D^{\text{min/liq}}$ high field strength elements (HFSE) such as titanite, rutile, ilmenite, amphibole or garnet in the source (Green & Pearson, 1986; Ryerson & Watson, 1987; Hoffman, 1988; Drummond & Defant, 1990), that retain the HFSE, producing HFSE-impooverished melts.

Based on ϵ_{Nd} of -2.5 to -3.7 at 2.2 Ga, Hackspacher *et al.* (1990) and Van Schmus *et al.* (1995) considered that a crustal component played an important role in the genesis of the Caicó Complex magmas. This interpretation, based only on ϵ_{Nd} values, is clearly in contrast to the trace element signatures discussed here, which suggest instead an enriched mantle source with very little or no crustal contamination. Consequently, the $\epsilon_{\text{Nd}}(t=2.2 \text{ Ga})$ of $+0.3$ to

-1.9 (see Table 5) should reflect the enriched nature of the source rather than contamination with older continental crust. Geochemical characteristics (metaluminous rocks, wide SiO₂ range, a very low proportion of garnet, or no garnet, in the source), geochronological data (U–Pb, Pb–Pb and whole-rock Rb–Sr and Sm–Nd isochrons with similar ages; no inherited zircon) and comparison with experimental results all show that the Caicó Complex orthogneisses mainly represent juvenile magmatism, with no, or very subordinate, crustal contribution.

Paleoproterozoic gneisses form *c.* 38% ($\sim 155\,760 \text{ km}^2$) of the exposed surface of the Precambrian rocks in NE Brazil. However, as the Neoproterozoic plutons, which make up about $34\,800 \text{ km}^2$ exposure, have Nd isotope signatures indicating a major contribution by 2.4–1.9 Ga sources (Neves, 2003), and 2.2 Ga detrital zircon in Meso- to Neoproterozoic supracrustal belts (Van Schmus *et al.*, 2003), the reconstituted Paleoproterozoic crust should represent more than 46% ($\sim 190\,560 \text{ km}^2$) of the exposed Precambrian units. The continental crust in NE Brazil has been modelled by gravity and isostasy studies by Castro *et al.* (1997a, 1997b), who concluded that it is $\sim 30 \text{ km}$ thick. Seismic refraction data also indicate a somewhat similar crust thickness ($\sim 34 \text{ km}$) in West Africa (Dorbath *et al.*, 1986). This estimated thickness should be considered a minimum value, as at least $\sim 23 \text{ km}$ (considering emplacement at about 7 kbar for the Caicó orthogneisses; see Table 2) have been eroded and incorporated into younger supracrustal belts (e.g. Seridó) and siliciclastic components of Phanerozoic cover. This indicates that a significant

volume ($\sim 10 \times 10^6 \text{ km}^3$ for a 53 km thick crust) of magma formed at $\sim 2.2 \text{ Ga}$, corresponding to the Caicó Complex.

Juvenile magmatic rocks of about 2.18–2.1 Ga age and a less voluminous extent of 2.35–2.2 Ga age cover huge areas extending for thousands of square kilometres. They are also known in the northeastern São Francisco (Conceição, 1997; Teixeira *et al.*, 2000), São Luís (Klein *et al.*, 2005b) and West African (Doumbia *et al.*, 1988; Abouchami *et al.*, 1990; Boher *et al.*, 1992; Toteu *et al.*, 2001; Gasquet *et al.*, 2002; Feybesse *et al.*, 2006) cratons, French Guyana (Gruau *et al.*, 1985; Vanderhaeghe *et al.*, 1998; Delor *et al.*, 2003; Ledru *et al.*, 2003; McReath & Faraco, 2006) and NE Brazil (Fetter *et al.*, 2000; Martins & Oliveira, 2003; Neves, 2003; Klein *et al.*, 2005a; Neves *et al.*, 2006). Based on geological and geochronological correlations, Neves (2003) interpreted that the cratons (São Francisco, Congo, West African, Amazonian) and the neighbouring Brasiliano–Pan-African belts (Borborema, Brasília–Ribeira, Nigerian) as part of the Atlantica supercontinent, which accreted at the end of the Eburnean cycle ($\sim 2.0 \text{ Ga}$). In the Birimian terrains of West Africa, Boher *et al.* (1992) concluded that juvenile crust formation spanned $< 50 \text{ Myr}$, a conclusion based on the similarity between U–Pb and Rb–Sr (2.19–2.16 Ga) ages, Sm–Nd ages ($T_{\text{DM}} = 2.34\text{--}2.14 \text{ Ga}$ in magmatic rocks) and synchronous metamorphism (isochron with 2.2 Ga in garnet-bearing pelite). In these areas, granite–greenstone-like associations were formed, and all $\sim 2.2\text{--}2.1 \text{ Ga}$ magmatic rocks have been derived from a depleted mantle source, with $\epsilon_{\text{Nd}}(t = 2.2 \text{ Ga})$ in the range $+0.4$ to $+6.8$, which drastically differs from our conclusions for the Caicó Complex.

Consequently, it can be proposed that this specificity could reflect local mantle heterogeneities, an enriched mantle source being located under NE Brazil. This assumption is strongly supported by the fact that at the Proterozoic–Paleozoic boundary (Brasiliano orogeny), all magmas produced from mantle melting also show these peculiar geochemical signatures (e.g. Sial *et al.*, 1989; Hollanda *et al.*, 2003). It is worth noting that this enriched mantle is also proposed as the source for Mesoproterozoic and Neoproterozoic plutonic as well as Cretaceous and Cenozoic volcanic rocks in NE Brazil (Sial, 1976; Bellieni *et al.*, 1992; Fodor *et al.*, 1998; Neves *et al.*, 2000; Mariano *et al.*, 2001; Hollanda *et al.*, 2006). It is, thus, suggested that the mantle enrichment process in NE Brazil is an ancient feature, probably dating back to at least late Archean times or shortly before the onset of Paleoproterozoic crust-forming events. A viable way to metasomatize the mantle is by hybridization of the depleted mantle through mixing with a slab-derived high-silica (TTG-like) adakite melt. Successive episodes of oceanic subduction during the Eburnean and Brasiliano orogenies enhanced this enrichment so that all magmas generated in this region show the LILE and HFSE characteristics described here.

CONCLUSION

Our main results can be summarized as follows.

- (1) Field, petrographic, geochemical and isotopic data show that the magmatic rocks of the Caicó Complex were generated by the same petrogenetic mechanisms.
- (2) They are metaluminous, high-K calc-alkaline LILE- and LREE-enriched magmas emplaced at about 2.2 Ga.
- (3) They have geochemical and isotopic characteristics of juvenile magmatism emplaced in a subduction-like tectonic setting, the most probable source being an enriched spinel- or garnet ($< 5\%$ garnet)-bearing lherzolite.
- (4) This tectonic setting favoured the hybridization of the depleted mantle source by slab-derived high-silica adakite melt, resulting in a metasomatized peridotite that generated by partial melting the parental magmas of the Caicó gneisses.
- (5) The petrogenetic model involves two stages: first, partial melting (10–20%) of an enriched lherzolite gave rise to a basic magma that subsequently evolved by high-pressure fractionation of olivine, thus resulting in the parental magmas of the Caicó Complex orthogneisses; second, each parental magma evolved by fractional crystallization at crustal pressures (5–8 kbar) of a combination of amphibole + plagioclase + magnetite $\pm$ pyroxenes, thus giving rise to the plutonic suite.
- (6) This juvenile magmatism extended throughout northeastern Brazil and has age and lithostratigraphic equivalents in French Guyana and in the West Africa and São Francisco cratons. Consequently, the Paleoproterozoic (2.2 Ga) juvenile magmatism represents a major continental accretion event far from the influence of older continental basement, and thus limiting contamination from it.

The data allow us to assign four specific features for the juvenile magmatism at the Archean–Proterozoic transition: (1) most of the geochemical and petrographic parameters are akin to those of modern granitoids; (2) granitoid magmas are mantle-derived, and recycling of continental crust is limited or absent; (3) the mantle can be either depleted (as in the West Africa, São Luís and northeastern São Francisco cratons, and French Guyana) or metasomatically enriched (as in the case studied here); (4) the metasomatic agent is believed to be a high-silica adakite (TTG-like) melt that hybridized with the depleted mantle. Finally, it should be stressed that the prevalence of wedge-dominated lithospheric mantle as the source for the granitoids of the Caicó Complex is comparable with processes responsible for the generation of modern juvenile granitoids, although the volume of magma generated resembles slab-dominated Archean continental crust-forming events.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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