



U–Pb ages and Hf-isotope data of detrital zircons from the late Neoproterozoic–Paleoproterozoic Minas Basin, SE Brazil



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ABSTRACT

Because of its world-class iron ore deposits and promising Au and U mineralizations, the late Neoproterozoic to Paleoproterozoic Minas Basin (Minas Supergroup, SE of Brazil) is one of the best-studied basins in South America. However, the lack of datable interlayered volcanic rocks prevented discourse over ages of the strata, the sources and the nature of its ore deposits. In this paper, we present detrital zircon U–Pb age patterns coupled with Lu–Hf data for 18 samples, representing different stages of the Minas Basin evolution (~2000 analyzed zircons). Age spectra for the main basal unit (Moeda Formation) show a classic rift-related detrital zircon pattern, characterized by multiple autochthonous sources, which in turn are much older than the age of deposition. Maximum age for the rifting event is constrained at ca. 2600 Ma. Detritus accumulated at the base of the Minas Supergroup were derived from Archean source rocks and their sedimentation was marked by differential uplift of the Archean crust, shortly after the 2730–2600 Ma high-K calc-alkaline magmatism (Mamona Event). The age of the BIF deposits is younger than 2600 Ma, most likely coinciding with the great oxygenation event between 2400 and 2200 Ma and the precipitation of banded iron deposits worldwide. Detrital zircons from the topmost units of the Minas strata suggest that tectonic inversion and closure of the basin took place at ca. 2120 Ma with the deposition of the synorogenic Sabará Group. Rhyacian zircon supply showing juvenile Hf signatures gives evidence of a late Rhyacian amalgamation between the Mineiro Belt and the craton. The ϵ_{Hf} signatures support the hypothesis that the Archean crystalline crust of the craton was mostly built by crust–mantle mixing processes, with a successive decrease of ϵ_{Hf} values in zircons crystallized after 3250 Ma and minor mantle-like additions after Paleoproterozoic times. Regionally, our dataset supports previous interpretations of a long-lived evolution of the southern São Francisco Craton comprising a succession of convergent island arcs, small microplate collisions, and development of Archean convergent and divergent basins that evolved between Archean and Paleoproterozoic times.

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1. Introduction

The Minas Basin in the Quadrilátero Ferrífero (QF), SE Brazil, is a distinctive record of a continental rift that evolved into passive margin along the southern part of São Francisco Craton (Alkmim and Martins-Neto, 2012). The opening of the basin took place around the Archean–Proterozoic boundary, following a protracted history of late-Archean magmatic events (Lana et al., 2013) that coincided in time and space, to produce important U and Au mineralization at the base of the sequence (Machado et al., 1996; Rosière et al., 2008; Fig. 1a and b). These processes also interacted

in such a way that made the crust rigid and stable enough to preserve world-class deposits of banded iron formation deposited in the central part of the basin (Romano et al., 2013). Although the geological processes that contributed to this exceptional accumulation of metals have been much debated ever since the early studies of Dorr (1969), uncertainties in the source and age of sedimentation of the various strata have largely restricted our understanding evolution of this region.

Field-based mapping and early geochronological studies have long proposed that much, if not all, the evolution of the basin occurred in the Paleoproterozoic (Machado and Carneiro, 1992; Babinski et al., 1995 Figs. 1b and 2a, b). Subsequent reconnaissance U–Pb detrital zircons studies by Machado et al. (1996) supported previous interpretations of a rift to passive margin basin that began sedimentation after ca. 2600 Ma, straddling the Archean–

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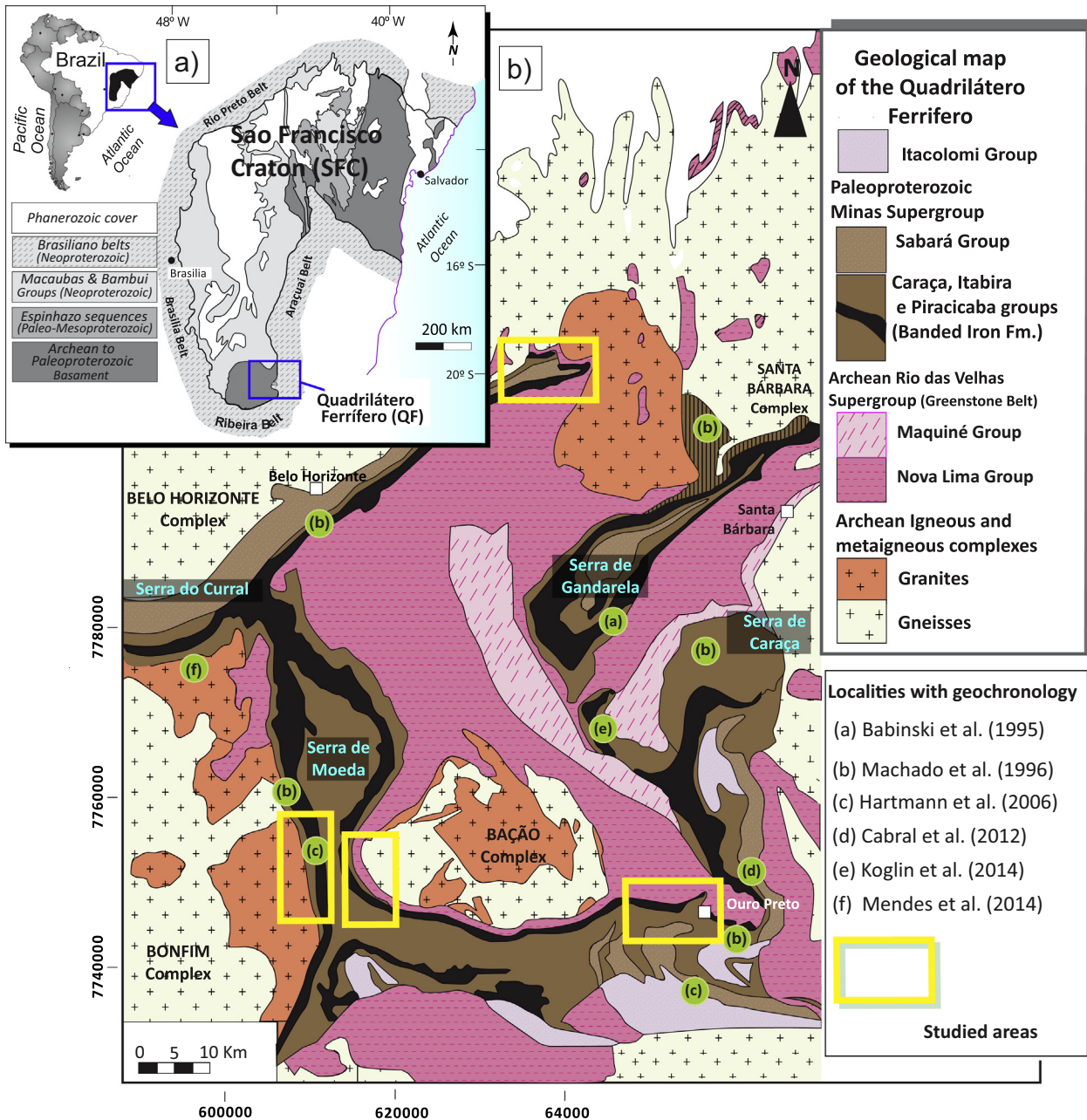


Fig. 1. a) Geological sketch of the São Francisco Craton showing the surrounding Ediacaran/Cambrian Brasiliano orogenic belts and in the south, the Quadrilátero Ferrífero (QF) district (blue box in b) (taken from Alkmim and Martins-Neto, 2012); b) Geological map with the main lithostratigraphic units of Quadrilátero Ferrífero. The regions considered in this study are also squared in yellow (based on Dorr, 1969; Farina et al., 2016 and references therein).

Proterozoic limit. Indeed, detailed work (U–Pb detrital zircon SHRIMP dating) by Hartmann et al. (2006) showed that the base of the sequence, Moeda Formation, should be younger than 2580 Ma, whereas the age of diagenesis of stromatolitic carbonates above Moeda Formation were dated as old as 2420 Ma (Pb–Pb isochron; Babinski et al., 1995), bracketing the age of the Cauê Banded Iron Formation –guide layer of the QF– (Fig. 2a). However, this Paleoproterozoic age range and the early view of a layer-cake stratigraphy for the basin was challenged by Cabral et al. (2012), and Cabral and Zeh (2015b). Cabral et al. (2012) obtained a U–Pb zircon age of ca. 2650 Ma for an alleged metavolcanic layer within the banded iron formation.

The closure of the Minas basin would have started after the deposition of the shallow to deltaic sequences – Piracicaba Group–, followed by a regional angular unconformity and the syn-

orogenic sediments of the Sabará Group (Fig. 2a; Reis et al., 2002). The passage from this coastal far sided environment to a chaotic deposit is still elusive. Available age dating of two single zircons detrital ages for the Sabará Group yielded ca. 2130 Ma (Machado and Carneiro, 1992; Machado et al., 1996).

One of the many problems in dating of the opening and the closure of the Minas Basin, as well as in constraining the age of the banded iron formation deposits, relates to the absence of fossils, interlayered volcanic beds, and of datable crosscutting igneous dykes or sills. Consequently, bracketing periods of sediment accumulation and timing the evolution of the Basin have been not easy (Fig. 2a). Important questions, such as the maximum age of deposition, source of sediments and tectonic framework of sediment accumulation, can nevertheless be quite satisfactorily addressed by combining a systematic dataset of detrital zircon ages (from

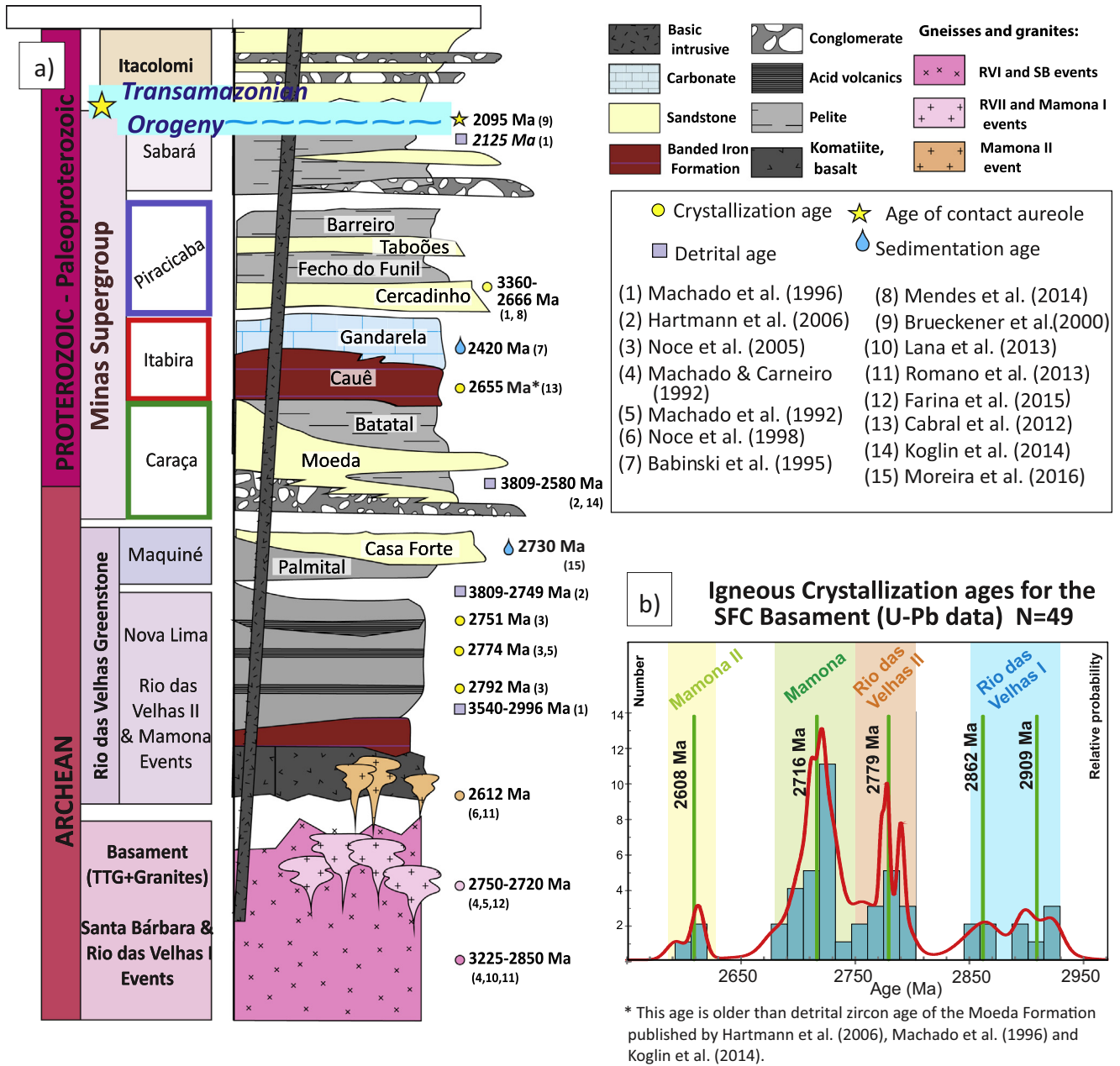


Fig. 2. a) Stratigraphic column with available age constraints and proposed tectonic models to explain the Archean and Paleoproterozoic rocks in the Quadrilátero Ferrífero (based on Dorr, 1969; Alkmim and Marshak, 1998; Alkmim and Martins-Neto, 2012 and references in the figure); b) Probability density diagram with five age populations of igneous rocks in the Southern São Francisco Craton (references herein and Farina et al., 2015): Santa Bárbara orthogneiss (SB), Rio das Velhas I TTG-resembling- Granite-Gneiss complex (RV I); Rio das Velhas 2 Granite- Gneisses (RV II) TTG-like- Granite-Gneiss complex, and high-K Granitoids and pegmatites (Mamona event I and II); Details in (Farina et al., 2015, 2016).

strategic areas of the QF) with a well constrained U–Pb and Hf-isotope database of the surrounding basement rocks.

In this paper, we present four stratigraphic logs across the Minas Supergroup from key areas of the Minas basin where the effects of the early tectonic events are believed to be minimum. The logs were tied with up to 2000 U–Pb detrital zircon ages determinations and 1100 Lu–Hf isotopic analyses (Fig. 1b). We combine this large dataset with U–Pb zircon ages of the surrounding basement rocks and underlying supracrustal rocks of the Rio das Velhas Greenstone Belt (Albert et al., 2016; Romano et al., 2013; Lana et al., 2013; Farina et al., 2016; Moreira et al., 2016) to explore: (1) the sources and depositional ages of the rift sediments and the overlying formations; (2) the sources and maximum ages of clastic deposits in some banded iron formation strata; (3) age con-

straints of the top units of the basin (Piracicaba and Sabará groups) to understand the significance of the discordance between the two cycles of the basin; (4) changes in nature and the age of the source (s) from the base to the top of the basin.

2. Background

The São Francisco Craton is located in the eastern portion of the Brazilian shield, encompassing several Archean blocks bounded by major 2100 to 2000 Ma suture zones (Almeida et al., 1981; Teixeira and Figueiredo, 1991; Barbosa and Sabaté, 2004). The southern part of the craton was built during a protracted magmatic evolution between 3220 and 2600 Ma (Figs. 1a and 2a). The construction

of the QF basement comprises a Paleo- to Mesoproterozoic stage of TTG-like medium-K magmatism and metamorphism (Carneiro, 1992; Noce et al., 1998; Teixeira et al., 1996; Romano et al., 2013; Lana et al., 2013) and a Neoproterozoic high-K granite magmatism stage (Farina et al., 2015), similar to the rocks produced in Phanerozoic convergent settings.

Recent field-based mapping, geochemistry and U–Pb geochronology (Lana et al., 2013; Farina et al., 2016) have divided the Archean evolution of the QF crystalline basement into several magmatic pulses. These are the Paleoproterozoic Santa Bárbara (3220–3200 Ma), the Mesoproterozoic Rio das Velhas I (2930–2900 Ma), the Neoproterozoic Rio das Velhas II (2800–2760 Ma) and the Mamona events (2750–2700 Ma and 2620–2580 Ma – referred here as Mamona I and II) (Fig. 2b).

The Rio das Velhas II and Mamona magmatic events (<2800 Ma) represent a subduction-collision cycle, contemporaneous with the deposition of gold-bearing re-sedimented, volcanic chemical, and mafic-ultramafic komatiitic associations at the base (Nova Lima Group, Baltazar and Zucchetti, 2007; Lobato et al., 2007) to continental clastic foreland deposits (Maquiné Group) of the Rio das Velhas Supergroup. The timing and conditions of metamorphic events related to the closure of the basin and intrinsic development of the Archean crust are still not well elucidated. U–Pb ages of syn-volcanic and clastic strata within the Nova Lima Group bracketed the felsic magmatic arc activity between 2790 and 2750 Ma and sedimentation as young as 2730 Ma for the siliciclastic rocks at the top (Noce et al., 2005; Moreira et al., 2016).

Shortly after the Mamona magmatic event, the São Francisco Craton crust experienced accumulation of a thick early Paleoproterozoic succession of clastic and chemical sediments of the Minas Supergroup, which is subdivided from base to top into the Caraça, Itabira, Piracicaba and Sabará groups (Dorr, 1969; Renger et al., 1995) (Fig. 1b). The Caraça Group (Vilaça, 1981) encompasses sandstones (Moeda Formation) and phyllites (Batatal Formation) that are observed throughout the QF. Batatal Formation marks a change from the clastic deposition of the Caraça Group to the biochemical accumulation of the overlying Itabira Group.

The Moeda Formation at the base of the Minas Supergroup, is further subdivided into three units, which from bottom to top consist of a basal sandstone and pyritiferous/auriferous metaconglomerate and (Unit I), intermediate phyllite and sandstones (Unit II) and a medium- to coarse-grained sandstone (Unit III) (Vilaça, 1981). The beginning of sedimentation of the Moeda Formation was proposed by Hartmann et al. (2006) to have started as early as 2580 ± 7 Ma based on U–Pb SHRIMP zircon dating of one sample from the western part of the Quadrilátero Ferrífero. This maximum depositional age overlaps well (within errors) with a range of detrital zircon ages obtained by Machado et al. (1996) and Neri et al. (2013). In contrast, recent U–Pb detrital zircon ages by Koglin et al. (2014) suggested a maximum age of sedimentation for the unit (II) at 2677 ± 6 Ma and top unit (III) at 2623 ± 14 Ma. Despite the presence of <2600 Ma zircons in some of their samples, Koglin et al. (2014) proposed that such zircons experienced partial Pb loss (Fig. 1b). Highly concordant zircons (95–98% of concordance) for a sample at the top of Moeda Formation (northwest of the Mariana syncline) within the range of 2530 and 2670 Ga were considered as altered by Cabral and Zeh (2015a) adding, even more, controversy to the depositional age of the unit.

After the marine sedimentation in the final stages of the Caraça Group (Batatal Formation), a major transgression is tracked leading to a period of chemical sedimentation. This event marked a change in the atmospheric conditions with the accumulation of an originally 250 m-thick package of Lake Superior-type banded-iron formation – the Cauê Formation – and stromatolite-rich carbonates of the Gandarela Formation. The Cauê Formation (Dorr, 1969; Klein and Ladeira, 2000) consists essentially of itabirites, i.e., the

local name for metamorphosed banded iron-formations, and is presently the most important economic unit of the Quadrilátero Ferrífero, hosting world-class hematite-rich iron ore deposits (Rosière et al., 2008). It is a greenschist- to amphibolite-facies metamorphosed hematite-rich rock that occurs in siliceous, dolomitic and amphibolitic varieties (Rosière et al., 2008). According to Spier et al. (2007), C and O isotopes and REE signatures suggest a marine origin for the sediments with very little terrigenous supply. Minor types of itabirites, including metavolcanic protoliths with N-MORB basalt affinity, were also proposed (Pires, 1983; Cabral and Zeh, 2015b). However, the proper identification of the primary lithologies is challenging due to the extended medium to high-grade Transamazonian (ca 2100 Ma) and Brasiliano (ca 480–680 Ma) metamorphic imprints and deep weathering that affected the sequences (Cabral and Zeh, 2015b). The depositional age of the Cauê Formation was conservatively bracketed between 2620 and 2420 Ma; i.e. between the maximum age of deposition of the top of the underlying Moeda Formation (Koglin et al., 2014) and the age of the overlying Gandarela Formation. This is inconsistent with U–Pb dating of zircon grains of 2655 ± 6 Ma obtained by Cabral et al. (2012) for an alleged metavolcanic layer. The interpretation of this age is controversial since it contradicts most of the already published data for the underlying Caraça Group.

The Gandarela Formation has a maximum average thickness of 750 m and is made up of dolomites, limestones, carbonaceous phyllites and dolomitic iron-rich formation in which stromatolitic structures are preserved (Souza and Müller, 1984). The contact between the Cauê and Gandarela formations is a 10 m-thick transitional zone of mostly dolostone. Age dating in the Gandarela Formation was provided by Babinski et al. (1995) who produced a Pb–Pb isochron age of 2420 ± 19 Ma. This age would be representing the sedimentation age of the carbonates, due to the preservation of organic structures and the absence of deformation.

The deltaic to shallow water marine sandstones and pelites of the Piracicaba Group (Dorr, 1969) overlie the Gandarela Formation through an erosive contact marked by the presence of a pebble-rich conglomerate that contains clasts from the underlying Itabira Group. Piracicaba Group is a ca. 1300 m-thick metasedimentary pile decreasing in grain size upwards mainly composed of quartz-rich ferruginous sandstones and conglomerates at the base interbedded with mudstones and highly pure sandstones at the top. The basal unit, Cercadinho Formation, comprises coarse to fine-grained hematite-rich sandstones, sandstones, silvery phyllites, and Fe-rich and non-rich phyllites and dolomites. Dorr (1969) pointed out that the absence of iron-rich levels within the sandstones of the Piracicaba Group suggests an important change in the prevailing atmospheric conditions. The base of the Piracicaba Group (Cercadinho Formation) contains detrital zircons with ages ranging from the Mesoproterozoic to the end of the Paleoproterozoic. The youngest zircon detrital populations for this unit in the Serra de Curral are ca. 2680 Ma and 2780 Ma (LA-ICPMS U–Pb dating; Mendes et al., 2014); however, these data are not useful to constrain the depositional age of the unit.

The stratigraphy of the Minas Supergroup is completed with the 3.5 km-thick Sabará Group (Reis et al., 2002). The contact with the underlying unit is erosive and marks a regional hiatus and a change in the overall conditions of sedimentation of the Minas Supergroup. The Supergroup comprises a coarsening upwards sequence of metapelites, wackes, lithic conglomerates, and diamictites (Renger et al., 1995; Reis et al., 2002) interpreted as a turbiditic, submarine fan deposit formed during the inversion of the Minas Supergroup passive margin (Alkmim and Marshak, 1998; Alkmim and Martins-Neto, 2012). Detrital zircon age distribution spectra for the Sabará Group show a few Proterozoic ages spreading between 2100 and 2500 Ma and a well-defined peak at 2850–

2900 Ma (Machado et al., 1996). This is remarkably different from the sources shown in the age distribution pattern collected close to the town of Ouro Preto obtained by Hartmann et al. (2006) which shows no Proterozoic ages and two major Archean peaks at ca. 2720 and 2890–2930 Ma. The depositional age of these sediments is additionally constrained by the single detrital idiomorphic zircon U–Pb TIMS in 2125 ± 4 Ma and 2131 ± 5 Ma (Machado et al., 1992, 1996). These ages are coeval with the climax of the magmatism in the terrains located to the east and south of the QF, interpreted respectively as continental and intra-oceanic arcs (Machado et al., 1992; Alkmim and Martins-Neto, 2012; Teixeira et al., 2015). On the top of the stratigraphic column of the QF and unconformably overlying the Minas Supergroup is the Itacolomi Group (Fig. 2a). Sericite bearing sandstones, non-sorted polymictic metaconglomerates, and minor phyllites built the 2 km-thick sequence (Dorr, 1969) that filled extensional structures

after 2100 Ma (Alkmim and Marshak, 1998). Age constraints on the deposition Itacolomi sediments are still loose. It was dated with a minimum zircon Pb–Pb age –no concordance control– as young as 2059 ± 58 Ma (Machado et al., 1996). Therefore, this foreland basin conditions that appear to be reflected towards the end of the Minas Supergroup and the beginning of the Itacolomi stage should show a change in the sediment source and/or in the character of the basin (Dorr, 1969) during the Transamazonian event.

3. Field observations

Samples from the Minas Supergroup were studied along profiles in different areas of the QF (Fig. 1b): western and eastern flanks of the Moeda Syncline (Figs. 3a–c), the Dom Bosco Syncline (Fig. 4a), and the northeast of the Serra de Curral (Fig. 1b).

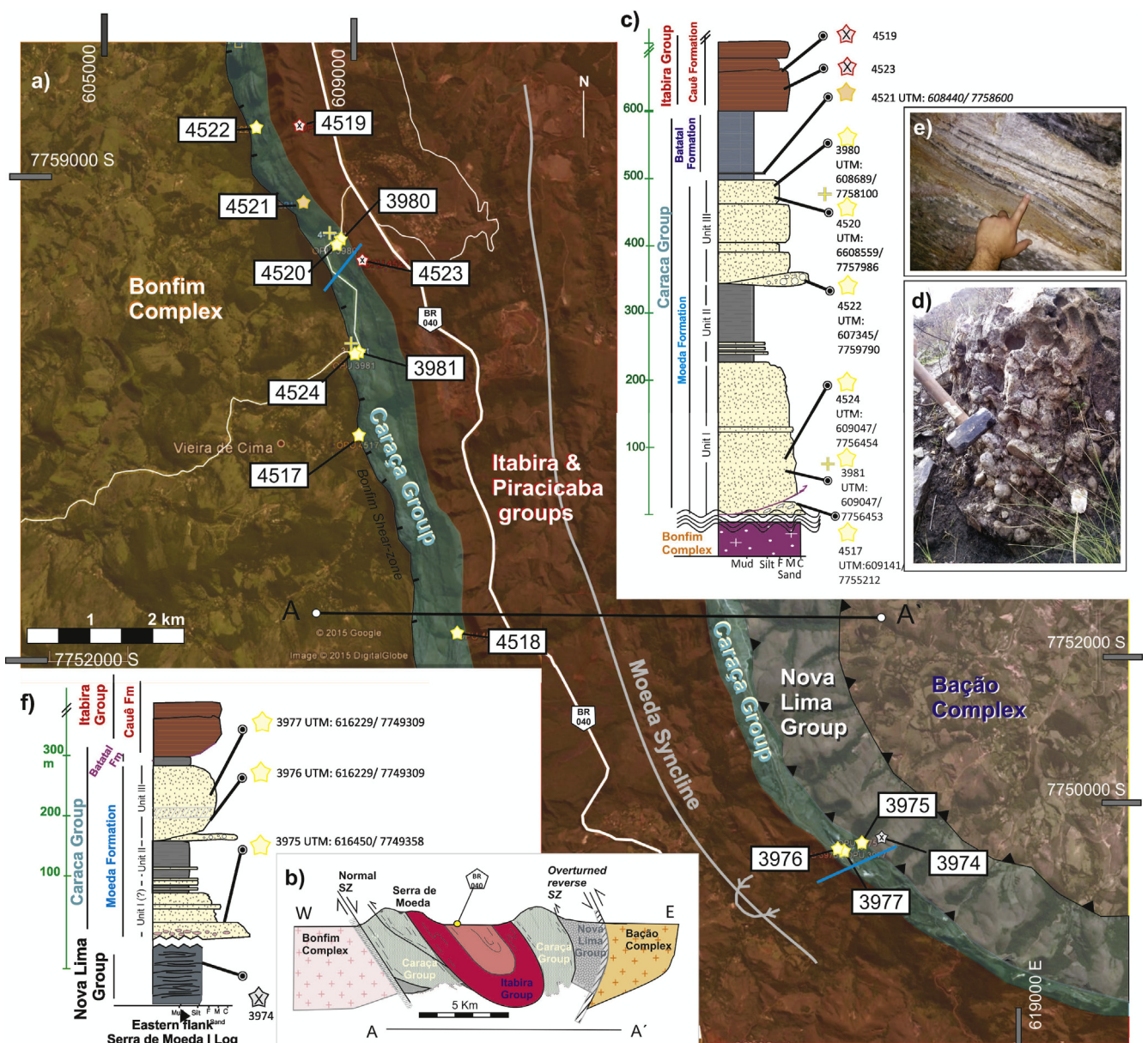


Fig. 3. West of the Iron Quadrangle- Moeda Syncline. a) Geological sketch of lithological distribution in of the Moeda Syncline. Sampling location is indicated. Image taken from GoogleEarth®; b);c)Schematic W-E cross section in the western flank of with lithologies sampled; Field images of the samples c) Quartz-rich lens within the Nova Lima Group, 15 m below the top contact with Minas Supergroup; d, e) Lithological variation of medium-grained quartz schists to pure sandstones in Moeda Formation; f) Clastic quartz-rich lens within the carbonaceous phyllites of the Itabira Group; e) Decimetric sequence of alternating sandstone- mica schists and ferruginous sandstones of the Piracicaba Group a few meters close to the base.

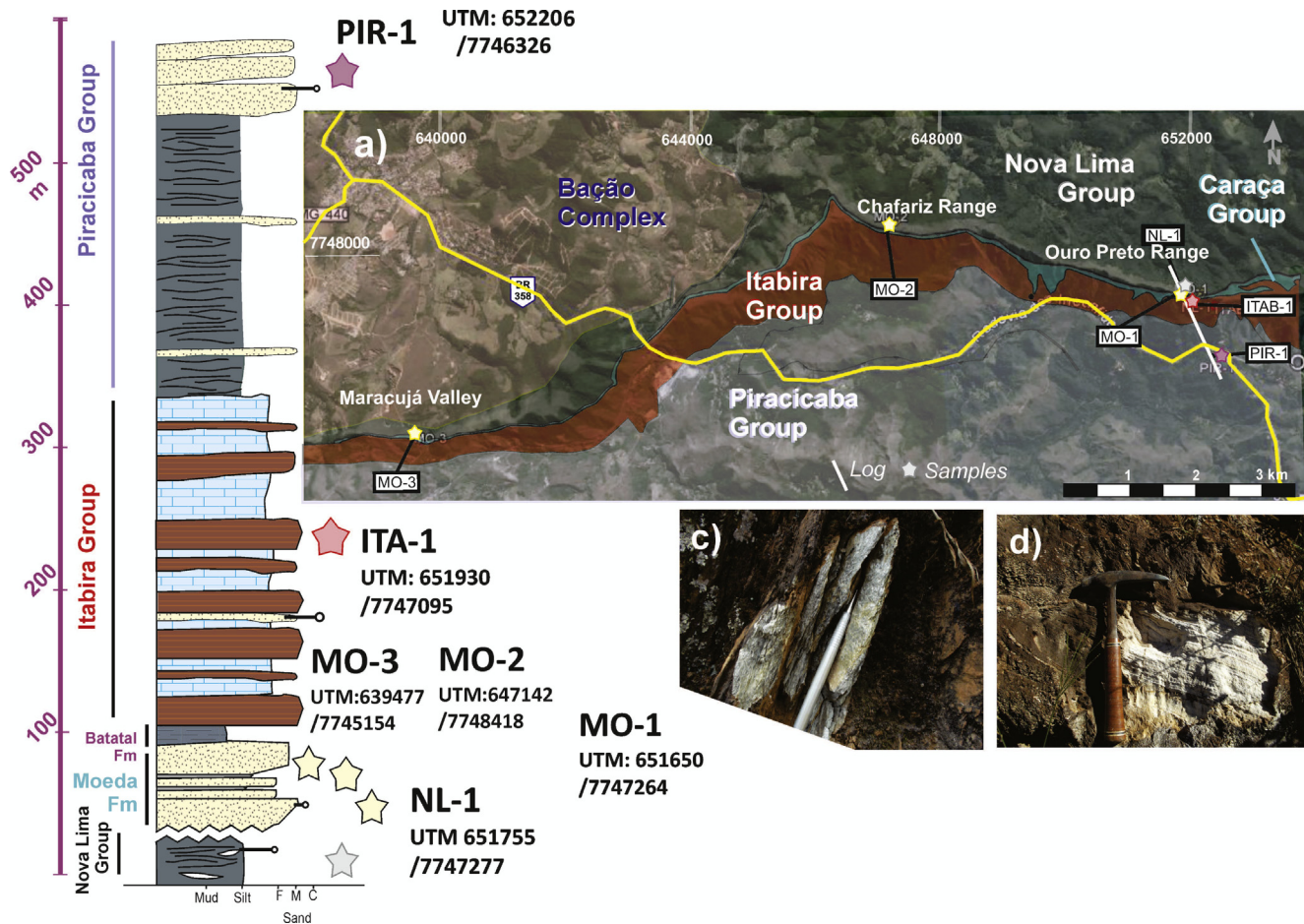


Fig. 4. a) Geological sketch of the units in the northern flank of the Dom Bosco syncline. Background image taken from GoogleEarth®; b) Schematic stratigraphic S-N section with indication of the sampling units and sites; c, d) Lithological variation of medium-grained quartz schists to pure sandstones in Moeda Formation.

The Moeda Syncline is a 40 km-long N-S trending west-verging fold (Figs. 1a and 3a, b) limited by meter-to tens of meter-wide ductile shear zones (Dorr, 1969; Hippertt and Davis, 2000). The core of the syncline exposes extensive outcrops of the Itabira and Piracicaba Groups, whereas the borders expose mainly the Moeda Formation and Rio das Velhas Supergroup. The syncline structure is bounded on either side by km-long shear zones (Hippertt and Davis, 2000), which deform some units of the Rio das Velhas and Minas Supergroup (Fig. 3b) as well as the neighboring granitoid domes (Bação to the east and Bonfim to the west). The western flank of the syncline exposes the best-recorded section of the Caraça Group and part of the Itabira Group. Here a >600 m-thick sequence is divided in three fining upwards cycles of clastic sediments (Fig. 3c). The base of the Moeda Formation (unit I) is represented by quartzitic microconglomerate composed by mm-wide round quartz in a fine-grained matrix. This section was sampled a few meters above the base (samples 3981 and 4524). Further north, along the Moeda/Mamona Granodiorite contact, a >15 m package of grayish pelites make up most of the intermediate member of the Moeda Formation (sample 4522; Fig. 3d). The sequence continues for 150 m upwards with massive m-thick beds of monotonous clean, well sorted and fine-grained sandstones, locally displaying cross-bedding. This sequence gives place to a 30 to 60 m-thick layer of metapelites of the Batatal Formation, which was sampled a few meters above the contact (sample 4521). In the sampling area, shales are interlaminated with iron oxides bearing layers and quartz-rich layers (Fig. 3e). This enrichment in iron oxides increases towards the upper conformable and gradational con-

tact with a >100 m-thick layer of banded iron formation. The eastern flank of the Moeda Syncline (Fig. 3a b and f) exposes felsic schists and poorly sorted *meta*-graywackes of the Nova Lima Group in contact with the basal orthoconglomerate of the Moeda Formation (sample 3975). The occurrence of the Nova Lima Group is restricted to a < 300 m-wide strip between the crystalline rocks of the Bação Complex and the Moeda Formation (Fig. 3a and b). The sequence continues for about 300 m upward with medium-grained quartzites interbedded with dm-scaled dark gray phyllites (samples 3977 and 3976, respectively 10 m below the top).

The Dom Bosco Syncline is a >40 km-long E-W trending keel structure in the southern parts of the QF. Akin to the Moeda Syncline, the Dom Bosco exposes extensive outcrops of the Itabira Group in the core and the Caraça/Nova Lima Groups along the flanks. It is bounded on either side by Archean Bação Complex and Paleoproterozoic calc-alkaline suites of the Mineiro Belt. Observations were taken along an 800 m-long profile (Fig. 4a and b), which corresponds to the E-W- trending Ouro Preto ridge – some 4 km to the west of Ouro Preto. The section comprises brownish highly foliated quartz-sericite schists of the Nova Lima Group. The contact between the Archean Greenstone Belt and the base of the Moeda Formation is highlighted by the presence of massive recrystallized quartz-rich veining. The Moeda Formation reaches 40 m in thickness and from base to top it is composed of variably sericitized sandstones grading to purer sandstones (Figs 4c and d) and thin beds of gray to bluish gray phyllites, alternating with sericite sandstones. Sample 3982/NL-1 belongs to a fine-grained sandstone layer within the Nova Lima Group. Sample

3983/MO-1 represents a fine-grained sandstone that was collected ca. 15 meters up from the base of the Moeda Formation (Fig. 4c). The Caraça Group is covered by a homogeneous sequence of laminated itabirites that grade upwards into more dolomite-rich itabirite levels. This sequence is interlayered with minor quartz-rich lenses (<5 m-thick). One of these lenses was sampled 40 meters above the base (Sample 3984/ITA-1). The continuity between the Itabira Group and the overlying Piracicaba Group was elusive across the section. The base of the Piracicaba Group is dominated by quartz-mica schists, schists interbedded with carbonaceous phyllites (200 m-thick), that grade to a pack of ferruginous sandstones (sample 3987/PIR-1) interbedded with silver phyllites at the top. Two other sandstone samples 3988/ MO-2 and 3989/ MO-3 were collected further west of the cross section ca. 5 and 12 km, respectively. The westernmost sample of the Moeda Formation belongs to a 50-metre thick pile of silicified sandstones interbedded in the middle with shales. The basal contact with the Nova Lima schists is abrupt. Sample 3989/MO-3 was collected from a sandstone level below the phyllites.

The Curral Homocline is a prominent E-W trending ridge, located in the northern part of the QF (Fig. 1b). Field observations and sampling were taken in central part of the Serra da Piedade located nearly 30 km to the east-northeast of Belo Horizonte in the easternmost end of the Curral homocline. There, the ridge is mostly dominated by the uppermost section of the Minas Supergroup. One sample of a grayish quartz mica schist –Sabarã Group (sample 4600)– was collected in the northeast of the QF.

4. Geochronology

4.1. Sampling Strategy, sample preparation and methods

The sampling strategy involved collecting 18 samples of several locality types of the main units of the Minas Supergroup (Moeda, Batatal, Cauê, Cercadinho and Sabarã units) and a clastic lens in Nova Lima Group. In each sampling site, up to 15 to 20 kg of sample were collected and screened for alterations in hand specimen. Rocks were crushed and pulverized and their heavy mineral fraction was separated via panning and magnetic methods. The non-magnetic fraction of zircons was handpicked disregarding color, shape or size. Zircons were mounted and imaged via cathodoluminescence (CL) and the Back-Scattered electron detector (BSED) using a JEOL 6510 Scanning Electron Microscope housed at the DEGEO- Escola de

Minas in the Universidade Federal de Ouro Preto. The BSED and the CL images were obtained to examine morphologic characteristics of zircon, internal zoning patterns and the possible presence of inclusions, cracks or damaged areas and to help discriminating regions with higher Hf or Pb content in the same zircon crystal.

Nearly 2000 U–Pb detrital zircon dates were obtained for this study - half of which were concordant (Supplementary data table A). U–Pb and Lu–Hf analysis at the Universidade Federal de Ouro Preto. U–Pb analyses were carried out using a ThermoScientific Element 2 sector field (SF) ICP-MS coupled to a CETAC LSX-213 G2+ laser ablation system and an Agilent 7700 Quadrupole (Q) ICP-MS coupled to a 213 nm NewWave laser. Lu–Hf analyses were done using Neptune Plus LA-MC-ICP-MS coupled to a PhotonMachines ArF 193 nm Laser ablation system (see Appendix A for details of the analytical conditions and data processing; see also Farina et al., 2015 for details).

The most suitable location of the analytical spot for U–Pb geochronology was selected on the acquired images selecting areas without inclusions, fractures and possibly with internal textures connected to precise forming process such as magmatic growth, metamorphic re-growth or re-crystallization. Dark areas (U-rich) in the CL-image were avoided to prevent getting information of out damaged areas (Pb-loss). After the isotopic analysis execution, the analyzed zircon grains were inspected to check the precise location of the spots with respect to micro-structural domains with the aim to recognize the origin of zircon crystals.

4.2. Estimation of maximum depositional ages from detrital zircons

To establish the maximum depositional U–Pb ages, we considered zircons that were <5% discordant or reversely discordant and used two approaches: (1) the youngest graphical peak in age probability defined by at least three overlapping ages and/ or (2) the weighted mean of the coherent group of youngest grain ages that overlap each other at 1 σ level of analytical error or acceptable MSWD values (Table 1). These methods were recently successfully combined but in restricted units of the Quadrilátero Ferrífero such as the Maquiné Group (Fig. 1b; Moreira et al., 2016). An alternative estimate based on the youngest single grain is compelling, especially when the number of zircons is low, but statistically unreliable (e.g. Dickinson and Gehrels, 2009) since it might yield to a younger depositional age than the true maximum depositional age (due to Pb loss or measurement statics). Previous U–Pb pioneer

Table 1
Summary of the new geochronological results of the Minas Supergroup.

Unit	Sample	Analyzed Zircons		Number of highly concordant zircons between 2580 and 2620 Ma	Mean age of the youngest cluster		Number of zircons that compose the PDP age	Youngest PDP Age	
		Total	Concordant		Age	±(Ma)		Age	±(Ma)
Nova Lima Gr	3982 /NL-1	87	52	0	2679	20			
Moeda Fm	3983 /MO-1	102	80	2	2594	17	8	2646	12
Moeda Fm	3988 /MO-2	87	69	2	2596	17	3	2600	25
Moeda Fm	3989 /MO-3	69	61	0	2695	17	32	2719	6
Moeda Fm	3987 /PIR-1	94	80	0	2666	41			
Moeda Fm	3975	204	109*	0	2636	21	26	2673	7
Moeda Fm	3976	140	44	3	2570	19	3	2582	20
Moeda Fm	3977	217	45	1	2585	17			
Moeda Fm	3980	111	59*	11	2567	18	9	2607	12
Moeda Fm	3981	86	59*	0	2652	19			
Moeda Fm	4517	46	30	3	2602	18	13	2640	12
Moeda Fm	4518	31	23	3	2580	20	3	2590	22
Moeda Fm	4520	216	135	22	2562	20	17	2585	9
Moeda Fm	4522	75	39	1	2619	19	8	2680	14
Moeda Fm	4524	196	114	0	2663	18	23	2689	7
Batatal Fm	4521	53	15	1	2559	22	6	2674	15
Cauê BIF	3984 /ITA-1	113	95		2453	18			
Sabarã Gr	4600	92	38						

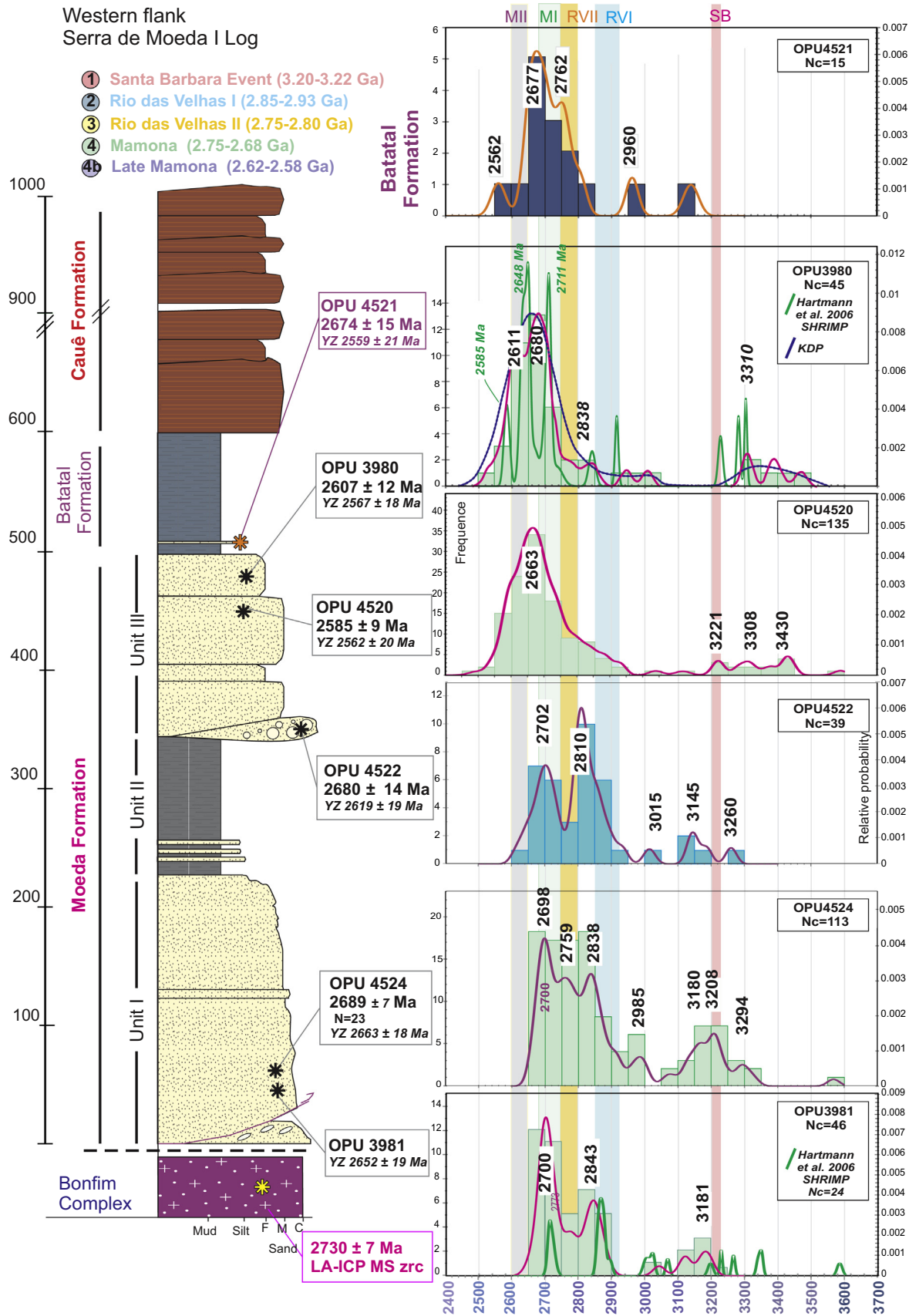


Fig. 5. Frequency histogram and probability density curves for the $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages of the samples collected in the western flank of the Moeda Syncline across the northernmost W-E log in the Minas Supergroup. Details of the samples are in the text. Age Display and Isoplot software (Sircombe, 2004; Ludwig, 2008, respectively) was used to build the graphs and evaluate the data. All weighted zircon age data was 95–105% concordant according to the ratio $^{206}\text{Pb}/^{238}\text{U}$ / $^{207}\text{Pb}/^{206}\text{Pb}$ and treated as sigma-1 errors. The age intervals indicated as (1)-Santa Bárbara, (2)- Rio das Velhas I, (3)- Rio das Velhas II, (4) Mamona, (4b) Late Mamona are based on the proposals of Lana et al. (2013) and Farina et al. (2015, 2016).

regional dating in the Minas Supergroup prioritized this approach based on having a low number of zircons but very precise dating (e.g. SHRIMP dating in Hartmann et al., 2006) or high number but without concordance control (e.g. Pb–Pb ages in Machado et al., 1996). Particularly, in the case of limited in number determinations (typically $N \leq 114$, Vermeesch, 2004; or $60 < N < 100$, Pullen et al., 2014), it might be argued as not statistically representative of the sources.

The extensive use of Probability Density Plot Diagrams (PDP) (Ludwig, 2008) started more than a decade ago (Gehrels et al., 2000; Dickinson and Gehrels, 2009) as an attempt to quantify the possible resemblance among detrital zircon spectra when populations are large enough. Recently, Vermeesch (2012) propose the Kernel density estimation method (KDE), a robust alternative to visualize detrital populations. We built our PDP only with highly concordant zircons between 95 and 105% of concordance and data out of single zircons (one point selected per zircon, with U/Th ratio >0.1 and usually the most concordant). Moreover, we compared the results of the PDP and KDE in order to increase the confidence in the populations.

The youngest data cluster shown in figures is calculated using the weighted average age (Isoplot 4.15; Ludwig, 2008) of youngest significant group with $N \geq 3$.

The probable age of the peaks was obtained with the Age Peak Excel Macro (Gehrels, 2009), AgeDisplay (Sircombe, 2004) and Isoplot 4.15. For comparison purposes with the Kernel density estimation method the software Densityplotter (Vermeesch, 2012) was used.

4.3. Zircon morphological features

Zircon crystals from the Nova Lima Group and Moeda Formation are transparent, brown-grayish and, in a lesser extent, pink

in color. Most of them are slightly rounded, prismatic 3:1 ranging in size from 400 to 100 μm and show well-defined complex oscillatory zoning in CL images. Most zircon cores and rim relations indicate magmatic origins. The pinkish group is characteristically short prismatic, small in comparison ($<150 \mu\text{m}$) and exhibits a sugar texture. Fractures within the crystals are common. On the other hand, zircons extracted from the Batatal phyllite are brownish, rounded and smaller than 100 μm . Sandstone lens of the Itabira Group yielded grayish rounded zoned zircons, with sizes varying from 200 to 50 μm . Sabará Group in the Serra de Piedade yielded transparent, round zircons which average size ca. 200 μm . Many of them are zoned with brighter external rim and marked by radiation-damage domains

4.4. U–Pb results

4.4.1. Moeda syncline

All samples from the Moeda Formation and the Batatal Formation are marked by similar age distribution patterns indicating little (if any) variation of the source throughout the deposition of these units (Figs. 5 and 6; Table 1). They show one broad, dominant peak, ranging from 2590 and 2800 Ma (Figs. 5 and 6), coincident with the ages of most of the calc-alkaline granites of the Mamona event (2610–2750 Ma) and granitoids of the Rio das Velhas II event (2780–2800 Ma). Other secondary peaks were found between 2830–2870 Ma and between 3150–3250 Ma, broadly coinciding with the Rio das Velhas I and Santa Bárbara magmatic events (Figs. 5 and 6). The same applies for samples collected in the eastern flank of the Moeda Syncline. The spectrum for the base of the Moeda Formation (3975) shows three age populations: the largest is the youngest with a mean age at 2676 Ma, followed by secondary clusters at 2755 and 2835 Ma ($N = 89$; out of 207 analysis; Table 1). Small groups of Mesoarchean zircons (3100 and 3300 Ma)

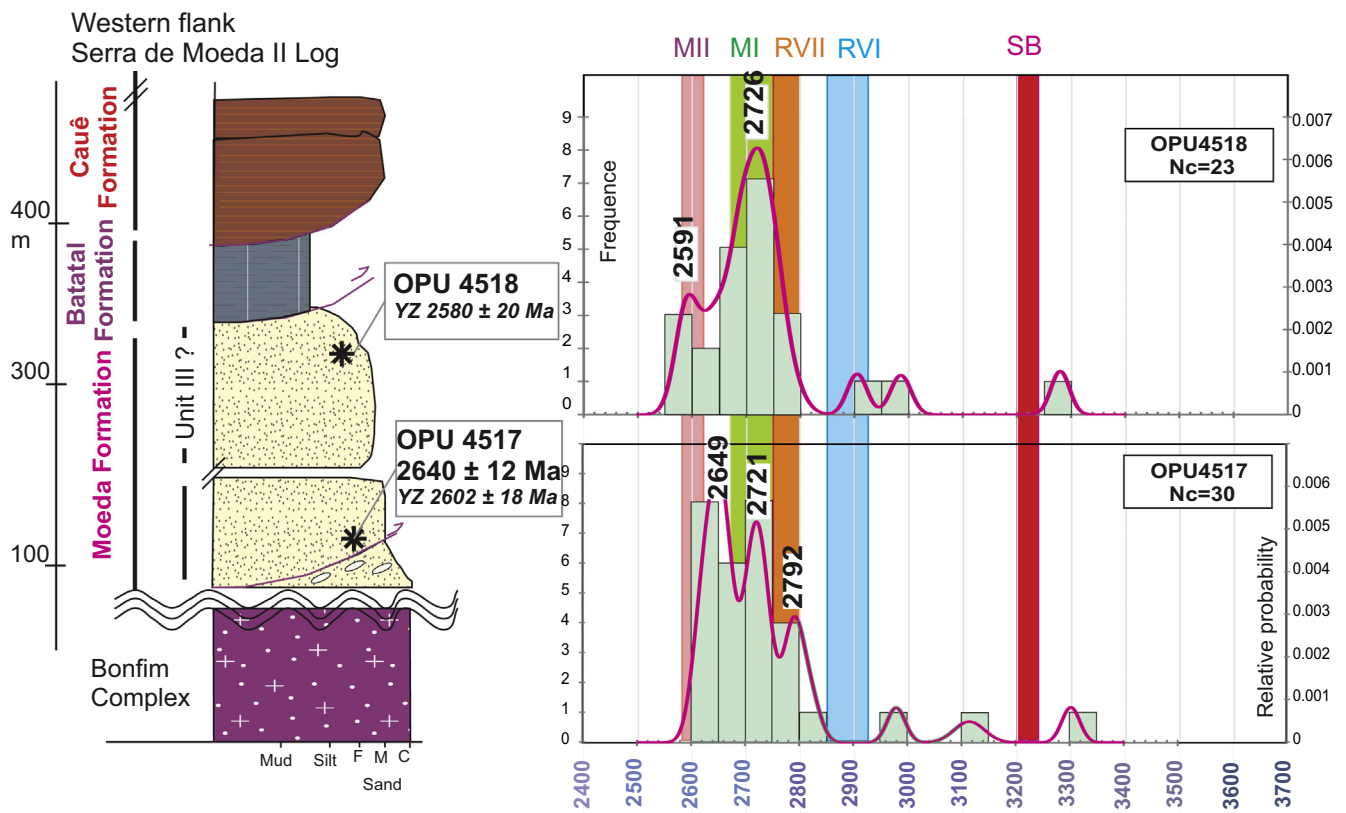


Fig. 6. Frequency histogram and probability density curves for the $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages of the samples collected in the western flank of the Moeda Syncline across the southernmost W–E log in the Minas Supergroup. Data in Supplementary material A.

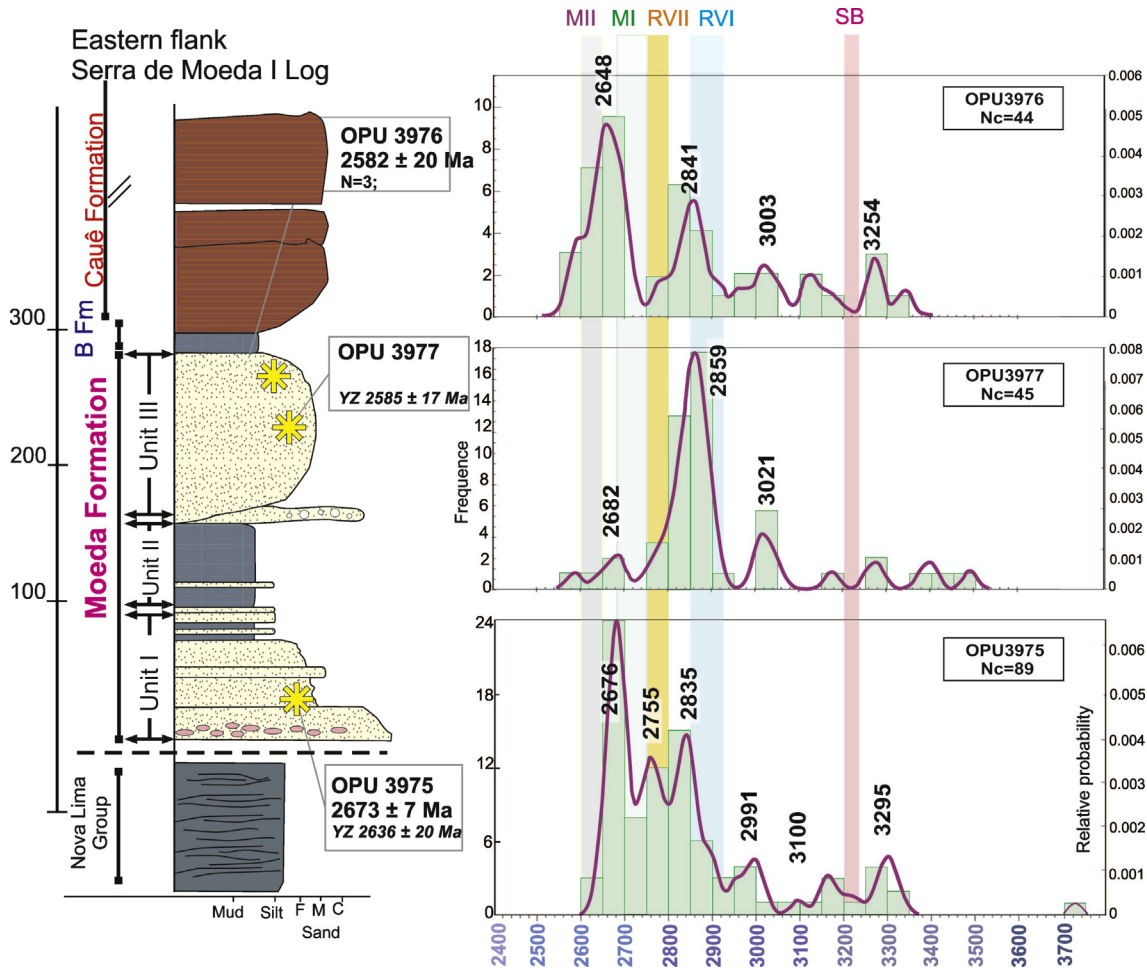


Fig. 7. Frequency histogram and probability density curves for the $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages of the samples collected in the eastern flank of the Moeda Syncline across the a W-E log in the Minas Supergroup. Data in Supplementary material A.

were also observed in most samples (Fig. 7). Eighty-nine concordant ages (347 in total) were obtained from single grains from the upper part of the eastern flank of the Moeda syncline section (samples 3977 and 3978 are coarse- and fine-grained sandstones, respectively; Fig. 7). Both samples record a bimodal distribution with averaged contributions between 2682 Ma and 2850 Ma. Subordinate peaks at ca. 3015 Ma as well as around 3260 Ma are also present. The top units of the eastern flank record a few number of zircons with ages in the interval of 2560 Ma and 2600 Ma (Fig. 7).

The maximum depositional age range of 2610–2590 Ma and the source matches with the results obtained by Hartmann et al. (2006) (Figs. 5–7). For instance, samples 4518, 3980, 4520, 3977, 3976 record between 1 and 7 zircons younger than 2600 Ma. Sample 3980 was collected from the locality studied by Hartmann et al. (2006); the comparison between these two spectra shows a high degree of overlap.

4.4.2. Dom Bosco Syncline

Zircons of a sandstone layer within the schist sequence of the Nova Lima Group (sample 3982) yielded three main modes at 2730 Ma, 2787 Ma, and 2870 Ma and minor early Mesoarchean ages between 3050 Ma and 3250 Ma (Fig. 8). This age spectrum is different from the samples from the Moeda Formation collected along the same profile (samples 3983, 3988, 3989) in that the Moeda samples lack a prominent peak at 2790 Ma, and that the

Rio das Velhas sample does not have zircons younger than 2720 Ma (Table 1).

The probability density plots for the Moeda Formation (samples 3983, 3988, 3989) depict a similar bimodal pattern with almost identical peaks between 2717 Ma and 2725 Ma and 2866 Ma and 2870 Ma within a total of 210 concordant zircons. All three samples record contributions of older sources. Two of these samples (3988, 3989) display a pronounced peak at ca. 3165–3170 Ma.

The age spectrum for the quartz-rich layer in the Cauê Banded Iron Formation (sample 3984) exhibits an asymmetric unimodal population at ca. 2791 Ma and a large tail that covers a wide range of ages until early Mesoarchean (Fig. 8). On the other hand, the base of the Piracicaba Group (Cercadinho Formation, sample 3987) contains zircons with ages ranging from the early Mesoarchean (youngest peak at 2721 Ma; Table 1) to the end of the Paleoproterozoic. The most abundant populations are found at ca. 2960 Ma and 2878 Ma (Rio das Velhas I event). Zircon ages among 2950 Ma and 3000 Ma have not been found among the basement populations in the QF (Fig. 2b).

4.4.3. Piedade Syncline

The probability density plot for the Sabará Group shows multiple clustering on the base of 38 concordant zircons of a population of 92 analyzed grains (sample 4600; Fig. 9). U/Th ratios for the zircons are above the limit proposed for metamorphic zircon rims. There are two groups of ages clustering in the late Paleoproterozoic (2120–2220 Ma) and Neoproterozoic (2600–2900 Ma). The largest

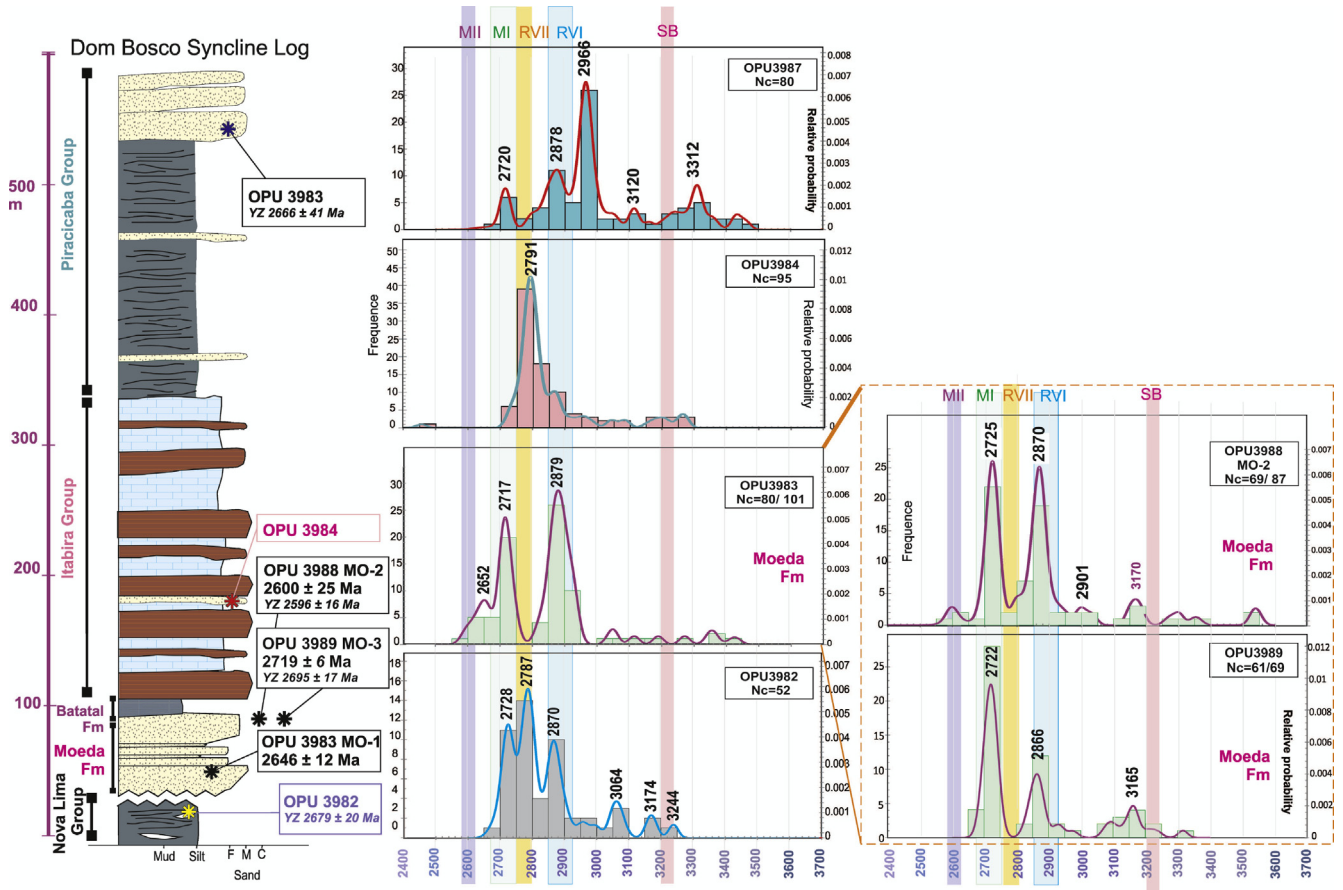


Fig. 8. Frequency histogram and probability density curves for the ²⁰⁷Pb/²⁰⁶Pb zircon ages of the samples collected in the southern flank of the Dom Bosco Syncline across the a N-S log in the Minas Supergroup. Details in Appendix A1–4 and data in Supplementary material A.

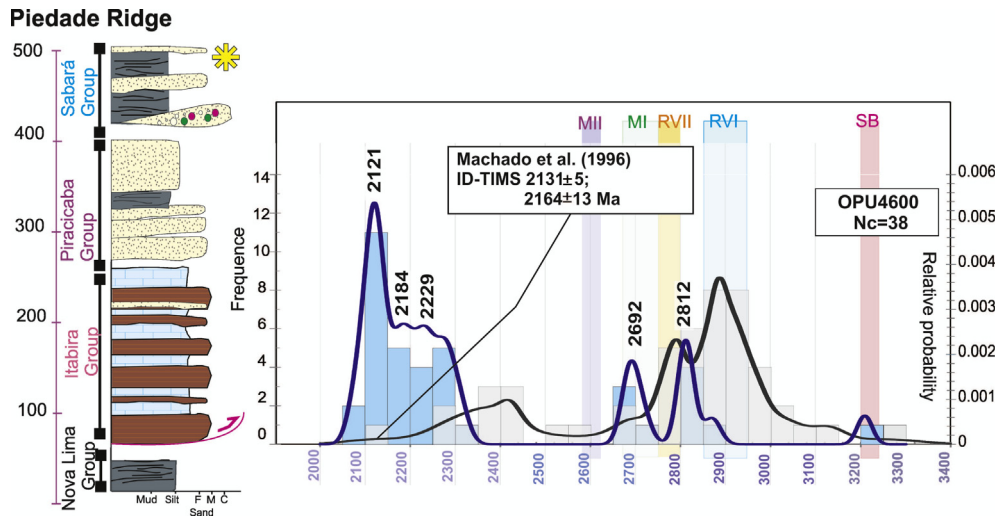


Fig. 9. Frequency histogram and probability density curve for the ²⁰⁷Pb/²⁰⁶Pb zircon ages of a sample of the Sabará Group collected in the Serra da Piedade (northeast of the Serra do Curral). Details in Appendix A1 and data in Supplementary material A.

contribution has a mode at 2121 Ma, interpreted as the maximum depositional age, followed by two other meaningful contributions at ca. 2180 Ma and 2220 Ma. Neoproterozoic ages are bimodally distributed with modes at 2692 Ma and 2812 Ma. A small number of zircon detrital ages (Machado et al., 1996) for another locality in the east of the Serra do Curral were produced via TIMS (Fig. 9). The maximum depositional age found here perfectly coincides with the

single zircon Pb–Pb ID-TIMS ages of 2131 ± 5 Ma and 2164 ± 13 Ma of Machado et al. (1996).

4.5. Lu–Hf isotope results

In order to characterize and trace potential primary magmas from the detrital zircons, the Lu–Hf isotope ratios were obtained

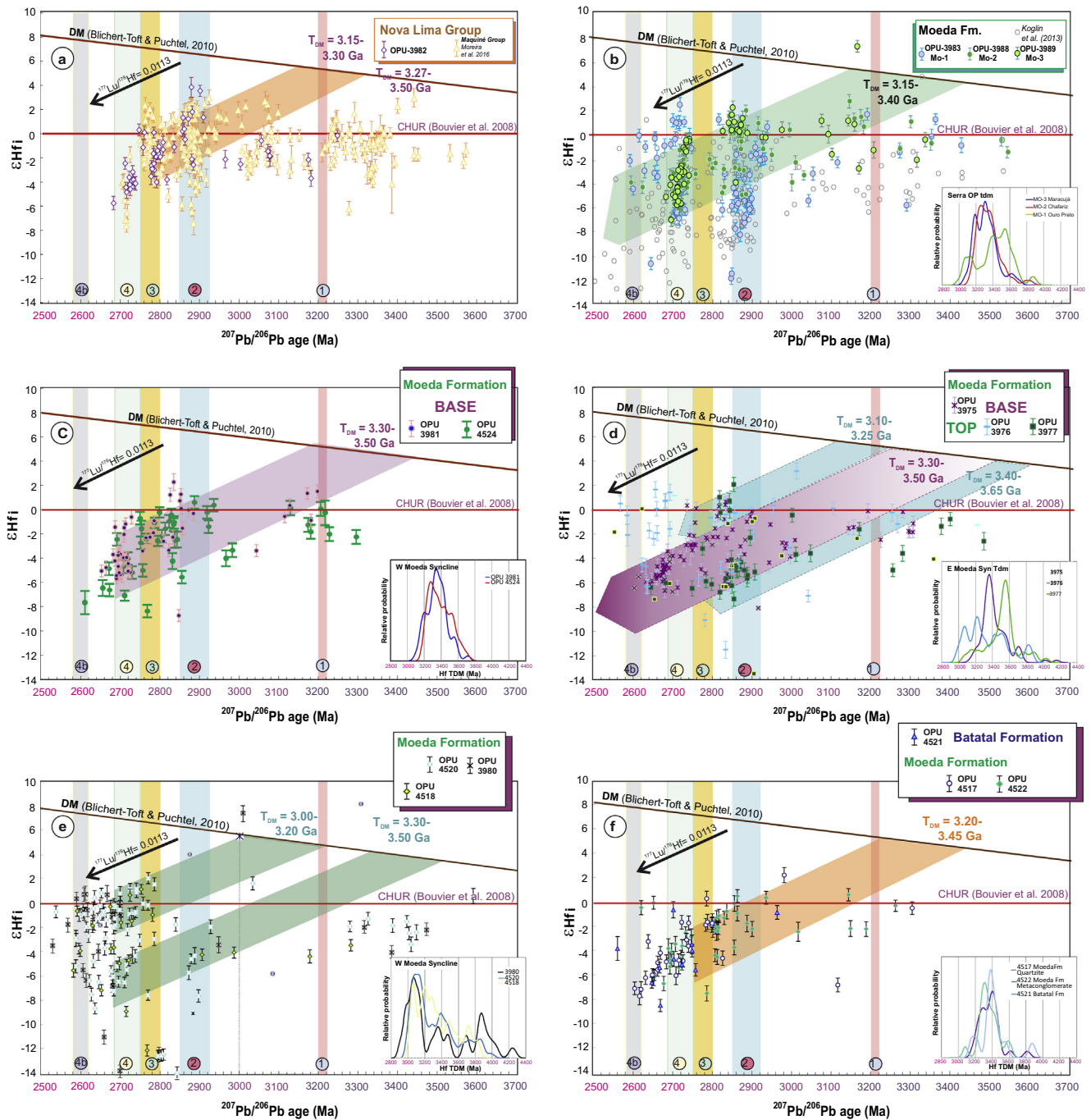


Fig. 10. $\text{Hf}(t)$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ age diagram showing results for detrital zircon from the Archean Rio das Velhas greenstone belt and base of the Minas Supergroup. a) Nova Lima Group and published data for the Maquiné Group (Moreira et al., 2016); b) Moeda Formation in the Serra de Ouro Preto and published data for the Ouro Fino Syncline (Koglin et al., 2014); c) Base of the Moeda Formation in the western flank of Moeda syncline (sample d); d) Base and top of Moeda Formation in the Eastern Flank; e) f) Top of Moeda and Batal formations in the western flank of Moeda syncline. Insets in each figure show the probability curves for the Lu-Hf model ages (T_{DM}). The age intervals indicated as (1)-Santa Bárbara, (2)- Rio das Velhas I, (3)- Rio das Velhas II, (4) Mamona, (4b) Late Mamona are based on the proposals of Lana et al. (2013) and Farina et al. (2015, 2016). See Supplementary Material B and Appendix A.5 for data and analytical procedures.

from a selection of highly concordant igneous zircons described above. Lu-Hf isotopes were obtained on zircons crystal areas that were proved to be highly concordant by laser ablation U-Pb method. Spatially, the U-Pb and Lu-Hf spot analyses have to be as close as possible in order to analyze domains of the zircon grain with the same isotopic characteristics.

Epsilon $\text{Hf}(t)$ vs. crystallization age as well as $2S T_{\text{DM}}$ model ages of the detrital zircons for the base and for the top of Minas Supergroup are presented in Figs. 10 and 11.

The detrital zircon grains of the Nova Lima Group collected from the three main magmatic events in the QF (Rio das Velhas I, II and Mamona events) exhibit a trend with decreasing $\epsilon_{\text{Hf}(t)}$ from older to younger grains (from +4 to -5 units) yielding Mesoarchean to Paleoproterozoic $2S T_{\text{DM}}$ model ages between 3100 and 3350 Ma. The $2S T_{\text{DM}}$ model ages bracket a possible age range comparable with the late Paleoproterozoic Santa Bárbara Event (Fig. 10a; Lana et al., 2013), for which one sample and several inherited grains in the crystalline basement rocks suggest a range of events from

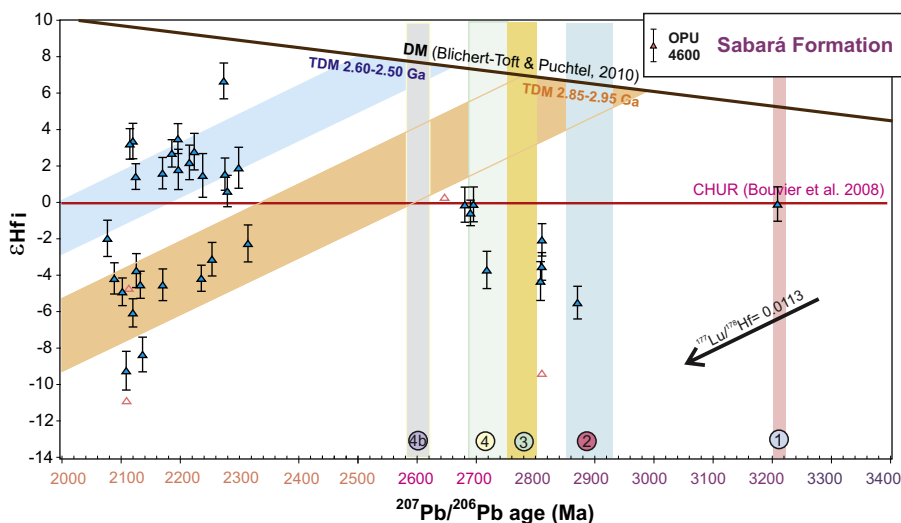


Fig. 11. $\text{Hf}_{(t)}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ age diagram showing results for detrital zircon from the Sabará Group mica schist. The age intervals indicated as (1)-Santa Bárbara, (2)- Rio das Velhas I, (3)- Rio das Velhas II, (4) Mamona, (4b) Late Mamona are based on the proposals of Lana et al. (2013) and Farina et al. (2015, 2016). See Supplementary Material B and Appendix A.5 for data and analytical procedures.

3200 to 3220 Ga (Machado and Carneiro, 1992; Lana et al., 2013). Zircons of the Moeda and Batatal Formations show a decrease in $\epsilon\text{Hf}_{(t)}$ from older to younger grains. This evolution trend is also supported by the variance in the $^{176}\text{Hf}/^{177}\text{Hf}_{(t)}$ against age diagram ensuring non-Pb loss effect had happened (e.g. Gerdes and Zeh, 2009). The late Mesoarchean to Paleoproterozoic (3100–3600 Ma) detrital zircon populations yielded mainly sub-chondritic $\epsilon\text{Hf}_{(t)}$, clustering between -3 and $+2$, with variations in 2S T_{DM} model ages within the Archean interval whereas younger populations (<3100 Ma) show a decoupled evolution that seems to reflect different contributions for the base and top units of the Moeda Formation (Fig. 10b–e).

In Serra de Ouro Preto, Hf isotopic compositions of detrital zircons from the Rio das Velhas I magmatism (2850–2930 Ma) for easternmost sample (3983) yielded a wide range of $\epsilon\text{Hf}_{(t)}$ values between -8 and $+2$, clustering within -6 and -2 , whereas for the westernmost samples (3988 and 3989) values are assembled between -5 and $+2$, clustering among the suprachondritic values (0 and $+2$) (Fig. 10b). Generally, the Neoproterozoic zircons (e.g., RVII and Mamona zircons) have $\epsilon\text{Hf}_{(t)}$ values bracketed between -7 and $+3$ units.

In the Moeda syncline, the Hf compositions of the detrital zircons of the samples collected at the base of the sections (3981, 4524; 3975; Fig. 8c and d, respectively) are identical. Zircon grains sourced by the Rio das Velhas I magmatic event for both flanks of the syncline yielded $\epsilon\text{Hf}_{(t)}$ values clustered between -2 and $+2$ units. Zircon populations amongst Rio das Velhas II and Mamona events, record $\epsilon\text{Hf}_{(t)}$ values between -3 and 0 and -8 and -2 , respectively. The detrital zircon grains of the top of the sequence in both flanks (samples 3976, 3977; 4918, 4920, 3980; Fig. 8d and e) from Rio das Velhas II, Mamona and younger sources, $\epsilon\text{Hf}_{(t)}$ clustered between -2 and $+2$ and -8 and -3 units. The more chondritic to subchondritic assortment has not been detected in the samples of the base.

For mica-schist of the Sabará Group, zircon grains with concordant U–Pb ages of the major age population at 2120 Ma show a wide range of $\epsilon\text{Hf}_{(t)}$ values between $+3$ and -9 (Fig. 11). On the other hand, zircon grains of the populations within the ~ 2180 and 2300 Ma interval cluster between $+7$ and 0 showing Late Neoproterozoic 2S T_{DM} model ages (2500–2650 Ma) corresponding to the Late Mamona Event. Few zircons with negative $\epsilon\text{Hf}_{(t)}$ values

of ca. -4 follow the crustal array of the more negative younger zircons (Fig. 11).

5. Discussion

When detrital zircon populations are large enough (between 60 and 100, Pullen et al., 2014) and a multi-sample approach is guaranteed, information from detrital zircons provides an excellent tool to characterize the source regions (Gehrels et al., 2000, 2011; Fedo et al., 2003; Hietpas et al., 2011) and to make stratigraphic correlations based on age spectra (e.g. Bahlburg et al., 2009; Gehrels et al., 2000; Gehrels, 2014). Thus, detrital zircon data can be used to understand (1) the relative contribution of the various sources into the basin, (2) observe the changes of the source as sedimentation progresses from base to top (e.g. Cawood et al., 2003; Park et al., 2010), (3) account for different sedimentation mechanisms operating on a single sedimentary succession (e.g. Zimmermann et al., 2015) and (4) make inferences about the tectonic environment in which the basin was created (e.g. Cawood et al., 2012) and about exhumation of surrounding tectonic terrains (Gehrels, 2014).

The broad spectra of ages displayed by all samples of the Moeda Formation reflect the multisource nature of the crystalline basement of the Southern São Francisco Craton. Among the main sources, the Mamona high-K granites made the most important contribution to a wide range of ages from 2750 Ma to 2620 Ma (Fig. 2b; Romano et al., 2013; Farina et al., 2015, 2016). Likewise, important contributions were made by granitoids of the Rio das Velhas I and II magmatic events that were emplaced at relatively narrow periods of time at ca. 2760–2800 Ma and 2860–2930 Ma. In contrast, most samples had small contributions from older granitoids such as those of the 3200–3220 Ma Santa Bárbara event (Lana et al., 2013; Romano et al., 2013). Older granitoids such as the Rio das Velhas I and Santa Bárbara were important contributions for the younger strata as the Piracicaba Formation (see also Machado et al., 1996), which may suggest some form of aging of the source as the sedimentation progressed (e.g., as the sedimentary strata get younger, the source gets older).

The age spectra for all units of the Moeda (units I/II/III) across the QF are substantially similar. Samples from important localities such as the Moeda and Dom Bosco Syncline (this study), the Bom

Sucesso Ridge (Neri et al., 2013), as well as the Serra do Curral, Caraça and Gandarela ridges (Machado et al., 1996; Koglin et al., 2014) all suggest that the initial sedimentation took place along one single rift system. The detrital ages from such samples define a flame-type spectrum that is similar in many ways to those from rift to passive margin basins (Cawood et al., 2012). Significantly, the age spectrum for all of the Moeda strata is marked by a wide range of sources that are substantially older than the onset of sedimentation (discussed below).

The typical broad age peak between 2770 Ma and 2590 Ma documented for the Moeda units (Figs. 5–8) is in sharp contrast with the spectra documented for the Archean Rio das Velhas Supergroup (i.e., Nova Lima and Maquiné groups) – the latter are mainly marked by narrow peaks at 2750–2770 Ma and older (Nova Lima Group, Machado et al., 1996) or unimodal populations at 2770 Ma (Maquiné Group, Moreira et al., 2016). This sharp difference demonstrates very clearly how the Minas and Rio das Velhas basins evolved separately in space and time. Significantly, one main critical difference between the two basins is the young population of zircons that range in age from 2700 Ma and 2600 Ma. Such detrital zircons show that the Mamona event (2730 Ma to 2600 Ma) is a fundamental marker of the São Francisco Craton as it separates the Archean Rio das Velhas from Minas Basin.

In summary, we propose that during the early stages of margin configuration, the source of detrital zircons correspond mostly to the calc-alkaline Mamona granites (2680–2750 Ma), Rio das Velhas I event (2850–2930 Ma) (Fig. 12). Given that the Mamona granitoids were upper crustal, sheet-like intrusions that were emplaced structurally above the TTG rocks (Romano et al., 2013), it is likely that these rocks were exhumed to surface level at the time of Minas rifting event (Fig. 12). Further modifications to the sources are seen with the deposition of the Piracicaba Formation, which benefited from much older granitoid sources such as the Rio das Velhas I and Santa Bárbara.

5.1. Maximum depositional age for the base of Minas basin

The maximum depositional age of the uppermost unit of Moeda sediments has been proposed by various studies at (1) 2650 Ma (Machado et al., 1996), 2580 Ma (Hartmann et al., 2006), 2620 Ma (Koglin et al., 2014) and (2) 2650 Ma (age of an alleged metavolcanic layer within the overlying Itabira Group (Cabral et al., 2012). Koglin et al. (2014) inferred that the deposition of the Moeda Formation should be bracketed between the youngest grains that they dated from the base of the formation at 2650 Ma and a supposedly 2610 Ma age from a crosscutting pegmatite studied by Noce et al. (1998). However, Noce et al. (1998) did not provide a crystallization age for the pegmatite. They dated two discordant grains from this pegmatite – at 2597 and 2667 Ma – and argued that both zircons dated could be inherited from the source (or entrained from pegmatite walls). Noce et al. (1998) also concluded that younger date should be taken as maximum crystallization age.

If we take the considerations about the disturbance of the U–Pb system monitored by Hf isotopes, as advised by Koglin et al. (2014), then the 2623 ± 14 Ma younger single detrital zircon age should be emphasized over the 2580 ± 10 Ma of Hartmann et al. (2006) as a maximum depositional age. However, the limited number of grains dated per sample in these previous studies (<60 concordant points/sample) does not allow a critical assessment of the youngest detrital zircon in the sequence. Despite the common sense that detrital zircon dating should involve between 60 and 100 analyses, enough for determining the presence of the main age groups (Pullen et al., 2014), minor age groups can only be detected by more than ~110 analyses for most samples (Vermeesch, 2004). This is particularly

true for rift-related/passive margin basins that are marked by their multitude of sources.

Here we have analyzed over 1600 zircons only in the Caraça Group (nearly three times more than all previous studies have done together). Our evidence from the top units of the Moeda Formation indicates there is an important zircon supply aged between 2580 Ma and 2620 Ma based on > 45 zircons. This is in agreement with ages published for the Moeda Formation samples in the southwestern most end of the QF (Lagoa da Prata unit in the base of the Bom Sucesso sequence) that yielded 2603 ± 7 Ma and 2616 ± 7 Ma (Neri et al., 2013) as well as in the Caraça/Gandarela ridges (Machado et al., 1996). The widespread occurrence of ca. 2600–2630 Ma zircons in the Moeda Formation requires that rifting of the Minas Basin occurred after 2600 Ma. Two main conclusions about the evolution of the Minas Basin can be drawn from this:

- 1) The maximum deposition age <2610 Ma implies that the rifting event took place after the last pulse of the Mamona granitoids, confirming early field evidence (Dorr, 1969; Renger et al., 1995; Machado et al., 1996; Noce, 2000) that the Minas Basin postdates the Archean evolution of the basement, for which the last magmatic pulse was dated at 2612 Ma (Noce et al., 1998; Romano et al., 2013) and 2593 ± 18 Ma (Romano et al., 1991). These granitoids are less regionally extensive than the >2680 Ma Mamona II granitoids, which explains the small amounts of detrital zircon of this age in the Moeda sequence.
- 2) The rifting of the Minas Basin post-date the stabilization of the Archean crust between 2700 and 2600 Ma (see Romano et al., 2013). We interpret that the Minas rifting was deprived of magmatism because the upper crust was shielded from the mantle by a dry lower crust and a dehydrated mantle keel. As discussed by Romano et al. (2013), the lower crust became depleted in radiogenic elements after the generation of the K-rich granites of the Mamona event and thus resilient to further melting during the rifting event.

We conclude that the onset of the Minas rifting event, which marks the initial evolutionary stages of the Minas Basin, is bracketed between the youngest population of zircons dated in nearly all samples of the Moeda Formation at ca. 2600 Ma and the 2420 Ma age of the carbonate sequences of the Gandarela Formation (Babinski et al., 1995). The sediments of the Moeda Formation were deposited after the Mamona event, which marks the stabilization of the Southern São Francisco Craton between 2700 and 2600 Ma and separates the evolution of the Minas Basin from the underlying greenstone belt succession (the Rio das Velhas Supergroup) (Fig. 12). As expected for a rift to passive margin basin, the Minas Basin is marked by a broad range of age spectra reflecting a wide range of sources that are older than the basin (Cawood et al., 2012).

5.2. The rift to passive margin transition

The lateral continuity of the metasediments along the interconnected synclines in the QF supports the idea of Dorr (1969) a blanket type deposit for the Caraça Group. Sedimentological studies on the base of the Minas Supergroup advocate for fluvial-intertidal environments, in which the cycles of finning upwards sandstones and metaconglomerates with occasional fine-grained transgressive lacustrine deposits of different thicknesses settled over a regional discordance (Canuto, 2010; Villaça, 1981). Canuto (2010) interpreted the laterally discontinuous basal layer of metaconglomerate and the following coarse sandstone, as markers of the

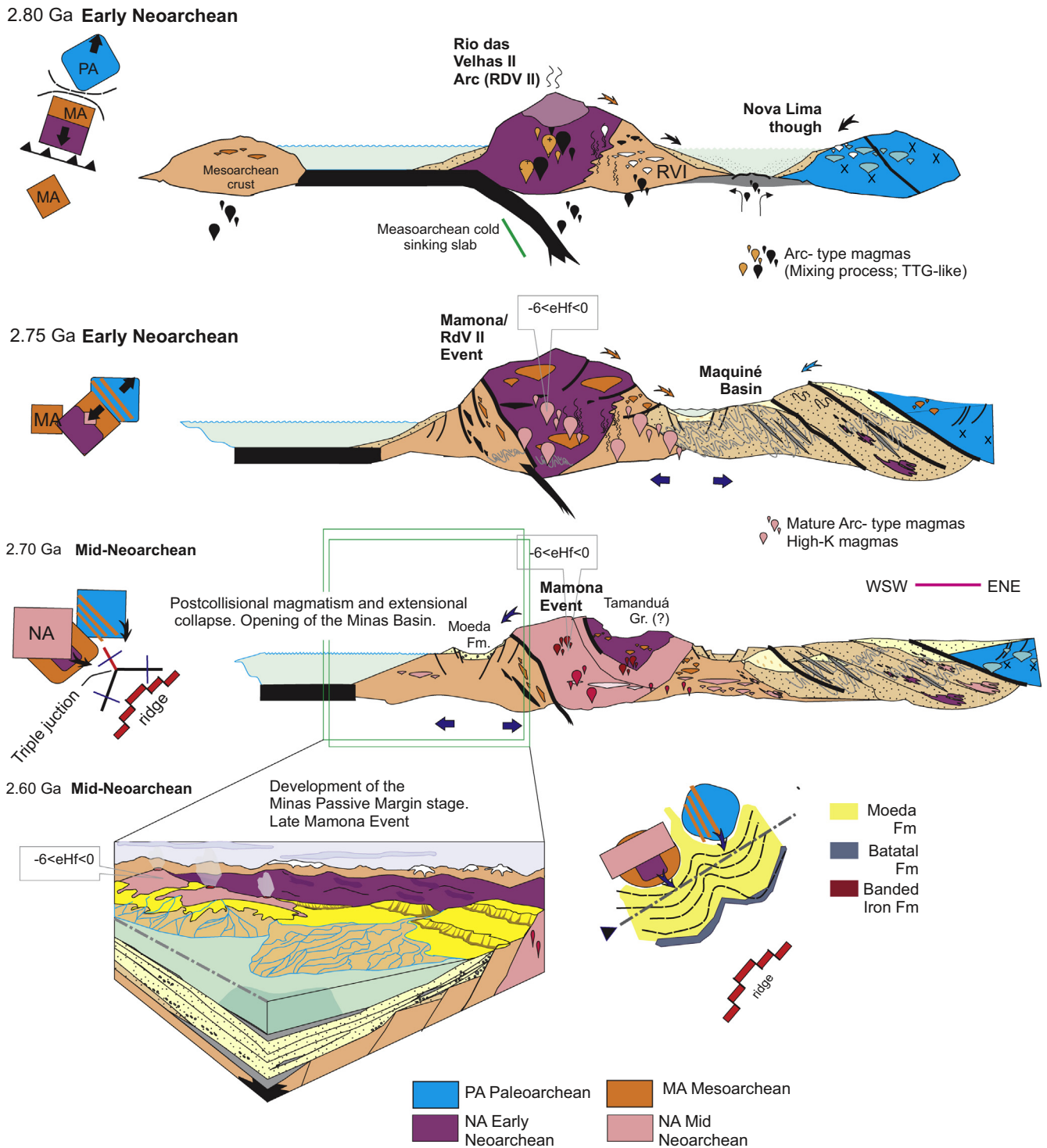


Fig. 12. Schematic cartoon of the Pre-Minas Basin development and tectonic scenario of the margin of the southern São Francisco Craton based on Alkmim and Martins-Neto (2012), Lana et al. (2013), Farina et al. (2015, 2016), and Moreira et al. (2016), among others and the integration with our isotopical data from the autochthonous sources of the Minas Basin. Early Neoproterozoic (ca. 2800 Ma) Stage: Rework of the Paleoarchean (PA, blue color) and Mesoarchean crust (MA, Rio das Velhas I Event in orange color) and arc type magma production minor addition of mafic melts. Beginning of the subduction and development of the Rio das Velhas Basin (Rio das Velhas II magmatism in purple color); Early Neoproterozoic (2750 Ma) Stage: Collision and Uplift, reactivation of older suture zones, change in the sources and mechanisms of magma production (High-K Mamona Event in pink and red color). Development of the Maquiné basin (Moreira et al., 2016). Mid Neoproterozoic to Paleoproterozoic (2750 to 2500 Ma) development of the Minas Basin extension and passive margin conditions. Schematic block diagram of the configuration of the open margin stage, extensional stage, sedimentation of the Moeda Formation with the development of large river systems. Shore/litoral environment and more marine conditions towards the S and SE (present coordinates). Rift drift transition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

initiation of an extensional system, indicating the lateral variations in the accommodation space created in the earliest stages of stretching.

The detrital zircon data for all the Moeda samples show that the evolution from rift to a passive margin was accompanied by minimal variation of the main source, which was in turn dominated

by the Mamona granitoids. Therefore the data (e.g., basal units) confirms the early observations of [Dorr \(1969\)](#) that the nature of the basal deposits, sources (in age and isotopic characteristics) as well as depositional ages are alike. Towards the top, the detrital record of the Moeda Formation shows the presence of all the basement sources and its relative contribution changed slightly towards younger zircons, particularly in the case of samples from the Moeda Syncline (Figs. 5–8). Significantly, the upper session is marked by a distinctive population within the younger zircons with chondritic Hf values (for instance, see the differences between the top and the lower cycles in Figs. 8b and d) evidencing that sources changed as the basin evolved from rift to a passive margin. We suggest that a topographic barrier was built and prevented the supply of other sources, perhaps the final uplift of the Mamona dominated terrains, or a change in the paleodrainage system occurred.

5.3. The maximum depositional age for the banded iron Formation and implications for global atmospheric changes

During passive margin stages, the Minas Basin was affected by a global shift of atmospheric oxygen and carbon that is testified by the widespread precipitation of the iron oxide-rich beds and carbonates of the Cauê and Gandarela formations ([Spier et al., 2007](#)). Apart from being one of the main sources of iron ore, the Cauê Banded Iron Formation records a major elevation in Cr supply into oceans, which was linked to aerobic bacterial oxidation at 2480 Ma ([Konhauser et al., 2011](#)). A study by [Morgan et al. \(2013\)](#) showed that part of the Cauê sequence is marked by negative $\delta^{13}\text{C}$ values, which is an indication of organic origin during the well established great oxidation event between 2450 and 2220 Ma ([Catling, 2014](#)). Additionally, carbon isotope data from the overlying 2420 Ma Gandarela Formation ([Babinski et al., 1995](#)) (which shows a gradational contact with the BIF) indicates major carbon isotope fluctuations and in the seawater composition from 2400–2200 Ma ([Sial et al., 2015](#); [Bekker et al., 2003](#)).

We argue that 2650 Ma age for the volcanic rock in the Cauê Formation ([Cabral et al., 2012](#)) is at odds with a number U–Pb detrital zircon studies in the Moeda Formation, which all give maximum deposition ages younger than 2650 Ma (e.g., [Machado et al., 1996](#); [Hartmann et al., 2006](#); [Neri et al., 2013](#); this study). More importantly, a number of papers and field-based stratigraphic studies (e.g., [Dorr, 1969](#); [Spier et al., 2007](#)) have long concluded that the deposition of the Moeda clastic sediments and precipitation of the Cauê iron formations are clearly distinct events in time and space. A lateral transition between the Caraça and Itabira groups is not documented in the QF. All previous mapping projects (synthesized in [Dorr, 1969](#)) and stratigraphic sections investigated here show that the pelites of the Batatal Formation separate the units of the Moeda Formation from the Cauê biochemical sediments in the QF. The Batatal formation is the ground truth that Moeda and Cauê are distinct units, and it also contains zircons younger than 2650 Ma. Thus, it is suggested that the ages from the volcanic layers in the Cauê Formation should be reevaluated.

5.4. The closure of the Minas Basin

The closure of the Minas Basin is marked by the regional 2nd order discordance followed by turbidite deposits of the Sabará Group and the intermontane sediments Itacolomi Group ([Dorr, 1969](#); [Machado et al., 1996](#); [Alkmim and Martins-Neto, 2012](#)). These deposits were formed during the inversion of the Minas Supergroup passive margin, followed by tectonic collapse and the development of the dome-keel structure ([Alkmim and Marshak, 1998](#)). We establish a maximum depositional age for the Sabará Group of ca. 2121 Ma, in agreement with the ID-TIMS U–Pb single zircon ages

of 2125 ± 4 Ma and 2131 ± 5 Ma ([Machado et al., 1992, 1996](#)) obtained in other localities of the Serra do Curral. In this sense, it is important to highlight that the felsic schist reported by [Hartmann et al. \(2006\)](#) as the Sabará Group close to Ouro Preto town matches with the pattern and maximum depositional ages for the Moeda Formation rather than for the Sabará Group. This is not surprising since lithologies are similar considering the strong effects of deformation and metamorphism in the southeast of the QF.

The inherited zircons spectra of the Sabará sediments shows two populations: a distinctive cratonic Paleoproterozoic source ranging from 2650 to 2950 Ma and a not local early Rhyacian source spreading in age from 2160 to 2320 Ma and (Fig. 11). The oldest zircon supply age range supports the observations of [Reis et al. \(2002\)](#) who indicates that the Sabará basin was infilled by the reworked older units of Minas Basin and the Rio das Velhas Greenstone Belt. Rhyacian crystallization ages were identified in the batholiths of the Mineiro Belt, southeast of the QF. Among these batholiths, the 2120–2150 Ma Ritópolis and Alto Maranhão batholiths ([Seixas et al., 2013](#)) in the Mineiro Belt domain. Rhyacian contribution (2160–2320 Ma) comprises igneous zircon cores crystallized mostly in juvenile magmas ($0 < \varepsilon_{\text{Hf}} < +8$) with ages of mantle extraction between 2450 and 2600 Ma and minor negative Hf-signatures ($-6 < \varepsilon_{\text{Hf}} < -3$) with late Mesoproterozoic Hf 2 s-TDM model ages. Other candidates for sourcing this synorogenic deposit are: (1) 2200–2230 Ma- Serrinha and Tiradentes juvenile suites and associated rocks ($-1 < \varepsilon_{\text{Nd}} < +7$; Syderian $T_{\text{DM}}\text{Nd}$ model ages in [Ávila et al., 2010](#)) and the older 2300–2350 Ma Ramos, Restinga de Baixo and Lagoa Dourada metaigneous rocks ([Seixas et al., 2012](#); [Ávila et al., 2014](#); [Teixeira et al., 2015](#)) in south-bordering Mineiro Belt. It is highly likely that both areas contributed to the Sabará basin.

The Rhyacian maximum depositional ages for the Sabará Group set an upper age constraint for the folding and thrusting upper crustal deformational event of the Transamazonian/Minas accretional orogeny and related metamorphism as younger than ≥ 2120 Ma. Moreover, the age of 2098 ± 33 Ma ([Brueckner et al., 2000](#)) in metamorphic contact aureole at its contact with the basement allows constraining the age of the dome and keel structure formation. Other clues of the collisional- related metamorphism are given for example by the multiple metamorphic overprints dated at 2140 and 2050 Ma in the Resende Costa Orthogneiss in the Mineiro Belt ([Teixeira et al., 2015](#)). Therefore, the sequential closure of the basin can be summarized as: ≤ 2120 Ma Sabará Group deposition, ca. 2100 Ma attachment of the Mineiro Belt (deformational pulse within Sabará Group. In summary, the deposition of the Sabará turbidites marks a major change in the source of Minas Supergroup sediments. The turbiditic pelites, greywackes, lithic conglomerates and diamictites of the Sabará Group were interpreted as representing synorogenic sediments ([Renger et al., 1995](#); [Reis et al., 2002](#)) shed from a colliding Mineiro and Mantiqueira magmatic arcs and spread over an evolving foreland basin onto the São Francisco Craton margin during the Rhyacian orogeny ([Alkmim and Martins-Neto, 2012](#)). The relaxation after the accretionary Minas belt might have cause the dome and keel building and the successful opening at ca. 1750 Ma of the Espinhaço basin in the eastern margin of the craton ([Machado and Abreu-Bentivi, 1989](#)). Final structure and massive fluid circulation were imprinted in the Neoproterozoic to Cambrian Brasiliano orogeny in the eastern and southeastern parts of the Quadrilátero Ferrífero.

6. Conclusions

A large data-bank of detrital zircon U–Pb partially coupled with Hf-data set for the Minas Supergroup has been obtained (>2000 analyzed zircons). The results obtained so far indicate that:

- The maximum depositional age for the Moeda Formation in the QF is conservatively reestablished as ≤ 2680 Ma for the base (unit I) and ≤ 2610 Ma for the top (unit III). Based on the widespread occurrence of *ca.* 2600–2630 Ma zircons in Moeda Formation we propose the rifting of the Minas Basin occurred after 2600 Ma.
- Detrital zircons from the Moeda Formation came from autochthonous sources recording populations identified in the Archean basement of the São Francisco Craton (Santa Bárbara, Rio das Velhas I, Rio das Velhas II, Mamona Granites).
- Hf isotopes applied on detrital zircon grains of the Moeda Formation indicate a major crustal reworking of Archean crust. However, slightly juvenile contributions have been detected for the Mamona (2730–2680 Ma) and late Mamona events (2620–2580 Ma).
- No lateral transitions have been documented so far between Moeda and Cauê formations in the Quadrilátero Ferrífero.
- The basin closed at *ca.* 2120 Ma with the deposition of the synorogenic Sabará Formation. The main source of the deposit is bracketed between 2120 and 2300 Ma and confirms a juvenile contribution from the Minerio Belt.

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Appendix A.

U–Pb isotope analyses

After cathodoluminescence imaging, in situ U–Pb isotope analyses of detrital zircons were undertaken at the Departamento de Geologia of the Universidade Federal de Ouro Preto (Brazil) in five analytical sessions: the first one in November 2013 and the second to the fifth in November 2014, February, May and June 2015, respectively. The analyses of the first session were performed using an Agilent 7700 Q-ICP-MS coupled to a 213 nm NewWave laser while the following sessions were produced using a ThermoScientific Element 2 sector field (SF) ICP-MS coupled to a CETAC LSX-213 G2+ laser system.

More than 800 reference materials and unknown zircons of the first U–Pb session were ablated by using a Q-ICP-MS small teardrop shape sample cell. The general operating conditions and U–Pb protocols are described in Moreira et al. (2016) and Takenaka et al. (2015). Acquisition time of the gas blank was 20 s, followed by a 40 s of measurement of U, Th and Pb signals during ablation, and a 30 s washout (Buick et al., 2011; Lana et al., 2013; Moreira et al., 2016). Laser ablation were set at 30 μm spot size, fluence between 6 and 8 J/cm^2 at a 10 Hz repetition rate using He mixed with Ar as a carrier gas. Times of signal integration were 15 ms for ^{206}Pb and ^{238}U , 40 ms for ^{207}Pb and 10 ms for ^{208}Pb , ^{204}Pb plus ^{204}Hg and ^{232}Th .

In sessions 2, 3 and 4, 1800 U–Pb analyses were carried out using a ThermoFinnigan Element 2 sector field ICP-MS coupled to

a CETAC 213 ultraviolet laser system (LA-SF-ICP-MS). Operating procedures and parameters were similar to those of Moreira et al. (2016) and Farina et al. (2015). Laser spot size and repetition rate were between 20 and 30 μm and 10 Hz, respectively. He and Ar carrier gases delivered the sample aerosol to the plasma. Each analysis consisted of 20 s gas blank analysis followed by 360 sweeps through masses 202, 204, 206, 207, 208, 232, 235, and 238, taking approximately 30 s using between 10 and 15% of the laser energy. Time-independent fractionation, laser induced elemental fractionation of Pb/U, background signal as well as common Pb were corrected by normalizing U/Pb and Pb/Pb ratios of the unknowns to the zircon standards and Pb composition model of Stacey and Kramers (1975), respectively. U and Th concentration were monitored by comparing to NIST 610 trace element glass. In order to test the validity of the applied methods and the accuracy and external reproducibility of the obtained U–Pb age data, we used GJ-1 zircon (608 ± 1 Ma; Jackson et al., 2004) or M127 (524 ± 1 Ma; Nasdala et al., 1998) as a primary reference material and every 10 to 15 unknowns and/or multiple analyses of Plešovice reference zircon (337 ± 1 Ma; Sláma et al., 2008), 91500 (1065 ± 1 Ma; Wiedenbeck et al., 1995) and of the in-house reference zircon Blue Berry for quality control (562 Ma Santos et al., 2017) every 10 to 20 unknowns. The LA-ICP-MS data were corrected and reduced using the software Glitter (Van Achterbergh et al., 2001) calculated and plotted on Concordia diagrams using the IsoplotEx 3.75 program (Ludwig, 2008). Uncertainties given for individual analyses (ratios and ages) are at the 1 sigma level.

The analytical data are reported in the Supplementary Material section A, including uncertainties at the 1σ level, and measurement errors.

Hf-isotopes analyses

Hf-isotope analyses herein reported were carried out using Thermo-Finnigan Neptune multicollector ICP-MS coupled to a Photon-Machines laser system that delivers a beam of 193 nm UV light from a frequency-quintupled Nd:YAG laser hosted also in Universidade Federal de Ouro Preto.

The analyses were achieved with a beam diameter of 50 μm , a repetition rate between 4 and 6 Hz and 50% of laser output. Depending on the conditions and Hf contents, the Hf signals were between 1 to 6 $\times 10^{-11}$ A and the ablation times lasted 60 s. Ar carrier gas transported from the ablated sample from the laser-ablation cell via mixing chamber to the ICPMS torch. The accurate measurement of $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in zircons requires corrections of the isobaric interferences of ^{176}Lu and ^{176}Yb on ^{176}Hf . Therefore, for this project we measured masses 172, 173 and 175–180 in static-collection mode and simultaneously monitored these isotopes. ^{177}Hf signal intensity was *ca.* 10 V. LA-ICP-MS data were reduced using In-house Excel Spreadsheets.

The accuracy and external reproducibility of the Lu–Hf results were guaranteed by bracketing every 50 unknowns with a bunch of standard zircons such as Temora (Black et al., 2003; Wu et al., 2006), GJ-1 (Jackson et al., 2004), Plešovice (Sláma et al., 2008), Mud Tank (Black and Gulson, 1978; Woodhead and Hergt, 2005), 91500 (Goolaerts et al., 2004), Blue Berry (Santos et al., 2017) which yielded $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.282658 ± 0.000026 ($n = 95$), 0.281985 ± 0.000042 ($n = 5$), 0.282478 ± 0.000018 ($n = 104$), 0.282496 ± 0.000027 ($n = 35$), 0.281671 ± 0.000023 ($n = 22$), respectively ($\pm 2\text{SD}$). These ratios are in good agreement with the accepted ratios data of 0.282000 ± 0.000005 (GJ-1), 0.282482 ± 0.000013 (Plešovice), 0.282680 ± 0.000031 (Temora), 0.282504 ± 0.000044 (Mud Tank), 0.282307 ± 0.000031 (91500) and 0.281674 ± 0.000018 (Blue Berry). See supplementary data B for detailed information.

For the calculation of the ϵ_{Hf} values, the chondritic values reported in Bouvier et al. (2008): $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785 \pm 11$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336 \pm 1$ are used. To calculate the model ages (T_{DM}) based on a depleted mantled source, the model with $(^{176}\text{Hf}/^{177}\text{Hf})_i = 0$ and a $^{176}\text{Lu}/^{177}\text{Hf}_{\text{DM}} = 0.0399$ (Blichert-Toft and Puchtel, 2010); this produces a value of $^{176}\text{Hf}/^{177}\text{Hf}$ (0.283294) similar to the average MORB over ca. 4560 Ma using the following equation:

$$T_{\text{DM}}(\text{Ga}) = [1/\lambda \ln\{(^{176}\text{Hf}/^{177}\text{Hf}_{\text{DM}(t)}) / (^{176}\text{Hf}/^{177}\text{Hf}_{\text{Sample}(t)}) / (^{176}\text{Lu}/^{177}\text{Hf}_{\text{DM}} - ^{176}\text{Lu}/^{177}\text{Hf}_{\text{AVC}}) + 1\} / 106 + \text{Age}(\text{Ma})] * 1/1000$$

The λ decay constant for ^{176}Lu used is $1.867E^{-11}$ (Söderlund et al., 2004) whereas the $^{176}\text{Lu}/^{177}\text{Hf}$ ratio for the average crust in the Paleoproterozoic to Archean is 0.0113 (as proposed by Scherer et al., 2001).

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.precamres.2017.01.026>.

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