The Statherian itabirite-bearing sequence from the Morro Escuro Ridge, Santa Maria de Itabira, Minas Gerais, Brazil

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ARTICLE INFO

Article history:

Received 8 June 2014

Accepted 18 December 2014

Available online 27 December 2014

Keywords:

Morro Escuro Ridge

Serro group

Itabirite

Geochemistry

ABSTRACT

The itabirite-bearing metasedimentary sequence from Morro Escuro Ridge comprises the basal units of the Espinhaço Supergroup and makes up a small tectonic inlier developed during one of the Brasiliano orogenic events (800–500 Ma), amongst horses of the Archean TTG gneisses, including sheared granites of the anorogenic Borrachudos Suite (~1700 Ma). The metasedimentary rocks are comprised of low-to intermediate-amphibolite facies schists, quartzites, conglomerates and banded iron formation (itabirite) correlatable with the sequences of the Serro Group, which underlies the metasedimentary rocks of the Espinhaço Supergroup in the Serra da Serpentina Ridge. A maximum Statherian deposition age (1668 Ma) was established using SHRIMP U–Pb isotopic constraints on zircon grains from conglomerate and quartzite units overlying the itabirite. The itabirite is predominantly hematitic and its geochemical characteristics are typical of a Lake Superior-type BIF deposited in a platformal, suboxic to anoxic environment distant from Fe-bearing hydrothermal vents. Close to the contact zone with amphibolites of the Early Neoproterozoic Pedro Lessa mafic suite, an increase of the magnetite content and crystallization of metasomatic Mg-hornblende and Ce-allanite can be observed. These mineralogical changes developed preferentially along the igneous contact zone but are probably co-genetic with the formation of alteration haloes in zircon grains during the Neoproterozoic Brasiliano orogeny (506 ± 6 Ma).

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1. Introduction

The Morro Escuro Ridge (MER) and similar ridges are discontinuously distributed in a large area reaching from the eastern border of Quadrilátero Ferrífero up to the town of Serro (Fig. 1). These ridges follow an arcuate structural trend that varies from NW–SE, N–S to NE–SW bordering the eastern to southeastern part of the São Francisco Craton (Fig. 1). The

structural framework of these geomorphological units is defined by intercalated thrust slices of metasedimentary structural units and granite-gneissic rocks of the basement developed during the Brasiliano Orogen (Araçuaí Orogenic Belt – Noce et al., 2007). The metasedimentary outcropping units are comprised mainly of a layer of metamorphosed banded iron formation, referred to as itabirite, found between thick psamo-pelitic units which have also locally undergone metasomatism and hydrothermal alteration, but without the formation of large, economically important high-grade iron ore bodies (>64 wt% Fe). The increasing global demand for iron, however, has made unenriched, medium-graded banded iron formations (<40 wt% Fe), such as those found at the Morro Escuro and similar ridges, important targets for exploration.

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Fig. 1. Regional map showing the location of the Morro Escuro Ridge and distribution of the main geological units, between the Quadrilátero Ferrífero and the location of Serro (based on Grossi-Sad et al., 1997; Pedrosa-Soares et al., 1994).

The age of these units and their depositional environment have been interpreted variously and controversially. Some authors, for instance, ascribe the Morro Escuro itabirite layer to the Paleoproterozoic Minas Supergroup (Itabira Group) or to the volcano-sedimentary unit from the Ganhães Complex assemblage (Grossi-Sad et al., 1997; Pedrosa-Soares et al., 1994) of Archean age (2867 ± 10 – Silva et al., 2002). Our recent results from field mapping in the MER, in combination with detailed petrographic, geochemical and isotopic studies of itabirite and its host rocks have allowed us to: 1) define a local stratigraphic column for that area (here called the Morro Escuro Ridge sequence) and distinguish it from the BIF-bearing Ganhães Complex and Minas Supergroup (2580 Ma to 2420 Ma – Hartmann et al., 2006) from the Quadrilátero Ferrífero mining district; 2) compare, discuss and suggest a correlation at a regional scale with the Statherian Serro Group that underlies the Espinhaço Supergroup at the Serra da Serpentina Ridge located at ca. 35 km NE (Fig. 1); 3) deliver a preliminary interpretation regarding the physical and chemical transformations undergone by the BIFs during the Brasiliano orogeny.

2. Regional geology

2.1. Structural setting

The Morro Escuro and similar itabirite ridges are widespread along the western and southern border of the Ganhães Block (Alkmim et al., 2007), which is a wide expanse of the basement of the Neoproterozoic Araçuaí Orogenic Belt (Fig. 1). Top-to-west thrust faults and east-vergent backthrusts (Dussin, 1994) developed during the Brasiliano orogeny (800–500 Ma), juxtaposing allochthonous slices comprised by BIF-bearing metasedimentary sequences inserted between granitic bodies of the Paleoproterozoic Borrachudos Suite and Archean TTG gneisses of the crystalline basement (Fig. 1) (Grossi-Sad et al., 1997; Pedrosa-Soares et al., 1994).

2.2. The crystalline basement

Archean crystalline rocks from the Dona Rita and Ganhães complexes (Grossi-Sad et al., 1997) make up the basement of the

São Francisco Craton (Fig. 1). The Guanhães Complex stretches over the central-eastern part of the state of Minas Gerais and is comprised mainly of an undivided assemblage of TTG (tonalite–trondhjemite–granodiorite) gneisses, migmatites and granitic bodies, commonly displaying mylonitic fabric, together with discontinuous strings of metasedimentary and metavolcanic rocks (Dussin et al., 2000; Noce et al., 2007). The Dona Rita Complex is a similar lithostratigraphic unit, indistinguishable from the Guanhães Complex, which crops out on the eastern border of the Craton (Guimarães, 1992; Grossi-Sad et al., 1997).

2.3. Itabirite-containing basins in the Southern São Francisco Craton

2.3.1. The siderian Minas basin

The Paleoproterozoic Minas Supergroup (2580 Ma to 2420 Ma – Hartmann et al., 2006) is located SW of the study area, in the Quadrilátero Ferrífero mining district. It is largely composed of metamorphosed carbonate-rich platform sequences as well as quartzites, metaconglomerates, phyllites, dolomites, and banded iron formations (itabirites) that host the largest and economically most important iron deposits in southern Brazil, including several high-grade (>60 wt% Fe) ore bodies (Rosière et al., 2008). The rocks of the Minas Supergroup are polydeformed and were affected by two main orogenic events the oldest one initiated at ca 2.1 Ga (Alkmim and Marshak, 1998), in the end of the Rhyacian Period with posterior tectonic reworking during the Brasília collage (Brito-Neves et al., 2014), resulting in a roughly bi-directional (NE–SW, NW–SE) domal structural pattern. Itabirites occur in three compositionally distinct lithofacies, namely quartz itabirite, dolomite-itabirite, and amphibole-itabirite.

2.3.2. The Statherian Espinhaço basin

The Espinhaço Supergroup (Pflug, 1968; Schöhl and Fogaça, 1979) is interpreted as being deposited in two younger intraplate basins of distinct ages: (i) the Lower Espinhaço Basin, which is marked by a volcano-sedimentary sequence with alluvial, fluvial and eolian sediments deposited from 1.68 Ga to 1.80 Ga; and (ii) the overlying Upper Espinhaço rift-sag Basin, which has a maximum deposition age of 1192 Ma (Chemale Jr. et al., 2012). The shallow marine sedimentary rocks from the Lower Espinhaço Basin are underlain by itabirite-bearing psamo-pelitic units and ultramafic rocks. A U–Pb age of 1715 ± 2 Ma was obtained from the igneous zircon grains of interlayered metarhyolite bodies (Machado et al., 1989), but the stratigraphic arrangement has been controversial. According to Almeida-Abreu et al. (1989) and Almeida-Abreu and Renger (2002, 2007), these units belong to the Serro Group (Fig. 1), which comprises, from bottom to top, the Alvorada de Minas Ultramafic Suite, quartzites from the Jacém Formation, and two BIF-bearing psamo-pelitic sequences: the Serra do Sapo and Itapanhoacanga formations. Rolim and Rosière (2011) have recently proposed a new stratigraphic grouping that would delineate two individual upper and lower BIF units separated by a psamitic layer.

2.4. Magmatic units

Anorogenic granitic bodies of the Borrachudos Suite (Fig. 1) occur along the eastern border of the São Francisco Craton, and were emplaced during a Paleoproterozoic plutonic event. This unit was dated by Silva et al. (2002) at 1740 ± 8 Ma using SHRIMP U–Pb in zircon crystals, and by Dossin et al. (1993) at 1729 ± 14 Ma using the zircon Pb–evaporation method.

Amphibolitic rocks were dated by Machado et al. (1989) at 906 ± 2 Ma, comprising the Pedro Lessa Suite associated with the rift volcanism of the Neoproterozoic Macaúbas Basin (Noce et al.,

1997). Younger, undeformed Mesozoic mafic dikes (120 Ma – Silva et al., 1995) were intruded during Pangaea breakup.

3. Sample selection and methodology

Our fieldwork activities in the studied area included surface geological mapping with detailed work conducted along profiles transversal to the ridge structure that include the description of 258 waypoints and 31 diamond drill cores with the collection of 69 samples for the preparation of thin and polished sections.

Whole rock chemical analyses from 30 collected samples (10 granite-gneiss, 4 mafic rock and 16 iron formation) were accomplished at the ACME Labs using the ICP-ES (Inductively Coupled Plasma Emission Spectrometry) method for major oxide elements and the ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) method for trace elements.

The chemical composition of several metamorphic minerals – amphibole, biotite, garnet, staurolite and plagioclase – was obtained using the JEOL JXA-8900RL electronic microprobe, at 15 kV accelerating voltage and 20 nA current, at the Instituto de Ciências Exatas of the Universidade Federal de Minas Gerais, for geothermobarometric calculations. The minerals were analyzed with WDS (Wavelength-Dispersive Spectrometers) for SiO₂, Al₂O₃, FeO, MgO, MnO, CaO, Na₂O, K₂O and TiO₂. A microcline standard was used for the analyses of Si and K, aluminum oxide (Al₂O₃) for Al, olivine for Fe and Mn, hornblende for Mg, anorthite for Ca, albite for Na and rutile for Ti.

The softwares TWQ 1.02 and TWQ 2.02 (Berman, 1991) were used for geothermobarometric calculations of maximum temperature (T) and pressure (P) with the purpose of establishing the metamorphic conditions using the Holand and Powell (1990) equations.

The Sm–Nd whole-rock isotopic analyses were carried out at the Laboratório de Geocronologia of the Universidade de Brasília on three amphibolite samples based on the method described by Gioia and Pimentel (2000). In this procedure, approximately 50 mg of powder sample is mixed with a tracer solution of ¹⁴⁹Sm and ¹⁵⁰Nd. The sample is dissolved in Savillex® capsules through successive acid attacks using HF, HNO₃ and HCl. The contents of Sm and Nd were extracted through a cationic exchange column made of Teflon® and packed with LN-Spec resin (liquid resin HDEHP acid di(ethylhexyl) phosphoric acid impregnated by powdered Teflon). The fractions of Sm and Nd were deposited on double rhenium filament arrangements with nitric acid and analyzed in metallic form in static mode, using the mass spectrometer Finnigan MAT-v262 multi-collector. The uncertainties for the ratios of Sm/Nd and ¹⁴³Nd/¹⁴⁴Nd are less than $\pm 0.5\%$ (2 σ) and $\pm 0.005\%$ (2 σ) respectively, based on repeated analyses using BHVO and BCR-1-1 international standards. The isotopic ratios are normalized for a ¹⁴⁶Nd/¹⁴⁴Nd value of 0.7219 and the disintegration constant used is $6.54 \times 10^{-12} \text{ a}^{-1}$.

SHRIMP (Sensitive High Resolution Ion Microprobe) U–Pb determinations of three samples were performed on detrital zircon crystals at Curtin University in Perth, Western Australia. The samples were processed with conventional crushing, grinding and screening methods at the LOPAG-DEGEO laboratory at the Universidade Federal de Ouro Preto. A heavy fraction concentration of 60–120 mesh was realized by panning. After the concentration, the three samples were sieved and washed to remove any very fine material (of clay and silt size). The 60–250 mesh fraction was treated with heavy liquid (TBE, tetra-bromo-ethane) to remove light minerals and a Frantz LB1 magnetic separator (to concentrate the less magnetic minerals such as zircon). Zircon was handpicked and organized in an epoxy mount, which was polished and carbon-coated for SEM (Scanning Electron Microscope) study. Back-

scattered images (BSE) were taken using a JEOL6400 SEM at the Centre for Analytical and Characterization Analyses at the University of Western Australia. Imaging of the zircon is critical for identifying internal features, such as the core and rims, and to avoid areas with high common lead content (inclusions, fractures, and metamict areas). Epoxy mounts (UWA 07-03) were coated with gold for SHRIMP analyses. Most SHRIMP analytical spots were in the diameter range of 20–30 μm but the analyses of hydrothermal zircon used a spot size of only 10 μm . Four scans were used for each spot analysis of detrital zircon and seven scans during the analyses of hydrothermal minerals. The following masses were analyzed for zircon: ($^{196}\text{Zr}_2\text{O}$, ^{204}Pb , background, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{238}U , ^{248}ThO , ^{254}UO), as well as $^{200}\text{TixOy}$, ^{204}Pb , background, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{238}U , ^{248}ThO , and ^{254}UO . The standards D23 and NBS611 were used to identify the position of the peak of the mass ^{204}Pb , whereas the calibration of the U content and the Pb/U ratio were conducted using the zircon standard BR266 (559 Ma, 903 ppm U). The $^{207}\text{Pb}/^{206}\text{Pb}$ ages are used for all detrital grains, but the $^{206}\text{Pb}/^{238}\text{U}$ ages are selected for hydrothermal zircon. Most of the data are concordant; the discordant data have been grouped with adjacent populations. All data on detrital zircon with common lead correction greater than 1% were rejected during the first scan. The uncertainties of individual ages are quoted at 1σ level, whereas the ages plotted are calculated at 2σ levels (about 95% confidence). SHRIMP data were reduced using SQUID software (Ludwig, 2001) and plots were prepared using ISOPLOT/Ex (Ludwig, 2003).

4. Geology of the Morro Escuro Ridge inlier

4.1. Tectonic structure

The MER is a small ENE-WSW elongated allochthonous shear-zone-bound inlier block, located between slices of the Archean basal Guanhães/Dona Rita Complex, and the Paleoproterozoic

Borrachudos Suite. The internal structure of the inlier is controlled by three sets of NE–SW trending folds (Fig. 2), which nucleated as fault propagation folds in three progressive deformation stages (D1, D2 and D3) during the Brasiliano orogeny (Pagung de Carvalho et al., 2014). The thrust faults verge towards the SE, differing from the general trend of the W-facing fabric of the eastern border of the Espinhaço Range.

4.2. Lithostratigraphic units

4.2.1. The Archean gneissic complex

TTG-type orthogneisses that crop out in the surroundings of the MER area are correlated with the Archean Guanhães/Dona Rita Complex (Guimarães, 1992) and interpreted as part of the basement of the metasedimentary rocks of the MER sequence. These rocks exhibit a medium grain size (0.01–1 mm), with granoblastic to granolepidoblastic fabric. The main minerals are quartz, plagioclase, microcline, muscovite and biotite. The accessories are chlorite, zircon, apatite, titanite, allanite, epidote, clinozoisite, rutile and opaque minerals (magnetite, hematite, ilmenite, pyrite, chalcopyrite, pyrrhotite).

4.2.2. The Borrachudos Suite

Structural slices of granite belonging to the Borrachudos Suite are also intercalated with the MER sequence. Such rocks exhibit textural features and a mineralogical composition very similar to those of the Guanhães/Dona Rita Complex, but with a distinct geochemical signature that indicates intrusion in an intraplate setting, as will be discussed further below.

4.2.3. The Morro Escuro Ridge sequence

NE–SW striking conformable strata comprise the supracrustal rocks informally named as the Morro Escuro Ridge sequence and subdivided into four meta-lithostratigraphic units (Fig. 3).

Fig. 2. Geologic map of the Morro Escuro Ridge. Adapted from Pagung de Carvalho et al., 2014.

Biotite-quartz schist unit: A wide mineralogical variety of aluminous schists comprise the lowest unit of the MER sequence, always in direct contact with the basement (Fig. 2). The fabric is dominantly granoblastic and lepidoblastic, but nematoblastic domains were also observed, with the development of a continuous to anastomosed schistosity that is locally crenulated. Biotite and quartz are the main components of the schists, although garnet, carbonaceous matter (graphite?), plagioclase, staurolite, amphibole, tourmaline, carbonate, muscovite, chlorite, ilmenite and magnetite can also be found as rock-forming minerals. Titanite, sulfides (chalcopyrite, pyrrhotite, pyrite, arsenopyrite, sphalerite), zircon, apatite, hematite, ilmenite, and epidote are accessory minerals. Several lithotypes can be distinguished by their mineral assemblages, such as garnet-biotite-quartz schist, biotite-garnet-staurolite-quartz carbonaceous schist, garnet-biotite-amphibole-quartz carbonaceous schist, magnetite-biotite-quartz schist, tourmaline-biotite-quartz schist and scattered lenses of amphibole-carbonate schist (Fig. 3).

The garnet composition is predominantly almandine (molar fraction 63.54–84.07), pyrope (6.28–24.51), grossularite (0.77–21.70) and spessartine (0–8.12). Biotite is Mg-rich. The analyzed plagioclase crystals have anorthite composition in the biotite-garnet-amphibole-quartz carbonaceous schists and andesine composition in the garnet-biotite-quartz schists. Magnesian hornblende is the most frequent amphibole with subordinate tschermakite (Leake et al., 1997).

The carbonatic schist comprises calcite, amphibole (tremolite-actinolite series) and ilmenite with hematite exsolution lamellae. The accessory minerals are sulfides (pyrrhotite, chalcopyrite, pyrite, arsenopyrite), magnetite, hematite and titanite.

Fig. 3. Simplified lithostratigraphic column of the Morro Escuro Ridge inlier.

Lower quartzitic unit: This unit comprises mica-quartz schist and quartzite layers that grade toward ferruginous schist near the contact with the overlying itabirite (Fig. 3). The biotite-quartz schists are fine-to medium-grained (0.01 mm–1.0 mm), showing lepidoblastic fabric. The rock-forming minerals are quartz, muscovite, biotite, kyanite and, locally, epidote, hematite (lamellar, granular), martite, magnetite and carbonate. The accessory minerals are ilmenite, apatite, tourmaline, zircon, titanite, chlorite and clinozoisite.

Upper quartzitic unit: The upper boundary of the overlying itabirite layer is defined by repeating mica-quartz schists and quartzite layers covered by coarse-grained quartzite (the diameter of grains reaches 0.5 cm). There is an intercalation of metaconglomerate with quartzose matrix and sub-rounded clasts of quartz, quartzite and iron formation with low sphericity. The main minerals in the matrix of the conglomerate are quartz, muscovite, kyanite, iron oxides (mainly lamellar hematite and magnetite) and, rarely, hornblende. The accessory minerals are zircon, hematite, apatite and epidote.

Banded Iron Formation unit: Banded iron formation occurs in the MER as a NE–SW trending layer that, together with the metaconglomerates, supports the ridge (Figs. 3, 4 and 5A). Considering the metamorphic grade of this rock, we have used in the present paper the term itabirite as proposed by Rosière et al. (2008) and Hagemann et al. (2008).

The primary banding of the iron formation is commonly transposed with extensive obliteration of sedimentary/diagenetic structures by axial plane schistosity (Fig. 5B and C) and the development of a structural layering defined by the alternation of millimetric bands of quartz and iron oxides (hematite and magnetite). Centimetric to millimetric intrafolial folds are ubiquitous (Fig. 5B). The foliation is cut across obliquely by shear zones with a thickness of mm or cm and a length of several meters, which commonly host lenticular bodies of quartz-free, high-grade (~64 wt% Fe) schistose ore. Grain size varies from fine to medium (0.01 mm–1.0 mm).

Textural and mineralogical characteristics of the Morro Escuro itabirite are homogeneous, distinguishing them from the Cauê Formation of Quadrilátero Ferrífero (Rosière and Chemale Jr., 2000), which exhibits a wider variety of compositional facies. Nevertheless, they are identical to the quartz itabirite of the Serro Group as observed in the Serra da Serpentina (Rolim and Rosière, 2011; Dossin, 1985; Dossin et al., 1987) and Serra do Sapo ridges (Zacchi, 2010). The fabric of the iron formation is mainly schistose with subordinate granoblastic domains. Granoblastic ore is composed of equidimensional crystals with triple-junction and straight-grain boundaries. However, anhedral hematite crystals with lobate embayments and inequidimensional irregular intergrowths with martite are also present. Schistose domains are composed of elongated platy crystals (Fig. 6). Magnetite and amphiboles usually occur close to the contact zones with mafic dikes.

Fig. 4. East-west view of the Morro Escuro Ridge, showing the distribution of the lithostratigraphic units.

Fig. 5. Macroscopic characteristics of the Morro Escuro itabirite. (A) Itabirite outcrop in the southern portion of the Morro Escuro Ridge (UTM–693721/7852255); (B) Detail depicting millimetric banding with intrafolial folds (UTM–695335/7853778); (C) Variation in thickness of bands from left to right indicates the transposition and obliteration of the itabirite layering to an homogeneous foliation.

Fig. 6. Photomicrographs showing the different textures of the itabirite. (A) Lamellar hematitic itabirite; (B) Lamellar hematitic itabirite with magnetite blasts; (C) Lamellar and granular hematitic itabirite; (D) Contact of the amphibolite (on the right) with magnetitic itabirite (on the left). Abbreviations: HemL – lamellar hematite, HemG – granular hematite, Mag – magnetite.

Table 1

Synkinematic mineral assemblages and metamorphic facies of each lithostratigraphic unit of the Morro Escuro Ridge. Abbreviations: Qz – quartz, Pl – plagioclase, Ms – muscovite, Bt – biotite, Mc – microcline, Ep – epidote, Grt – garnet, Ky – kyanite, St – staurolite, Gr – graphite, Hbl – hornblende, Cb – carbonate, Tr – tremolite, Act – actinolite, Hem – hematite, Mag – magnetite.

Unit	Paragenesis	Facies
Archean Complex and Borrachudos Suite	1) Qz + Pl + Mc + Bt + Ms ± Ep	Amphibolite
Biotite-quartz schist	1) Qz + Bt + Grt + Ky + Ms	Amphibolite
	2) Qz + St + Grt + Bt + Gr	
	3) Qz + Hbl + Gr + Grt + Bt + Ms + Pl	
	4) Qz + Bt + Pl	
	5) Qz + Bt + Grt + Ep	
	6) Qz + Bt + Grt + Pl + Gr + St + Ep	
	7) Cb + Tr/Act	
Mica-quartz schist	1) Qz + Ms + Ep ± Bt	Greenschist to
	2) Qz + Ms + Ky ± Ep	Amphibolite
Itabirite	1) Qz + Hem + Mag ± Hbl	Amphibolite
Metaconglomerate	1) Qz + Ms ± Ep ± Hbl	Amphibolite
	2) Qz + Ms + Ky + Hbl	
Amphibolite	1) Hbl + Pl + Qz ± Bt ± Ep	Amphibolite

Magnetite appears as relicts in martite or as subhedral crystals (0.01 mm–4.0 mm of diameter) grown in a finer-banded hematite matrix (Fig. 6D). Magnesium-hornblende and, subordinately, tschermakite and epidote, comprise <10 vol% of the rock. The accessory minerals of the itabirite are sericite, chlorite, apatite and, very rarely, rutile, epidote (Ce-allanite), pyrite and chalcopyrite.

4.2.4. Intrusive mafic rocks

There are two generations of intrusive mafic rocks in the studied area (Fig. 3). The oldest is represented by tabular-shaped bodies of orthoamphibolite of the Pedro Lessa Suite (Dussin, 1994), which are in structural contact with all previously described units. The amphibolite is fine-to medium-grained, rarely coarse-grained, with a nematogranoblastic texture. It is composed mainly of hornblende, plagioclase, quartz, biotite, epidote, titanite, and ilmenite with hematite exsolution lamellae. The accessory minerals are sulfides (pyrite, chalcopyrite, pyrrhotite, arsenopyrite, pentlandite, sphalerite and bornite), magnetite, apatite, allanite, zircon and rutile.

Massive dark green isotropic gabbroic dikes comprise the younger set of undeformed Mesozoic mafic dikes (Silva et al., 1995) that preferentially cut through the gneiss. They exhibit a fine phaneritic, subophitic, equigranular fabric and are mainly composed of plagioclase, clinopyroxene, olivine and opaque minerals.

5. Metamorphism

The mineral assemblages (Table 1) in the different lithostratigraphic units consistently constrain the regional metamorphic grade to the amphibolite facies. The association staurolite ± garnet ± biotite ± muscovite ± quartz ± plagioclase that defines the S₁-foliation of the pelitic schists, indicates conditions of the staurolite and, more rarely, the kyanite zone (Yardley, 2004).

Geothermobarometric calculations were based on microanalysis of the core of synkinematic garnet, biotite, plagioclase and amphibole crystals selected from three samples of biotite schist (Appendix A). Three independent reactions were obtained from the plagioclase-bearing carbonaceous schist (Sample 010-133,35, Table 2), exhibiting a minimum temperature of 512 °C (±50 °C) and a maximum pressure of 5.9 ± 1 kbar (Fig. 7). Calculations from the other samples (Table 2) delivered a single reaction and a maximum temperature of 560 °C (±50 °C). These values also indicate that the MER metasedimentary rocks experienced low-to intermediate-amphibolite facies conditions.

6. Geochemistry of the basement

All granitic rocks that crop out in the MER and surroundings are strongly foliated and exhibit similar textural features and mineral assemblages, but could be distinguished based on their geochemical characteristics (Appendix B – chemical results). In the Rb vs. Y + Nb diagram (Fig. 8) after Pearce et al. (1984) one set of rocks plot largely in the WPG field (within-plates – intraplate granites), similar to the results from other granite bodies from the Borrachudos Suite (Dussin, 1994; Fernandes, 2001; Oliveira, 2002). The other points fall distinctly within the VAG (volcanic arc granites) field and indicate a distinct origin for the orthogneisses that are therefore ascribed to the basal Archean Complex (Guanhães/Dona Rita complexes) (Fig. 8).

The chondrite-normalized REE spidergrams for the different granitic rocks from the MER also exhibit very distinctive patterns: ΣREE values for the WPG granite data range from 164.0 to 1050.1. The plots display a strong negative Eu anomaly ($Eu/Eu^*_{(CN)} = Eu_{(CN)}/Sm_{(CN)} + Gd_{(CN)}$), varying from 0.07 to 0.24, and a relative enrichment of the LREE (La/Yb_(CN) ratio) that fluctuates between 4.48 and 14.25. These values are similar to those reported by several authors (e.g. Dussin, 1994; Fernandes, 2001; Oliveira, 2002), for the typical granites from the Borrachudos Suite (Fig. 9). Distinctively, the samples that plot in the VAG field exhibit a less pronounced Eu anomaly (0.31–0.49), higher La/Yb_(CN) ratios (10.49–150.85) and smaller ΣREE values (51.0–289.4).

7. Geochemistry of the itabirite

Whole-rock chemical analyses of the itabirite from the MER were carried out on 16 drill core samples, collected below the weathering zone (Appendix C). The SiO₂ and Fe₂O₃ content varies from 47.9 to 67.8 wt% and from 28.5 to 51.4 wt%, respectively, similar to other BIFs worldwide (see Gutzmer et al., 2008 and references therein). The corresponding Fe_{total} content varies from 19.9 to 36.0 wt%. According to Klein (2005), the average bulk chemistry of unenriched BIFs from the Archean and the Paleoproterozoic are always found to be similar, with Fe_{total} ranging from about 20 to 40 wt%. The CaO, MgO, MnO, Al₂O₃, Na₂O, K₂O, P₂O₅, TiO₂, Cr₂O₃ contents are less than 1 wt%. In most samples, the MgO, Na₂O, K₂O (<0.01%) and Cr₂O₃ (<0.002%) values are below the detection limit (Appendix C). Two samples (008-701 and 009-001- Fig. 10) collected near the contact layer with the amphibolite dikes contain magnesian hornblende and display anomalously high grades of

Table 2

Geothermobarometric results obtained in three samples of biotite-quartz schist.

Sample code	Rock	Analyzed minerals	Temperature (°C)	Pressure (Kbar)
001-106,15	biotite-garnet-staurolite-quartz schist carbonaceous	garnet/biotite	530–550	–
010-501	garnet-biotite-quartz schist with plagioclase	plagioclase/garnet/biotite	530–560	–
010-133,35	biotite-garnet-amphibole-quartz carbonaceous schist with plagioclase	garnet/amphibole/biotite/plagioclase	512	5.9

Fig. 7. P-T Diagram prepared from the microanalysis of garnet, biotite, plagioclase and amphibole from the biotite-garnet-amphibole-quartz carbonaceous schist with plagioclase, using the TWQ 1.02 software. Abbreviations: Phl – phlogopite, Ann – annite, Prg – pargasite, Alm – almandine, Prp – pyrope, Grs – grossularite, Qz-a – alpha quartz, An – anorthite, Ab – albite, Tr – tremolite.

MgO, Al_2O_3 , Na_2O and K_2O , which indicate metasomatic alteration of the itabirite.

The large variations in the Fe content of the highly deformed MER itabirite may be the result of two distinct factors: 1) the primary composition of the BIF; 2) selective leaching of quartz (or carbonates) supported by localized pressure solution as an effective deformation mechanism. There is much evidence of metasomatism and hydrothermal alteration in the area as discussed below, but without any significant Fe-enrichment. Some deposits of friable intermediate-to high-grade (50–60 wt% Fe) iron ore on the eastern border of the Quadrilátero Ferrífero district have undergone considerable enrichment by pressure solution along shear zones, which was further enhanced by weathering and selective erosion (elutriation) of the fine recrystallized quartz grains along the foliation planes (Rosière et al., 2008), but this is not the case of the MER itabirite, where supergene enrichment was ineffective.

7.1. Rare earth elements

Rare-earth elements (REE) are useful as pathfinders of the deposition environment of BIF, due to their low mobility during metamorphism (e.g. Taylor and McLennan, 1985; Elderfield and Sholkovitz, 1987; McLennan and Taylor, 1991), except in cases of metasomatism or when the fluid/rock ratio is very high (e.g. Elderfield and Sholkovitz, 1987; Michard, 1989). The calculated

Fig. 8. Rb vs. (Y + Nb) Diagram for geotectonic classification (Pearce et al., 1984). Circles represent granites of the Borrachudos Suite sampled at the MER; the data fall within the WPG field (intraplate granites). Data points from Archean Complex (triangles) fall within the VAG field (volcanic arc granites).

--○-- samples with similar pattern to Borrachudos Suite

—○— samples with distinct pattern to Borrachudos Suite

Fig. 9. Chondrite-normalized REE spidergrams (Evensen et al., 1978) of granites and basement gneiss.

Fig. 10. Major whole rock oxide element content (wt%) of the itabirite from Morro Escuro Ridge.

Σ REE + Y (rare-earth elements plus yttrium) values for the Morro Escuro itabirite vary from 2.0 to 126.5 ppm. The highest values (Fig. 11, Appendix C) were detected in the Mg-hornblende-bearing samples from the amphibolite contact zone (see above).

Chondrite-normalized (Taylor and McLennan, 1985) REE + Y spidergrams from the Morro Escuro itabirite display an anomalously high LREE/HREE ratio ($(\text{Pr}/\text{Yb})_{\text{CN}} = 0.57\text{--}4.03$), as depicted in Fig. 11A. The Eu anomaly is slightly negative ($\text{Eu}/\text{Eu}^*_{\text{CN}} = 0.27\text{--}0.65$). PAAS – normalized (Post-Archaean Average Australian Sedimentary Rocks – McLennan, 1989) diagrams exhibit the typical relative HREE enrichment ($(\text{Pr}/\text{Yb})_{\text{SN}} = 0.10\text{--}0.71$, Fig. 11B) and, in most cases, a positive but weak Eu anomaly ($\text{Eu}/\text{Eu}^*_{\text{SN}} = 0.90\text{--}1.91$) with an average of 1.6, close to the value of 1.5 which is considered by Planavsky et al. (2010) to be characteristic of late Paleoproterozoic iron formations.

The shale-normalized Ce anomaly is slightly negative, close to 1 ($\text{Ce}/\text{Ce}^*_{\text{SN}} = 0.66\text{--}5.86$) and independent of the Al_2O_3 content, but it may show positive values in Ce-allanite-bearing samples (samples 009-001 and 007-701 – Appendix C). The discriminative binary plot of $\text{Ce}/\text{Ce}^*_{\text{SN}}$ vs. $\text{Pr}/\text{Pr}^*_{\text{SN}}$ (Bau and Dulsky, 1996)

demonstrates that the $\text{Ce}/\text{Ce}^*_{\text{SN}}$ values of the Morro Escuro itabirite are close to 1 with a positive La anomaly, consistent with deposition in an environment of suboxic to anoxic waters (Fig. 13). The values of the Y anomaly ($\text{Y}/\text{Y}^*_{\text{SN}}$) vary between 0.83 and 1.97 and the Y/Ho ratio from 26.25 to 47.00.

Some Y/Ho values fall in the chondritic range ($24 < \text{Y}/\text{Ho} < 34$) near or inside the “shale” field in the plot $\text{Ce}/\text{Ce}^*_{\text{SN}}$ vs. Y/Ho (Fig. 14). It is possible that samples (002-701, 007-701, 009-001), with low Y/Ho (< 34), might have been slightly contaminated by clays. The majority of the calculated values, however, are hyperchondritic (Bau et al., 1996) and consistent with an overall absence of fine detritic components, which is also corroborated by the low contents of Al_2O_3 (0.07–1.53%), TiO_2 ($< 0.01\text{--}0.06\%$), Th ($< 0.2\text{--}13.7$ ppm), Hf ($< 0.1\text{--}0.8$ ppm), Sc ($< 1\text{--}2$ ppm) in all samples.

7.2. Similarities with other BIF sequences

The REE + Y data from the Morro Escuro itabirite are very similar to the analytical results found in BIFs from the Serro (Appendix D) and Itabira Groups (Spier et al., 2007), with a weak

Fig. 11. Distribution pattern of the REE + Y values of the itabirite from Morro Escuro Ridge normalized to the values of chondrite (A) and PAAS (B).

Fig. 12. Diagram of $\text{Eu}/\text{Eu}^*_{(\text{CN})}$ vs. $(\text{Sm}/\text{Yb})_{(\text{CN})}$ (Alexander et al., 2008), depicting the distribution of the Morro Escuro itabirite data in relation to the Fe-rich hydrothermal deposits of low T (Puteanus et al., 1991), hydrothermal fluids of low T (Michard et al., 1983), PAAS, hydrogenetic Fe–Mn crusts (Bau et al., 1996), Pacific seawater (Alibo and Nozaki, 1999), Serro Group in the Morro do Pilar region and Itabira Group from the Minas Supergroup (Spier et al., 2007).

positive Eu anomaly, a distinguished positive Y anomaly and low $(\text{Pr}/\text{Yb})_{(\text{SN})}$ ratios (Table 3 and Fig. 15). These data plot as typical shale-normalized spidergrams similar to most Paleoproterozoic BIFs worldwide, such as the late Archean Witwatersrand BIFs, the early Paleoproterozoic Brockman and Kurunam iron formations and the late Paleoproterozoic Lake Superior Biwabik BIF (Table 3 and Fig. 16).

In contrast, the Neoarchean jaspilites from the Carajás Mineral Province and the 3.8 Ga old Isua BIFs (Moorbath et al., 1973) exhibit the highest Eu anomaly and ΣREE values (Figueiredo e Silva et al., 2008; Dymek and Klein, 1988). The REE contents of Rapitan-type Neoproterozoic BIFs from the Urucum district (755–730 Ma) are also high, but a positive Eu anomaly is absent (Klein and Ladeira, 2004).

8. Geochronology

8.1. U–Pb SHRIMP

The maximum depositional age for the upper quartzitic unit of the MER sequence was determined according to the youngest detrital zircon grain. Two populations of grains from the

Fig. 13. Discriminative diagram of $\text{Ce}/\text{Ce}^*_{(\text{SN})}$ vs. $\text{Pr}/\text{Pr}^*_{(\text{SN})}$ for La and Ce anomalies (Bau and Dulsky, 1996). The circles represent the Ce-allanite bearing samples.

Fig. 14. $\text{Ce}/\text{Ce}^*_{(\text{SN})}$ vs. Y/Ho diagram (Pecoits, 2010). The circles represent the Ce-allanite bearing samples.

metaconglomerate layer and one from the overlying quartzite of the same stratigraphic unit (see position on Fig. 3) were investigated and the SHRIMP results delivered three fairly homogeneous histograms. The single values are presented in Appendix E.

In one of the metaconglomerate samples (PTG106), the grains are subrounded to rounded, although some prismatic crystals were also observed, indicating short transport distance from the source. The youngest age found in a population of 30 grains was 1668 ± 23 Ma, which points to a Late Paleoproterozoic (Statherian) maximum sedimentation age. Another younger grain of 1623 Ma was 32% discordant and had to be excluded. Most of the population is Archean (43% of sample), but with a significant population of Statherian zircon grains (33% of sample), followed by 23% Rhyacian grains (Fig. 17A).

Thirty-one analyses were performed on thirty zircon grains in the second conglomerate sample (PTG93) and showed the youngest age of 1753 ± 32 Ma. 43% of the zircon grains are Archean and 57% are Paleoproterozoic and the main peak ages are at 1764, 2055, 2145, 2680, 2855, and 3114 Ma (Fig. 17B). One of the grains (e.4 – Appendix E) exhibited an alteration halo with very low Th/U ratio (0.005) and an age of 506 ± 6 Ma.

The quartzite sample (PTG226) is comparatively zircon rich with well-rounded grains. Thirty-three crystals were analyzed, with ages varying from 1728 ± 16 Ma (Statherian) up to 3266 ± 10 Ma (Paleoarchean – Fig. 17C). The main sources of this quartzite are Archean rocks (73% of the detrital material), with age peaks at 2589, 2796, 2800, and 2908 Ma. Six zircon grains (18%) are Rhyacian, with a peak at 2140 Ma. Only one grain is Statherian (1728 Ma) and two are Orosirian (1806 Ma and 1967 Ma).

8.2. Sm–Nd

Geochemical analyses of the orthoamphibolites from the Pedro Lessa Suite (906 Ma; Machado et al., 1989) in the MER indicate tholeiitic basaltic composition with subalkaline to alkaline affinity (Silveira Braga, 2012). The model-ages (T_{DMM} – depleted mantle MORB model) calculated from the Sm–Nd isotopic analyses (Table 4) of three samples vary from 1.46 to 1.78 Ga. The expected model ages would be slightly older than the crystallization age (~1000 Ma), considering the juvenile input from the mantle-derived basaltic magma. The relatively old T_{DMM} model ages in the 1.46–1.78 Ga range, however, suggest that the mantle-derived magma was isotopically contaminated by host rocks along the ascent pathway, particularly in the samples 7-02 and 11-505. Isotopic contamination is a common feature of basaltic magmas (e.g.: Bacon et al., 1994; Paslik et al., 1996; Baker et al., 2000), especially when the upper part of the magma trajectory is dominated by sedimentary rocks, which in the present case would be the units of

Table 3

Average values of the RRE + Y grades in itabirite from: Morro Escuro Ridge; Itabira Group (avg. data from [Spier et al., 2007](#)); Serro Group (Morro do Pilar region); Urucum (avg. data from [Klein and Ladeira, 2004](#)); Carajás (avg. data from [Figueiredo e Silva et al., 2008](#)); Isua (avg. data from [Polat and Frei, 2005](#)); Witwatersrand Supergroup (South Africa), Kuruman (South Africa), Brockman (Western Australia), Biwabik (USA) (single analyses from [Planavsky et al., 2010](#)). The average value from the Morro Escuro Ridge was calculated excluding the Ce-allanite- and amphibole-bearing samples (007-701, 008-701, 009-001).

	Brazilian BIFs						Worldwide BIFs				
	Morro Escuro	Itabira group – quartz itabirite	Itabira group – dolomite-itabirite	Serro group	Urucum	Carajás	Biwabik	Brockman	Kuruman	Witwatersrand	Isua
(Pr/Yb) _(SN)	0.28	0.33	0.27	0.39	0.35	1.18	0.78	0.25	0.20	0.44	0.60
Eu/Eu _(SN)	1.53	1.57	1.65	1.31	1.29	3.07	1.19	1.81	1.64	1.76	3.03
Ce/Ce _(SN)	1.14	0.81	0.82	0.99	1.65	0.74	0.89	0.80	0.78	0.86	0.91
Y/Ho	39.53	35.17	37.20	41.43	–	–	38.30	40.14	50.74	33.13	43.99

the Espinhaço Supergroup. The $\epsilon_{\text{Nd}}(t = 1000)$ values are in the +3.57 and –0.64 range, indicating less contamination of the juvenile mafic magma in sample 5-513 and more contamination in samples 7-02 and 11-505.

The geochemical characteristics and ages are similar to those obtained by [Dussin \(1994\)](#), [Silva et al. \(1995\)](#), [Babinski et al. \(2005\)](#), [Gradim et al. \(2005\)](#) and [Martins \(2006\)](#) for the source magma from the Tonian mafic rocks associated with the rift phase volcanism of the Macaúbas Basin ([Dussin, 1994](#); [Noce et al., 1997](#)).

9. Discussion and conclusions

The lithostratigraphic units that crop out in the MER inlier comprise metagranitic-gneissic rocks, an itabirite-bearing psammo-pelitic metasedimentary sequence and meta-amphibolitic dikes/sills, which underwent low-to intermediate-grade metamorphism ([Tables 1 and 2](#)). The tectonically intercalated and strongly sheared slices of the Borrachudos Suite granite could be distinguished from the equally common Archean TTG orthogneiss through comparative analyses of our geochemical data with earlier results from both units as delivered by different authors ([Dussin, 1994](#); [Fernandes, 2001](#); [Oliveira, 2002](#)) ([Figs. 8 and 9](#)).

SHRIMP data of detrital zircon grains of the BIF-related upper quartzitic unit of the MER sequence suggest a maximum upper Statherian age (1668 Ma) for the supracrustal rocks, much younger than the Guanhães Complex (2867 ± 10 , [Silva et al., 2002](#)) as purported by [Grossi-Sad et al. \(1997\)](#), and than the quartzites from the Lower Paleoproterozoic Minas Supergroup. These results also indicate that the psammitic layer is correlatable with the basal units of the Espinhaço Supergroup (Bandeirinha and São João da Chapada Formations) that, according to [Chemale Jr. et al. \(2012\)](#), were deposited between 1800 Ma and 1680 Ma. The recurrent main age peaks obtained in the three histograms ([Fig. 17](#)) are also in agreement with the evidence of these authors that suggested long periods of intense felsic activity during the Rhyacian and Archean times.

The associated itabirite layer has a relatively simple mineralogical composition with quartz and specularite as oriented plates that usually define a transposition foliation. The psammitic rocks as well as the itabirite have undergone an intense but progressive shear deformation with the generation of rootless intrafolial folds and a pervasive schistosity related to the development of Brasiliano orogenic thrust planes ([Pagung de Carvalho et al., 2014](#)). Syn- and post-tectonic blastesis and secondary grain growth of magnetite/

Fig. 15. Average (REE + Y)_{SN} spidergrams from Brazilian BIFs: Urucum ([Klein and Ladeira, 2004](#)), Serro Group near Morro do Pilar, Cauê Formation of the Itabira Group, Quadrilátero Ferrífero ([Spier et al., 2007](#)), Carajás ([Figueiredo e Silva et al., 2008](#)).

Fig. 16. Comparative plot of Morro Escuro rare earth distribution with (REE + Y)_{SN} spidergrams from BIFs worldwide: Isua (avg. data from [Polat and Frei, 2005](#)); Witwatersrand Supergroup (South Africa), Kuruman (South Africa), Brockman (Western Australia), Biwabik (USA) (single plots from [Planavsky et al., 2010](#)).

Fig. 17. Probability diagrams for the ages obtained in zircon grains from the metaconglomerate (A and B) and the quartzite (C).

martite blasts have further contributed to the destruction of primary features of the rocks.

The total obliteration of sedimentary features from all units and the limited geographic extension of the sequence prevent a more definitive conclusion about the basinal environment and stratigraphic position. Nevertheless, the structural characteristics, the compositional and mineralogical homogeneity of the itabirite layer, its association with the Statherian quartzites and metaconglomerates and the lack of extensive carbonate layers supports its correlation with the itabirite from the Serra Group (Grossi-Sad et al., 1997), as described at the Serra da Serpentina and Serra do Sapo ridges and other similar ridges such as those in the Morro do Pilar (Dossin, 1985; Zacchi, 2010; Rolim and Rosière, 2011) and also precludes a correlation with the complex variegated and polydeformed Minas Supergroup.

The geochemical characteristics and the lithologic association of the Morro Escuro itabirites are similar to other Paleoproterozoic sequences (Figs. 15 and 16) deposited in suboxic to anoxic platformal settings (Ce anomaly ~1 – Table 3 and Appendix C). REE + Y spidergrams from the analyzed samples compose a coherent group (Fig. 11A and B) but nonetheless, the wide variation of the values still needs to be elucidated. The low contents of Al₂O₃, TiO₂, Th, Hf and Sc and the hyperchondritic Y/Ho signature (Fig. 14) indicate a significant absence of terrigenous components and possibly

deposition under a shallow marine environment not very distant from the coastline. Pronounced Eu/Eu*_(CN) is observed in modern marine environments in high temperature (>250 °C) hydrothermal fluids, such as those typically emanating from mid-ocean ridges and back-arc spreading centers (Alexander et al., 2008). The positive but less expressive Eu anomaly (Eu/Eu*_(CN)) and the intermediate to low values of (Sm/Yb)_{CN} (Fig. 12) obtained from the Morro Escuro samples indicate the influence of a low temperature hydrothermal input (<200 °C) (Alexander et al., 2008; Danielson et al., 1992; Bau et al., 1996), or, alternatively, a weak contribution of high temperature fluids, due to its distal position with respect to the source vents. The similar and even lower Eu/Eu*_(CN) values from the Serra BIFs (Fig. 12) reinforce the correlation of both units, suggesting similar basin conditions or even greater distances of the deposition site from the hydrothermal source.

The alteration halo of zircon overgrowth with a very low Th/U ratio (0.005) of age 506 ± 6 Ma observed in one of the detrital zircon grains (e.4 – Appendix E) is caused by syn-metamorphic hydrothermal growth during the Brasiliano orogeny (from 800 to 500 Ma). This feature is often related to the presence of fluids and sometimes is called “hydrothermal zircon”. The local presence of Ce-allanite, responsible for the anomalous positive Ce/Ce*_(SN) values observed in two itabirite samples, and the relative enrichment of MgO and

Table 4

Sm–Nd isotopic data of amphibolite from the Morro Escuro Ridge. T_{DM}* = depleted mantle model, T_{DM}** = depleted mantle MORB model.

Sample	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd (±2SE)	T _{DM} * (Ga) (t = 1000 Ma)	T _{DM} ** (Ga) (t = 1000 Ma)	εNd (t = 1000 Ma)
7-02	5.817	25.881	0.1359	0.512261 ± 3	1.52	1.78	−0.64
11-505	11.083	54.928	0.122	0.512175 ± 2	1.43	1.65	−0.71
5-513	7.949	31.906	0.1506	0.512564 ± 3	1.15	1.46	+3.57

alkalis with the formation of Mg-hornblende and tschermakite, also indicate metasomatic alteration. These localized alteration events are probably coeval and suggest the presence of pegmatites and granites during the Brasiliano orogeny (Ribeiro-Althoff et al., 1997; Fernandes et al., 2000; Preinfalk et al., 2002). The alterations are possibly controlled by shear zones but also by the discontinuities along the contact zone of the Early Mesoproterozoic amphibolite dikes that might have contributed elements such as Mg for the hornblende in the itabirite. Despite the indications of metasomatism and hydrothermal alteration, large, economically important high-grade iron ore bodies (>64 wt% Fe) could not be found even after long and intensive detailed prospective campaigns.

The structural and metamorphic transformations of the supra-crustal rocks that took place throughout the evolution of the Espinhaço fold and thrust belt may have occurred during different pulses of the Brasiliano orogen. Both supracrustal rocks and basement units were involved in the development of imbricated tectonic slices and obliterated the internal structures. Major crustal thickening related to the stacking of the tectonic slices during successive orogenic pulses resulted in increasing metamorphic grade reaching temperatures which ranged from 512° to 560 °C (± 50 °C) and a pressure of 5.9 ± 1 kbar at the base of the MER. Olivo et al. (2011) interpret the wide variety of ages and cooling rates, observed in Ar–Ar geochronologic studies in metamorphic biotite, muscovite and hornblende crystals, as the result of a slow and gradual cooling process during erosional events after the tectonic uplift.

Acknowledgments

The authors would like to express their gratitude to TERRATIVA MINERAIS S.A., represented by Mr. I. G. Wender, which generously contributed to this project's financing, Centaurus Metals, particularly to Dr. K. Petersen, for supplying part of the samples, to the CNPq (Pr. nr. 472602/2009-8.) and FAPEMIG (Pr. Nr. APQ-00557-12) for additional funds. U–Pb analyses were performed using a SHRIMP II probe at the John DeLaeter Centre of the Curtin University, Perth Western Australia. We also thank S. Hagemann and an anonymous reviewer for constructive criticism and R. Fuck and J. Kellogg for the editorial handling.

Appendix A. Chemical composition of minerals

Garnet			
Sample	010-133,35	001-106,15	010-501
wt%			
SiO ₂	38.53	37.57	38.75
Al ₂ O ₃	20.98	21.49	21.79
MgO	1.95	3.86	2.91
CaO	7.39	0.33	6.18
MnO	1.45	0.04	1.20
FeO	29.22	36.39	30.69
Total	99.52	99.67	101.51
Si	3.07	3.01	3.03
Al _{IV}	–0.07	–0.01	–0.03
Al _{VI}	2.04	2.04	2.03
Fe ⁺²	1.95	2.44	2.01
Mg	0.23	0.46	0.34
Mn	0.10	0.00	0.08
Ca	0.63	0.03	0.52
Py	7.96	15.71	11.53
Al	66.97	83.25	68.21
Sp	3.37	0.09	2.69
Gr	21.70	0.96	17.58

Plagioclase		
Sample	010-133,35	010-501
wt%		
SiO ₂	43.90	59.61
Al ₂ O ₃	36.36	25.98
FeO	0.02	0.12
CaO	19.52	7.73
Na ₂ O	0.24	6.11
K ₂ O	0.00	0.02
Total	100.04	99.56
Si	8.11	10.63
Al	7.92	5.46
Fe	0.00	0.02
Ca	3.86	1.48
Na	0.08	2.11
K	0.00	0.00
Ano	97.84	41.09
Ab	2.14	58.77
Or	0.02	0.13

Biotite			
Sample	001-106,15	010-501	010-133,35
wt%			
SiO ₂	36.78	38.99	36.85
TiO ₂	1.86	1.44	2.30
Al ₂ O ₃	18.49	18.54	16.27
FeO	15.39	12.52	17.24
MgO	13.40	15.23	13.09
MnO	0.00	0.03	0.05
Na ₂ O	0.19	0.58	0.15
K ₂ O	9.47	8.14	9.39
H ₂ O ⁺	2.77	2.84	2.73
Total	98.35	98.48	98.08
Si	5.37	5.56	5.45
Al _{IV}	2.63	2.44	2.55
Al _{VI}	0.55	0.68	0.29
Ti	0.20	0.15	0.26
Fe ⁺²	1.88	1.49	2.13
Mn	0.00	0.00	0.01
Mg	2.92	3.24	2.88
Na	0.05	0.16	0.04
K	1.76	1.48	1.77
H ₂ O	2.70	2.70	2.70
%H ₂ O	2.77	2.84	2.73

Amphibole	
Sample	010-133,35
wt%	
SiO ₂	47.35
TiO ₂	0.30
Al ₂ O ₃	9.90
FeO	12.83
MgO	13.58
MnO	0.26
CaO	11.49
Na ₂ O	0.48
K ₂ O	0.31
H ₂ O ⁺	2.11
Total	98.59
Si	6.73
Al	1.66
Ti	0.03
Fe ⁺²	1.53
Mg	2.88
Mn	0.03
Ca	1.75
Na	0.13
K	0.06
OH	2.00
%H ₂ O	2.11

Appendix B. Chemical composition of the granite and gneiss

Sample	Detection limit	006-501	018-003	172-001	048-004	179-001	060	011-001	007-501	036-003	177-002
wt%	%										
SiO ₂	0.01	74.87	87.03	75.61	72.15	74.48	74.44	72.75	71.82	71.58	72.06
Al ₂ O ₃	0.01	11.93	7.12	13.13	14.77	13	13.67	14.47	14.98	13.4	14.48
Fe ₂ O ₃	0.01	2.2	1.09	2.31	1.83	2.29	1.34	1.35	2.02	3.26	2.12
MgO	0.01	0.54	0.24	0.19	0.5	0.34	0.27	0.3	0.88	0.42	0.57
CaO	0.01	0.71	0.04	2.32	1.74	0.96	0.92	1.1	0.94	2.06	2.18
Na ₂ O	0.01	1.84	0.28	3.84	4.47	2.98	3.59	4.44	3.24	2.27	4.48
K ₂ O	0.01	6.57	3.15	1.86	3.39	4.77	5.12	3.94	4.76	5.6	2.18
TiO ₂	0.01	0.22	0.1	0.24	0.25	0.24	0.15	0.19	0.23	0.38	0.24
P ₂ O ₅	0.01	0.02	0.04	0.05	0.07	0.06	0.06	0.05	0.07	0.1	0.08
MnO	0.01	0.04	0.02	0.03	0.02	0.04	0.03	0.03	0.03	0.04	0.02
Cr ₂ O ₃	0.002	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
LOI	−5.1	0.9	0.8	0.2	0.6	0.7	0.3	1.2	0.9	0.5	1.5
Sum		99.84	99.93	99.77	99.77	99.8	99.86	99.77	99.85	99.6	99.86
ppm											
Rb	0.1	287.4	161.5	43.9	78.5	164.8	231.6	116.7	125.2	192.3	70.5
Nb	0.1	35.5	9.7	26.9	3.3	6.4	10.5	7	5	31.1	3.3
Y	0.1	84	102	95.2	5.4	13.3	27.1	9.7	8.3	139	5
La	0.1	110.9	59	82.3	75.9	78.9	36.8	49.3	11.8	227.1	27.4
Ce	0.1	233.7	50.8	234.8	141.5	133.1	73.9	96.2	22.1	470.8	50.5
Pr	0.02	23.7	20.43	19.42	12.75	14.16	7.66	9.28	2.29	49.4	4.9
Nd	0.3	85.5	79.2	70.9	39.1	45.4	24.5	29.3	8	176.9	15.9
Sm	0.05	16.01	17.99	13.97	4.73	6.4	4.55	4.23	1.54	31.35	2.29
Eu	0.02	0.68	2.82	2.22	0.89	1.13	0.48	0.87	0.36	2.89	0.65
Gd	0.05	15.18	18.02	13.78	2.62	4.18	4.23	2.62	1.37	28.28	1.6
Tb	0.01	2.54	3.31	2.65	0.29	0.53	0.75	0.36	0.24	4.6	0.22
Dy	0.05	14.46	18.89	16	1.11	2.44	4.29	1.84	1.25	26.08	1.02
Ho	0.02	2.98	3.58	3.47	0.18	0.44	0.89	0.3	0.24	5.2	0.17
Er	0.03	8.38	9.71	10.15	0.44	1.16	2.63	0.77	0.75	13.44	0.43
Tm	0.01	1.22	1.41	1.44	0.07	0.18	0.4	0.12	0.13	1.85	0.06
Yb	0.05	7.7	8.89	8.69	0.34	1.15	2.55	0.69	0.76	10.77	0.38
Lu	0.01	1.15	1.2	1.29	0.07	0.2	0.4	0.1	0.13	1.45	0.06
ΣETR		524.10	295.25	481.08	279.99	289.37	164.03	195.98	50.96	1050.11	105.58
^a La/Yb _(CN)		9.73	4.48	6.40	150.85	46.36	9.75	48.28	10.49	14.25	48.73
^b Eu/Eu* _(CN)		0.07	0.24	0.24	0.35	0.31	0.16	0.37	0.37	0.15	0.49

Notes.

bdl – below detection limit.

^a ^bChondrite normalization based on [Evensen et al. \(1978\)](#).

^bEu/Eu*_(CN) = Eu_(CN)/Sm_(CN) + Gd_(CN).

Appendix C. Chemical composition of the itabirite from Morro Escuro Ridge.

Sample	Detection limit	001-701	002-701	003-701	004-701	005-701	006-701	007-701	008-701	010-701	011-701	013-701	014-701	015-701	002-001	009-001	013-001
wt%	%																
SiO ₂	0.01	48.13	50.7	51.38	52.93	50.43	60.25	59.28	67.83	47.9	61.06	52.71	50.04	52.46	53.62	52.43	59.07
Al ₂ O ₃	0.01	0.08	0.1	0.07	0.16	0.08	0.17	0.26	1.53	0.09	0.22	0.17	0.09	0.07	0.31	0.36	0.22
Fe ₂ O ₃	0.01	51.39	48.51	48.32	45.47	48.99	37.97	39.17	28.52	51.47	38.17	46.63	49.78	47.09	44.37	44.29	40.13
MgO	0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.74	bdl	bdl	bdl	bdl	bdl	0.04	0.25	bdl
CaO	0.01	0.02	bdl	0.09	0.34	0.1	0.02	0.1	0.38	0.09	bdl	0.13	0.06	0.03	0.99	0.82	0.04
Na ₂ O	0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.2	bdl	bdl	bdl	bdl	bdl	0.02	0.06	bdl
K ₂ O	0.01	bdl	0.01	bdl	bdl	bdl	0.02	0.02	0.4	bdl	bdl	bdl	bdl	bdl	0.02	0.02	0.04
TiO ₂	0.01	bdl	bdl	bdl	0.01	bdl	<0.01	0.01	0.06	bdl	0.01	0.01	bdl	bdl	0.04	0.03	0.02
P ₂ O ₅	0.01	0.06	0.05	0.04	0.27	0.09	bdl	0.11	0.14	0.07	0.04	0.12	0.07	0.04	0.71	0.49	0.04
MnO	0.01	0.06	0.03	0.07	0.03	bdl	0.03	0.01	0.18	0.08	0.03	0.02	0.04	0.01	0.07	0.06	0.04
Cr ₂ O ₃	0.002	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.003	bdl	bdl	0.002
LOI	−5.1	0.2	0.6	0	0.8	0.3	1.5	1.1	0	0.3	0.5	0.2	−0.1	0.3	−0.2	1.2	0.4
Sum		99.94	99.99	99.99	100.01	100.01	100.01	100.01	99.99	100.00	100.01	100.00	100.00	100.00	99.97	100.01	
ppm	ppm																
Hf	0.1	0.1	bdl	bdl	0.1	0.1	<0.1	0.1	0.8	bdl	0.2	bdl	bdl	bdl	0.2	0.3	0.2
Th	0.2	bdl	bdl	bdl	0.3	<0.2	<0.2	2.9	1.6	bdl	0.3	bdl	bdl	bdl	0.6	13.7	0.7
Sc	1	bdl	bdl	bdl	bdl	bdl	bdl	1	2	bdl	1	bdl	bdl	bdl	1	2	
Y	0.1	2.9	4.2	2.6	12.1	4.1	2.8	4.4	12.3	3.7	13.9	9.4	2.9	1.4	8.3	29.6	6.2
La	0.1	0.8	1.9	0.8	2	1.9	1.9	3.3	6.4	0.8	3	2	0.6	0.4	3.3	5.8	3.6
Ce	0.1	1.2	4.5	1	3.9	2.9	3	19.5	15.7	1.3	5.4	3	0.8	0.7	7.3	69.5	6.8
Pr	0.02	0.17	0.69	0.15	0.53	0.4	0.38	0.62	1.65	0.17	0.61	0.41	0.11	0.08	0.79	1.29	0.74
Nd	0.3	0.6	3.7	0.7	2.3	1.9	1.4	2.3	6.3	0.6	2.3	1.7	0.5	bdl	3.1	4.7	2.7
Sm	0.05	0.17	1.01	0.14	0.55	0.27	0.27	0.48	1.34	0.19	0.47	0.4	0.16	0.08	0.61	1	0.51
Eu	0.02	0.07	0.2	0.06	0.22	0.1	0.11	0.15	0.51	0.08	0.2	0.19	0.07	0.04	0.2	0.34	0.18
Gd	0.05	0.22	1.31	0.18	0.84	0.33	0.33	0.44	1.46	0.28	0.71	0.59	0.23	0.11	0.63	1.26	0.57
Tb	0.01	0.04	0.2	0.03	0.15	0.06	0.05	0.07	0.24	0.05	0.14	0.11	0.04	0.03	0.1	0.3	0.1
Dy	0.05	0.28	0.99	0.21	1.08	0.33	0.34	0.42	1.53	0.31	1.02	0.71	0.26	0.19	0.66	3.03	0.61
Ho	0.02	0.08	0.16	0.06	0.28	0.09	0.08	0.13	0.36	0.08	0.33	0.2	0.07	0.04	0.2	0.97	0.16
Er	0.03	0.25	0.39	0.2	0.88	0.31	0.26	0.46	1.12	0.28	1.14	0.67	0.25	0.16	0.64	3.42	0.5
Tm	0.01	0.04	0.05	0.04	0.14	0.04	0.04	0.07	0.18	0.05	0.18	0.1	0.04	0.02	0.11	0.59	0.09
Yb	0.05	0.27	0.31	0.23	0.86	0.3	0.28	0.52	1.23	0.3	1.11	0.65	0.3	0.14	0.8	4.1	0.53
Lu	0.01	0.05	0.05	0.05	0.14	0.06	0.04	0.09	0.21	0.06	0.18	0.11	0.06	0.03	0.13	0.63	0.09
ΣETR		4.24	15.46	3.85	13.87	8.99	8.48	28.55	38.23	4.55	16.79	10.84	3.49	2.02	26.87	126.53	23.38
^a Pr/Yb _(SN)		0.20	0.71	0.21	0.20	0.43	0.43	0.38	0.43	0.18	0.18	0.20	0.12	0.18	0.32	0.10	0.45
^b Eu/Eu* _(SN)		1.74	0.90	1.89	1.57	1.61	1.91	1.60	1.80	1.69	1.60	1.86	1.80	1.66	1.61	1.28	1.61
^c Ce/Ce* _(SN)		0.75	0.88	0.66	0.87	0.77	0.81	3.13	1.11	0.81	0.92	0.76	0.71	0.90	1.04	5.86	0.96
^d Y/Y* _(SN)		1.53	0.83	1.83	1.75	1.88	1.35	1.48	1.32	1.86	1.87	1.97	1.70	1.28	1.79	1.35	1.57
Y/Ho		36.25	26.25	43.33	43.21	45.56	35.00	33.85	34.17	46.25	42.12	47.00	41.43	35.00	41.50	30.52	38.75
^e Pr/Yb _(CN)		1.14	4.03	1.18	1.12	2.41	2.46	2.16	2.43	1.03	0.99	1.14	0.66	1.03	1.79	0.57	2.53
^f Eu/Eu* _(CN)		0.55	0.27	0.58	0.49	0.51	0.56	0.49	0.55	0.53	0.53	0.60	0.56	0.65	0.49	0.46	0.51
^g Ce/Ce* _(CN)		0.37	0.46	0.32	0.44	0.37	0.39	1.51	0.56	0.40	0.45	0.37	0.34	0.44	0.52	2.88	0.47

Notes.

The negative sign of the loss on ignition (LOI) value indicates that there were no volatiles in the sample.

^{a b c d}PAAS normalization values based on McLennan (1989).

^{e f g}Chondrite normalization based on Taylor and McLennan (1985).

^bEu/Eu*_(SN) = Eu_(SN)/0.66Sm_(SN) + 0.33Tb_(SN).

^cCe/Ce*_(SN) = Ce_(SN)/0.5La_(SN) + 0.5Pr_(SN).

^dY/Y*_(SN) = Y_(SN)/0.5Dy_(SN) + 0.5Ho_(SN), ^eEu/Eu*_(CN) = Eu_(CN)/Sm_(CN) + Gd_(CN).

^gCe/Ce*_(CN) = Ce_(CN)/La_(CN) + Pr_(CN).

bdl – below detection limit.

Appendix D. Chemical composition of the itabirite from Morro do Pilar region

Sample	Detection limit	006-502	011-502	013-503	014-503	016-502	016-504	016-505	017-505	018-503	019-502	023-503	024-502	012-502
wt%	%													
SiO ₂	0.01	49.48	51.36	54.87	49.27	53.24	45.41	56.14	52.68	54.73	70.38	50.39	55.81	53.34
Al ₂ O ₃	0.01	0.13	0.11	0.24	0.29	0.33	0.13	0.15	0.39	0.16	0.68	1.88	1.52	0.11
Fe ₂ O ₃	0.01	50.03	48.12	44.11	49.79	45.32	54.10	43.16	46.24	44.64	27.97	43.73	41.49	46.36
MgO	0.01	bdl	0.04	bdl	0.06	bdl	bdl	bdl	0.12	bdl	0.02	1.23	0.07	bdl
CaO	0.01	bdl	0.03	bdl	0.02	bdl	bdl	0.04	0.02	bdl	0.01	0.41	bdl	bdl
Na ₂ O	0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.02	bdl
K ₂ O	0.01	0.01	bdl	0.05	0.05	0.03	bdl	0.02	0.06	bdl	0.10	0.21	0.44	bdl
TiO ₂	0.01	bdl	bdl	bdl	0.02	0.01	bdl	bdl	0.03	bdl	0.03	0.07	0.07	bdl
P ₂ O ₅	0.01	0.03	0.04	0.03	0.02	0.02	0.03	0.05	0.02	0.02	0.02	0.07	0.03	0.03
MnO	0.01	0.06	0.06	0.03	0.05	0.02	0.02	0.10	0.04	0.02	0.32	0.67	0.05	0.02
Cr ₂ O ₃	0.002	bdl	bdl	0.002	0.003	0.002	bdl	0.003	bdl	bdl	bdl	0.007	bdl	0.004
LOI	−5.1	0.2	0.2	0.6	0.4	1.0	0.3	0.3	0.4	0.4	0.4	1.3	0.4	0.1
Sum		99.94	99.96	99.93	99.97	99.97	99.99	99.96	100.00	99.97	99.93	99.97	99.90	99.96
ppm	ppm													
Hf	0.1	0.4	0.2	0.1	bdl	0.1	bdl	0.2	0.7	bdl	0.5	0.8	0.7	0.2
Th	0.2	0.3	bdl	0.3	0.4	0.3	bdl	bdl	1.1	0.2	0.7	2.1	2.4	0.3
Sc	1	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1	2	1	bdl
Y	0.1	4.4	3.8	2.5	4.6	1.3	2.8	7.3	3.9	2.1	7.2	10.6	3.4	9.5
La	0.1	1.0	0.8	2.1	3.8	1.1	0.4	1.1	2.7	1.7	2.6	3.9	3.4	1.7
Ce	0.1	1.5	1.2	3.5	5.8	1.6	0.5	1.8	5.8	7.5	5.1	8.5	6.3	2.6
Pr	0.02	0.20	0.15	0.41	0.67	0.14	0.07	0.27	0.64	0.29	0.58	0.95	0.63	0.33
Nd	0.3	0.8	0.7	1.9	2.9	0.5	0.4	1.4	2.5	1.1	2.5	3.7	1.9	1.5
Sm	0.05	0.20	0.15	0.45	0.61	0.10	0.11	0.45	0.41	0.31	0.50	1.05	0.31	0.39
Eu	0.02	0.06	0.06	0.11	0.16	0.03	0.05	0.20	0.09	0.03	0.21	0.28	0.07	0.10
Gd	0.05	0.31	0.24	0.60	0.48	0.09	0.20	0.58	0.35	0.28	0.77	1.19	0.28	0.67
Tb	0.01	0.05	0.04	0.08	0.07	0.02	0.03	0.10	0.06	0.04	0.13	0.19	0.05	0.14
Dy	0.05	0.38	0.35	0.34	0.42	0.13	0.21	0.66	0.36	0.23	0.93	1.08	0.36	0.94
Ho	0.02	0.09	0.10	0.07	0.10	0.03	0.06	0.18	0.09	0.05	0.22	0.27	0.08	0.24
Er	0.03	0.32	0.27	0.18	0.32	0.11	0.17	0.50	0.31	0.15	0.66	0.80	0.29	0.78
Tm	0.01	0.05	0.05	0.03	0.06	0.02	0.03	0.08	0.05	0.03	0.11	0.12	0.05	0.11
Yb	0.05	0.29	0.29	0.20	0.35	0.12	0.18	0.56	0.29	0.15	0.71	0.82	0.33	0.61
Lu	0.01	0.05	0.05	0.03	0.07	0.03	0.03	0.10	0.06	0.02	0.13	0.13	0.06	0.10
ΣETR		5.30	4.45	10.00	15.81	4.02	2.44	7.98	13.71	11.88	15.15	22.98	14.11	10.21
^a Pr/Yb _(SN)		0.22	0.17	0.65	0.61	0.37	0.12	0.15	0.70	0.62	0.26	0.37	0.61	0.17
^b Eu/Eu* _(SN)		1.23	1.59	1.16	1.45	1.36	1.79	1.93	1.12	0.52	1.69	1.26	1.11	0.87
^c Ce/Ce* _(SN)		0.77	0.79	0.87	0.83	0.90	0.68	0.76	1.02	2.44	0.96	1.02	0.99	0.80
^d Y/Y* _(SN)		1.89	1.60	1.29	1.79	1.66	1.97	1.68	1.72	1.56	1.27	1.56	1.60	1.59
Y/Ho		48.89	38.00	35.71	46.00	43.33	46.67	40.56	43.33	42.00	32.73	39.26	42.50	39.58
^e Pr/Yb _(CN)		1.25	0.94	3.71	3.47	2.11	0.70	0.87	3.99	3.50	1.48	2.10	3.46	0.98
^f Eu/Eu* _(CN)		0.37	0.48	0.32	0.44	0.47	0.51	0.60	0.35	0.15	0.52	0.38	0.36	0.30
^g Ce/Ce* _(CN)		0.37	0.38	0.42	0.40	0.42	0.33	0.38	0.50	1.16	0.47	0.51	0.47	0.39

Notes.
a b c d) PAAS normalization values based on McLennan (1989).
e f) g) Chondrite normalization based on Taylor and McLennan (1985).
^bEu/Eu*_(SN) = Eu_(SN)/0.66Sm_(SN) + 0.33Tb_(SN).
^cCe/Ce*_(SN) = Ce_(SN)/0.5La_(SN) + 0.5Pr_(SN).
^dY/Y*_(SN) = Y_(SN)/0.5Dy_(SN) + 0.5Ho_(SN).
^fEu/Eu*_(CN) = Eu_(CN)/Sm_(CN) + Gd_(CN).
^gCe/Ce*_(CN) = Ce_(CN)/La_(CN) + Pr_(CN).
bdl – below detection limit.

Appendix E. U–Pb–Th SHRIMP data

U–Pb–Th SHRIMP data of detrital zircon grains from sample PTG106.

Spot	U ppm	Th ppm	²³² Th/ ²³⁸ U	²⁰⁶ Pb ppm	4f ²⁰⁶ %	²⁰⁷ Pb/ ²⁰⁶ Pb	±	²⁰⁷ Pb/ ²³⁵ U	±	²⁰⁶ Pb/ ²³⁸ U	±	Error correlation	²⁰⁸ Pb/ ²³² Th	±	Age ²⁰⁶ Pb/ ²³⁸ U	±	Age ²⁰⁶ Pb/ ²⁰⁷ Pb	±	Disc. %
D.1-1	262	214	0.84	71.1	0.00	0.10667	0.65	4.6463	1.53	0.3159	1.39	0.907	0.0913	1.57	1770	22	1743	12	–2
D.1-2	294	154	0.54	102.8	0.22	0.17350	0.53	9.7109	1.38	0.4059	1.28	0.925	0.1036	1.77	2196	24	2592	9	15
D.1-3	194	135	0.72	65.4	0.00	0.13824	0.81	7.4771	1.58	0.3923	1.36	0.860	0.1075	1.72	2133	25	2205	14	3
D.1-4	109	65	0.62	29.9	0.00	0.10692	0.97	4.7228	1.79	0.3204	1.50	0.839	0.0895	1.95	1791	24	1748	18	–3
D.2-1	101	42	0.44	30.5	0.50	0.13282	1.55	6.4144	2.18	0.3503	1.53	0.702	0.1084	3.87	1936	26	2136	27	9
D.2-4	400	50	0.13	165.9	0.03	0.19986	0.35	13.3016	1.29	0.4827	1.24	0.962	0.1289	2.46	2539	26	2825	6	10
D.3-1	208	84	0.42	90.0	0.12	0.19636	0.66	13.6141	1.49	0.5029	1.33	0.895	0.1285	1.92	2626	29	2796	11	6
D.3-2	301	228	0.78	155.4	0.03	0.26162	0.32	21.6967	1.32	0.6015	1.28	0.971	0.1522	1.40	3036	31	3257	5	7
D.3-3	122	62	0.52	58.5	0.20	0.22055	0.64	17.0043	1.60	0.5592	1.47	0.916	0.1408	2.43	2863	34	2985	10	4
D.5-1	119	60	0.52	54.1	0.06	0.19991	0.60	14.6355	1.59	0.5310	1.48	0.927	0.1420	1.86	2746	33	2825	10	3
D.5-2	111	118	1.10	34.2	0.00	0.12553	0.85	6.2057	1.74	0.3586	1.51	0.872	0.0974	1.78	1975	26	2036	15	3
D.5-3	224	118	0.54	97.5	0.02	0.18515	0.45	12.9330	1.40	0.5066	1.32	0.946	0.1346	2.27	2642	29	2700	7	2
D.5-5	74	34	0.47	35.8	–0.14	0.20712	0.90	16.1018	1.92	0.5638	1.70	0.883	0.1505	2.93	2882	39	2883	15	0
D.6-1	134	95	0.73	34.4	0.12	0.10657	0.95	4.3834	1.75	0.2983	1.47	0.842	0.0842	1.86	1683	22	1742	17	3
D.6-4	121	110	0.93	55.0	0.08	0.19941	0.62	14.5081	1.59	0.5277	1.47	0.922	0.1405	1.73	2732	33	2821	10	3
D.6-3	159	153	0.99	38.1	0.27	0.10239	1.26	3.9253	1.91	0.2781	1.44	0.751	0.0786	1.90	1582	20	1668	23	5
D.6-2	40	33	0.85	10.4	0.06	0.10690	2.33	4.4365	3.11	0.3010	2.05	0.660	0.0824	3.55	1696	31	1747	43	3
D.7-1	255	77	0.31	109.9	0.06	0.19860	0.40	13.7201	1.54	0.5010	1.48	0.965	0.1264	2.12	2618	32	2815	7	7
D.7-2	108	59	0.57	39.5	0.02	0.14303	0.73	8.4108	1.82	0.4265	1.66	0.916	0.1177	2.01	2290	32	2264	13	–1
D.7-3	270	26	0.10	76.0	0.02	0.12781	0.56	5.7634	1.65	0.3271	1.55	0.941	0.1014	3.19	1824	25	2068	10	12
D.8-1	275	229	0.86	114.6	0.13	0.18335	0.54	12.2479	2.59	0.4845	2.54	0.978	0.1214	2.67	2547	53	2683	9	5
D.8-2	202	258	1.32	106.7	0.02	0.26831	0.48	22.7538	1.52	0.6150	1.44	0.948	0.1570	1.58	3090	35	3296	8	6
D.8-3	315	287	0.94	79.4	0.14	0.12017	0.82	4.8525	1.52	0.2929	1.28	0.840	0.0834	1.58	1656	19	1959	15	15
D.8-4	264	242	0.95	79.0	0.06	0.12455	0.74	5.9707	1.57	0.3477	1.38	0.882	0.0934	1.63	1924	23	2022	13	5
D.9-1	656	126	0.20	105.4	0.36	0.09993	1.03	2.5690	1.59	0.1865	1.21	0.760	0.0533	4.06	1102	12	1741	19	32
D.9-2	236	141	0.62	60.9	0.04	0.10630	1.03	4.4089	1.69	0.3008	1.34	0.792	0.0830	1.96	1695	20	1737	19	2
D.9-3	89	75	0.88	24.2	0.45	0.10740	1.86	4.6584	2.54	0.3146	1.73	0.681	0.0842	2.73	1763	27	1756	34	0
D.10-1	152	164	1.12	39.7	0.14	0.10539	1.13	4.4228	1.86	0.3044	1.48	0.795	0.0841	1.85	1713	22	1721	21	0
D.10-2	65	26	0.41	32.8	0.12	0.22360	0.91	18.0096	2.03	0.5842	1.81	0.894	0.1492	2.74	2966	43	3007	15	1
D.12-2	73	43	0.61	20.2	0.15	0.10714	1.43	4.7641	2.23	0.3225	1.72	0.768	0.0894	2.55	1802	27	1751	26	–3

Notes: Isotopic ratios errors in %.

All Pb in ratios are radiogenic component. All corrected for ²⁰⁴Pb.

disc. = discordance. As $100 - 100 \{ [t^{206}\text{Pb}/^{238}\text{U}] / [t^{207}\text{Pb}/^{206}\text{Pb}] \}$.

4f²⁰⁶ = (common ²⁰⁶Pb)/(total measured ²⁰⁶Pb) based on measured ²⁰⁴Pb.

Uncertainties are 1σ; n.a. = not available.

U–Pb–Th SHRIMP data of detrital zircon grains from sample PTG93.

Spot	U ppm	Th ppm	²³² Th/ ²³⁸ U	²⁰⁶ Pb ppm	4f ²⁰⁶ %	²⁰⁷ Pb/ ²⁰⁶ Pb	±	²⁰⁷ Pb/ ²³⁵ U	±	²⁰⁶ Pb/ ²³⁸ U	±	Error correlation	²⁰⁸ Pb/ ²³² Th	±	Age ²⁰⁶ Pb/ ²³⁸ U	±	Age ²⁰⁶ Pb/ ²⁰⁷ Pb	±	Disc. %
E.1-1	311	98	0.33	92.6	−0.01	0.12559	0.53	6.00	1.39	0.3466	1.28	0.924	0.0972	1.63	1918	21	2037	9	6
E.1-2	39	26	0.696	10.2	0.00	0.10721	1.73	4.5694	2.72	0.3091	2.10	0.772	0.0889	2.97	1736	32	1753	32	1
E.1-3	117	37	0.323	31.9	0.91	0.18179	1.62	7.8879	2.24	0.3147	1.55	0.690	0.1216	5.91	1764	24	2669	27	34
E.2-1	362	158	0.452	131.5	0.04	0.16960	0.51	9.8920	1.37	0.4230	1.27	0.928	0.1102	1.59	2274	24	2554	9	11
E.2-2	194	145	0.772	83.8	0.09	0.21483	0.49	14.8491	1.42	0.5013	1.34	0.939	0.1405	1.58	2619	29	2942	8	11
E.2-4	294	147	0.517	123.6	0.00	0.18287	0.45	12.3209	1.35	0.4887	1.28	0.942	0.1323	1.45	2565	27	2679	7	4
E.3-1	278	128	0.477	130.6	0.02	0.20086	0.38	15.1436	1.40	0.5468	1.35	0.962	0.1437	1.56	2812	31	2833	6	1
E.3-2	196	178	0.940	62.4	0.05	0.12918	0.90	6.6152	1.63	0.3714	1.35	0.832	0.1050	1.57	2036	24	2087	16	2
E.3-3	244	101	0.428	67.0	0.00	0.12344	0.61	5.4396	1.52	0.3196	1.39	0.915	0.1150	1.64	1788	22	2007	11	11
E.4-1	1208	6	0.005	84.6	−0.04	0.05726	1.03	0.6440	1.58	0.0816	1.20	0.760	0.0422	42.32	506	6	502	23	−1
E.4-2	114	95	0.864	40.2	0.15	0.13834	0.96	7.8163	1.76	0.4098	1.47	0.838	0.1140	1.95	2214	28	2207	17	0
E.4-3	101	83	0.842	43.9	0.08	0.19787	0.72	13.7271	1.65	0.5031	1.48	0.900	0.0848	8.40	2627	32	2809	12	6
E.5-1	144	124	0.885	44.6	0.00	0.12579	0.76	6.2288	1.62	0.3591	1.44	0.885	0.0990	1.69	1978	24	2040	13	3
E.5-2	49	40	0.856	16.5	0.30	0.13025	1.81	7.0573	2.60	0.3930	1.87	0.719	0.1112	3.00	2137	34	2101	32	−2
E.5-3	77	52	0.705	27.4	0.29	0.13350	1.67	7.6021	2.33	0.4130	1.63	0.699	0.1134	3.20	2229	31	2144	29	−4
E.6-1	127	103	0.839	34.2	0.08	0.10772	1.26	4.6621	1.94	0.3139	1.48	0.761	0.0890	2.06	1760	23	1761	23	0
E.6-2	143	61	0.440	61.7	0.04	0.18461	0.64	12.8018	1.56	0.5029	1.42	0.911	0.1352	3.25	2626	31	2695	11	3
E.6-3	157	126	0.832	40.0	0.10	0.10776	1.30	4.4101	1.94	0.2968	1.44	0.740	0.0881	2.47	1675	21	1762	24	5
E.6-4	102	70	0.708	28.2	0.11	0.10863	1.38	4.8156	2.07	0.3215	1.54	0.744	0.0908	2.37	1797	24	1777	25	−1
E.7-1	125	195	1.61	39.6	0.77	0.12699	3.16	6.41	3.57	0.3661	1.67	0.468	0.1037	2.84	2011	29	2057	56	2
E.7-2	80	17	0.223	26.8	0.33	0.13328	1.30	7.1350	2.20	0.3883	1.78	0.807	0.1029	6.12	2115	32	2142	23	1
E.7-3	313	162	0.536	126.4	0.03	0.17640	0.40	11.4273	1.51	0.4698	1.46	0.965	0.1283	1.63	2483	30	2619	7	5
E.8-1	87	71	0.842	45.0	0.02	0.23919	0.60	19.7697	1.80	0.5995	1.70	0.942	0.1639	1.90	3028	41	3115	10	3
E.8-2	83	45	0.557	42.4	0.26	0.26882	0.66	22.0542	1.93	0.5950	1.82	0.940	0.1553	2.67	3010	44	3299	10	9
E.8-3	70	38	0.565	25.3	0.36	0.14654	1.36	8.4990	2.30	0.4206	1.85	0.805	0.1096	3.56	2263	35	2306	23	2
E.8-4	102	80	0.811	35.6	0.21	0.14232	0.92	7.9195	1.95	0.4036	1.71	0.880	0.1092	2.16	2185	32	2256	16	3
E.9-1	101	41	0.417	33.3	0.19	0.13135	1.15	6.9519	2.06	0.3838	1.70	0.828	0.1092	3.18	2094	30	2116	20	1
E.9-2	70	74	1.091	37.1	0.07	0.23736	0.68	20.1939	1.92	0.6170	1.79	0.934	0.1627	2.08	3098	44	3102	11	0
E.9-3	380	111	0.303	128.8	0.05	0.20350	0.36	11.0705	1.53	0.3945	1.48	0.972	0.1014	1.79	2144	27	2854	6	25
E.9-4	81	35	0.448	39.4	0.08	0.21746	0.69	16.9792	1.88	0.5663	1.75	0.931	0.1505	2.55	2893	41	2962	11	2
E.9-5	242	232	0.990	73.9	0.02	0.13348	0.56	6.5372	1.68	0.3552	1.58	0.943	0.0895	4.39	1959	27	2144	10	9

Notes: Isotopic ratios errors in %.

All Pb in ratios are radiogenic component. All corrected for ²⁰⁴Pb.disc. = discordance, as 100 − 100{[²⁰⁶Pb/²³⁸U]/[²⁰⁷Pb/²⁰⁶Pb]}.4f²⁰⁶ = (common ²⁰⁶Pb)/(total measured ²⁰⁶Pb) based on measured ²⁰⁴Pb.

Uncertainties are 1σ; n.a. = not available.

U–Pb–Th SHRIMP data of detrital zircon grains from sample PTG226.

Spot	U ppm	Th ppm	²³² Th/ ²³⁸ U	²⁰⁶ Pb ppm	4f ²⁰⁶ %	²⁰⁷ Pb/ ²⁰⁶ Pb	±	²⁰⁷ Pb/ ²³⁵ U	±	²⁰⁶ Pb/ ²³⁸ U	±	Error correlation	²⁰⁸ Pb/ ²³² Th	±	Age ²⁰⁶ Pb/ ²³⁸ U	±	Age ²⁰⁶ Pb/ ²⁰⁷ Pb	±	Disc. %
C.1-1	169	77	0.47	81.7	0.11	0.20991	0.53	16.3015	1.52	0.5632	1.42	0.938	0.1383	2.01	2880	33	2905	9	1
C.1-2	220	227	1.07	101.0	0.06	0.20335	0.44	14.9962	1.44	0.5349	1.37	0.952	0.0739	1.63	2762	31	2853	7	3
C.1-3	226	15	0.07	105.5	0.08	0.19831	0.43	14.8660	1.43	0.5437	1.36	0.954	0.0907	5.46	2799	31	2812	7	0
C.1-4	44	18	0.42	15.0	0.14	0.13289	1.58	7.2243	2.53	0.3943	1.98	0.782	0.1087	3.99	2143	36	2136	28	0
C.1-5	269	104	0.40	120.4	0.04	0.20349	0.42	14.6081	1.41	0.5206	1.34	0.955	0.1092	1.89	2702	30	2854	7	5
C.2-1	152	53	0.36	71.9	−0.04	0.21055	0.56	16.0259	1.66	0.5520	1.57	0.942	0.1438	2.09	2834	36	2910	9	3
C.2-2	172	86	0.52	80.9	0.08	0.20849	0.55	15.7529	1.64	0.5480	1.54	0.941	0.1418	1.99	2817	35	2894	9	3
C.2-3	212	141	0.69	94.6	−0.01	0.18558	0.50	13.3223	1.63	0.5206	1.55	0.952	0.1382	1.73	2702	34	2703	8	0
C.2-4	253	224	0.92	85.0	0.00	0.13344	0.59	7.1984	1.60	0.3912	1.48	0.929	0.1067	1.65	2129	27	2144	10	1
C.2-5	85	58	0.71	48.5	−0.02	0.26320	0.66	24.1981	1.83	0.6668	1.71	0.933	0.1751	2.04	3293	44	3266	10	−1
C.2-6	188	87	0.48	52.7	0.11	0.11039	0.89	4.9742	1.76	0.3268	1.52	0.863	0.0905	2.11	1823	24	1806	16	−1
C.2-7	154	60	0.40	69.8	0.05	0.20291	0.78	14.7563	1.73	0.5274	1.54	0.892	0.1351	2.09	2731	34	2850	13	4
C.2-8	192	89	0.48	89.7	0.06	0.21145	0.49	15.8564	1.66	0.5439	1.58	0.956	0.1363	1.90	2800	36	2917	8	4
C.2-9	165	284	1.78	50.5	0.18	0.17468	0.76	8.5627	1.75	0.3555	1.57	0.900	0.0825	1.80	1961	27	2603	13	25
C.2-10	178	223	1.29	56.8	0.09	0.19055	0.63	9.7244	2.05	0.3701	1.95	0.952	0.0448	2.91	2030	34	2747	10	26
C.2-11	136	84	0.64	69.6	0.22	0.21472	0.60	17.5761	1.74	0.5937	1.63	0.939	0.1526	2.09	3004	39	2942	10	−2
C.3-1	267	188	0.73	65.4	−0.06	0.10579	0.89	4.1626	1.63	0.2854	1.37	0.840	0.0798	1.77	1618	20	1728	16	6
C.3-2	237	64	0.28	79.7	0.03	0.13292	0.64	7.1552	1.51	0.3904	1.37	0.906	0.1062	2.15	2125	25	2137	11	1
C.3-3	135	82	0.63	62.4	0.03	0.19610	0.65	14.5802	1.68	0.5392	1.54	0.922	0.1419	2.02	2780	35	2794	11	0
C.3-4	185	55	0.31	61.5	0.05	0.13241	0.76	7.0793	1.59	0.3878	1.40	0.879	0.1091	2.32	2112	25	2130	13	1
C.3-5	90	44	0.50	39.5	0.04	0.17887	0.82	12.5456	1.77	0.5087	1.57	0.886	0.1357	2.22	2651	34	2642	14	0
C.4-1	87	50	0.59	39.5	−0.05	0.20573	0.78	14.9321	1.79	0.5264	1.61	0.901	0.1372	2.18	2726	36	2872	13	5
C.4-2	404	71	0.18	104.1	0.08	0.12076	0.80	4.9966	1.54	0.3001	1.32	0.856	0.0552	5.75	1692	20	1967	14	14
C.4-3	254	125	0.51	117.2	0.08	0.20033	0.57	14.8316	1.52	0.5370	1.41	0.928	0.1299	1.89	2771	32	2829	9	2
C.4-4	289	199	0.71	88.7	0.29	0.13311	0.91	6.5390	1.59	0.3563	1.31	0.821	0.1017	2.13	1965	22	2139	16	8
C.4-5	119	57	0.49	55.7	−0.05	0.20991	1.58	15.7216	2.23	0.5432	1.58	0.707	0.1434	2.68	2797	36	2905	26	4
C.4-6	258	84	0.34	115.0	0.01	0.19598	0.58	14.0441	1.50	0.5197	1.39	0.924	0.1362	2.06	2698	31	2793	9	3
C.4-7	192	124	0.67	87.0	0.11	0.20324	0.52	14.7589	1.50	0.5267	1.40	0.937	0.1329	1.71	2727	31	2852	9	4
C.4-8	193	226	1.21	81.0	0.16	0.19640	0.60	13.2197	1.58	0.4882	1.47	0.926	0.1170	1.69	2563	31	2797	10	8
C.5-1	77	47	0.64	35.3	0.12	0.22630	0.72	16.7187	1.94	0.5358	1.81	0.928	0.1463	2.38	2766	41	3026	12	9
C.5-2	186	66	0.37	56.5	0.20	0.12896	0.92	6.2799	1.81	0.3532	1.56	0.861	0.0724	3.58	1950	26	2084	16	6
C.5-3	379	94	0.26	123.1	0.16	0.17144	0.45	8.9267	1.57	0.3776	1.50	0.957	0.0355	7.27	2065	27	2572	8	20
C.5-4	196	35	0.18	81.1	0.08	0.17064	0.55	11.3460	1.62	0.4822	1.53	0.942	0.1213	3.30	2537	32	2564	9	1

Notes: Isotopic ratios errors in %.

All Pb in ratios are radiogenic component. All corrected for ^{204}Pb .disc. = discordance, as $100 - 100\{t[^{206}\text{Pb}/^{238}\text{U}]/t[^{207}\text{Pb}/^{206}\text{Pb}]\}$. $4f^{206}$ = (common ^{206}Pb)/(total measured ^{206}Pb) based on measured ^{204}Pb .Uncertainties are 1 σ ; n.a. = not available.

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