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Author Statement

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LA-ICP-MS U-Pb dating of rutiles associated with hydrothermal mineralization along the southern Araçuaí Belt, SE Brazil

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Abstract

The presence of hydrothermal rutile enables the dating of mineralization related to hydrothermal processes. Refinement of the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technique is key to enabling the quick analysis of individual rutile crystals in high spatial resolution and dating of crystals with low U contents, as a prerequisite for the reliable characterization of hydrothermal deposits. For this study rutile crystals were selected from quartz and topaz veins that extend along the southeastern portion of the Araçuaí Belt, part of the long-lived (630 - 490 Ma) polyphase Brasiliano Orogen that formed during West Gondwana amalgamation. The purpose was to allow a systematic evaluation of in situ dating of hydrothermal rutile by LA-ICP-MS. U-Pb ages from different rutiles range between 527 ± 6 Ma and 487 ± 5 Ma, indicating that different parts of the orogen were affected by episodic fluid flow under oxidizing conditions over a similar time interval. Our U-Pb dating results of rutiles associated with the Imperial Topaz mineralization in the Quadrilátero Ferrífero (southern portion of the São Francisco Craton, SE Brazil) constrains the age of those deposits to 500-498 Ma, which is within the range of U-Pb ages of hydrothermal systems and mineralized zones previously reported for the region. The chemical composition of the studied hydrothermal rutiles, as determined by electron microprobe and LA-ICP-MS analysis, together with their U-Pb ages, suggests that the extensive fluid production required to form the hydrothermal deposits was generated from multiple sources. Fluid production was related to extensional collapse of the Araçuaí Orogen. The findings of this research clearly shows the utility of U-Pb rutile dating via LA-ICP-MS for geochronological study of a range of hydrothermal deposits.

Keywords: Hydrothermal rutile, U-Pb dating, LA-ICP-MS, Araçuaí Orogen, Southern Espinhaço Range, Quadrilátero Ferrífero

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1. Introduction

Rutile (TiO_2) commonly occurs as a metamorphic accessory phase in moderate- to high-pressure metapelitic rocks and in high-pressure metamorphosed mafic rocks, and as a detrital heavy mineral in clastic sedimentary rocks. Rutile also occurs rarely in magmatic rocks as well as in hydrothermal veins or alteration assemblages (e.g., Force, 1980; Okamoto and Maruyama, 2004; Choukroun et al., 2005; Scott and Radford, 2007; Rapp et al., 2010; Pereira et al., 2019; Gonçalves et al., 2019). Some studies also document the formation of rutile at low P-T conditions ($< 350 - 400^\circ\text{C}$, $< 2.0 - 3.5$ kbar) in hydrothermal deposits (e.g., Cabral et al., 2015a; Pereira et al., 2019).

The Ti substitution by trace elements in rutile is controlled by the size, valence and crystal field effects of the substitute element (Scott, 2005), such as Ta, Nb, Fe, Sn, Cr, Cu, V, Sb, W and Zr. Zack et al. (2002) showed for eclogites that 1 modal-% of rutile can incorporate more than 90% of the whole rock content of Ti, Nb, Ta, Sb and W and 5–50% of the whole rock content of V, Cr, Mo and Sn. Because the diffusivities of the trace elements of interest for volume diffusion are very low at the appropriate temperatures (e.g., Cherniak et al., 2007), rutile is an important controller of trace elements, such as Nb and Ta, in the continental crust (e.g., Zeh et al., 2018; Pereira et al., 2019), and for distinguishing between detrital rutile formed from mafic versus felsic source rocks (e.g., Zack et al., 2004). The occurrence of rutile in a range of rock types buffers the Ti content of co-existing quartz, and the temperature-dependence of the Ti-content of quartz in equilibrium with rutile has been experimentally determined (Wark and Watson, 2006; Thomas et al., 2010). In the case of hydrothermal rutilated quartz-veins, which commonly lack other assemblages useful for geothermometry, Ti-in-quartz thermometry has been successfully applied to estimate temperatures of vein formation (Gonçalves et al., 2019).

Rutile can also accommodate small amounts of uranium in its structure (generally 3 to 130 $\mu\text{g.g}^{-1}$), enough for U-Pb dating (e.g., Meinhold, 2010). However, it is important to note that the U contents of some crystals are too low (< 0.1 ppm) to be datable, as is the case of some hydrothermal rutiles (Zack et al., 2011). Metapelitic rocks from the granulite facies are more likely to contain datable rutile than coexisting metabasic rocks (Zack and Kooijman, 2017). Several factors seem to be important parameters for controlling the U content in rutile, such as whole rock U content, coexisting accessory phases, temperature and oxygen fugacity (Zack and Kooijman,

2017), but there is no predictive model available for understanding high U concentrations in rutile. An advantage of LA-ICP U-Pb dating is that the initial common lead correction for most rutiles can be routinely applied via ^{208}Pb due to its extremely low Th/U ratios (usually < 0.003) (Zack et al., 2011). The closure temperature for Pb diffusion in rutile is strongly dependent on grain size. For a cooling rate of $1\text{ }^{\circ}\text{C Ma}^{-1}$ and spherical geometry, Cherniak (2000) determined closure temperature values of $567\text{ }^{\circ}\text{C}$ for $70\text{ }\mu\text{m}$ -size grains and $617\text{ }^{\circ}\text{C}$ for $200\text{ }\mu\text{m}$ -size grains. This implies that the U-Pb dating of low-T ($< 400\text{ }^{\circ}\text{C}$) hydrothermal rutile should yield crystallization ages and, consequently, the timing of a given hydrothermal mineralization, instead of representing cooling ages. In addition, rutile is a relatively inert and resistant mineral, and therefore fulfills the basic requirements for a good U-Pb geochronometer.

The relatively common occurrence of rutile makes it suitable for dating metamorphic and some magmatic rocks, and constraining sedimentary provenance, and this tool has been used by many researchers (e.g., Bibikova et al., 2001; Hirdes and Davis, 2002; Li et al., 2003, 2011). Although there are many occurrences of rutile associated with hydrothermal deposits (e.g., Williams and Cesbron, 1977; Rice et al., 1998; Clark and Williams-Jones, 2004), there are relatively few publications related to hydrothermal rutile dating compared to those of metamorphic rutile (Richards et al., 1988, Wong et al., 1991, Machado et al., 1992, Davis et al., 1994, Doyle et al., 2015, Pi et al., 2017). When compared to zircon and monazite, rutile still receives less attention as a geochronometer. An important reason is the generally low U content of rutile and its higher susceptibility to metamorphic disturbances (e.g., Cherniak, 2000), which has resulted in numerous unsuccessful U/Pb dating attempts. However, rutile has the advantage of wider geological distribution, particularly in the case of hydrothermal environments.

Pioneering studies in the past performed rutile U-Pb dating by thermal ionization mass spectrometry (TIMS) to constrain metamorphic cooling histories (e.g., Mezger et al., 1989) or to date xenoliths in kimberlite (e.g., Davis, 1997). More recently, high spatial resolution U-Th-Pb dating techniques (LA-ICP-MS: laser ablation-inductively coupled plasma-mass spectrometry and SHRIMP/SIMS: secondary ionization mass spectrometry) have been developed for *in situ* geochronology of metamorphic and detrital rutile: Clark et al. (2000), Schmitt and Zack (2012) and Pi et al. (2017) using SHRIMP/SIMS; Storey et al. (2007), Allen and Campbell (2007), Birch et al. (2007) and Zack et al. (2011) using LA-quadrupole (Q)-ICP-MS; Kooijman et al. (2010) using

LA-single collector sector field (SF)-ICP-MS; and Vry and Baker (2006) and Gonçalves et al. (2019) using laser ablation (LA)-multi collector (MC)-ICP-MS. One of the advantages of LA-ICP-MS U-Pb rutile dating when compared to SIMS/SHRIMP is that, for the latter, differences in the crystal orientation of the rutile grain fragments embedded in the epoxy puck or in thin section can result in a significant range of dates for a single rutile generation (e.g., Taylor et al., 2012; Zack and Kooijman, 2017). This effect needs to be corrected for SIMS studies, while it does not appear in the LA-ICP-MS technique. There are only a few U-Pb geochronological studies of hydrothermal rutile by LA-ICP-MS (Zack et al., 2011; Cabral et al., 2013a; Pereira et al., 2019; Gonçalves et al., 2019). This technique is ideal for dating rutile crystals with low U because of the high precision, high sample throughput, and high spatial resolution as a prerequisite for a reliable characterization of hydrothermal deposits.

The Brazilian portion of the Araçuaí-West Congo orogenic system (Fig. 1), referred to as the Araçuaí Orogen (e.g., Pedrosa-Soares et al., 2011; De Campos et al., 2016; Richter et al., 2016; Melo et al., 2017), was affected by a massive circulation of hydrothermal fluids between 530 Ma and 480 Ma, beginning with a stage of extensional collapse (Alkmim et al., 2006; Peixoto et al., 2018; Gonçalves et al., 2019). This process was responsible for the generation of the Eastern Brazilian Pegmatite Province (Pedrosa-Soares et al., 2011), for the Au mineralization in the Southern Espinhaço Range (geomorphological representation of the Araçuaí Belt) and Quadrilátero Ferrífero (southern São Francisco craton) (Cabral et al., 2012, 2015b) and for the generation of a large number of metre- to kilometre-scale quartz veins (Scholz et al., 2012). The presence of hydrothermal minerals, such as rutile, allows the dating of these processes, as well as the mineralizations associated with them.

In this paper, the *in situ* dating of hydrothermal rutile by LA-ICP-MS is systematically evaluated and verified by comparison to ages obtained by ID-TIMS. A variety of rutile, with sufficiently high U concentration for U-Pb geochronology, was selected from quartz and topaz veins that extend along the southeastern portion of the Araçuaí Belt. The aim was to determine U-Pb ages of rutiles formed during the hydrothermal events that generated these quartz veins and the topaz deposits, Imperial variety, in the Quadrilátero Ferrífero, showing that it is possible to date hydrothermal rutile with accuracy and precision using the *in situ* LA-ICP-MS technique.

2. Geological background and sample description

The Araçuaí Belt (Almeida, 1977), is one of the external domains of the Araçuaí-West Congo Orogen (AWCO), the Brasiliano-Pan-African orogenic system (630 - 490 Ma) developed between the São Francisco (eastern Brazil) and Congo (central West Africa) cratonic regions during the West Gondwana amalgamation (e.g., Uhlein et al., 1986; Pedrosa-Soares et al., 1992, 2001, 2008; Alkmim et al., 2006). The main structural elements of the Araçuaí Belt include a system of faults and folds that affect the basement gneisses and Proterozoic metasedimentary rocks along the Southern Espinhaço Range and the eastern portion of the Quadrilátero Ferrífero mining district in the state of Minas Gerais, Brazil (Fig. 1).

The external belt of the AWCO has as its western boundary São Francisco craton, which is marked by reverse or thrust faults that juxtapose the Meso- and Neoproterozoic rocks involved in the belt with basement inliers or Ediacaran units of the São Francisco basin (Reis et al., 2017, Alkmim et al., 2017). To the east, the Araçuaí Belt is bounded by the orogen's crystalline core, consisting essentially of high-grade metamorphic rocks and Ediacaran to Cambrian granites (e.g., Pedrosa-Soares et al., 2011; Gradim et al., 2014; Gonçalves et al., 2016; Richter et al., 2016; Tedeschi et al., 2016; Melo et al., 2017; Narduzzi et al., 2017).

After the collision and crustal thickening of the Araçuaí Orogen, a gravitational collapse occurred, which was responsible for an intense fluid flow (e.g., Alkmim and Marshak, 1998; Gonçalves et al., 2019) and generation of numerous quartz veins that cut greenschist-facies metasediments involved in the fold and thrust belts in the outer portion of the orogen (Gonçalves et al., 2018). These veins are concordant or discordant to the foliation and show strong lithostructural control (Chaves et al., 2003; Chaves, 2007; Chauvet et al., 2001).

In the Quadrilátero Ferrífero, these quartz veins are associated with gold mineralization of the Ouro Preto region (e.g., Chauvet et al., 2001; Cabral et al., 2013b) and the southern flank of the Mariana Anticline (Fig. 1), and important occurrences of topaz, Imperial variety, distributed along the northeastern area of the Dom Bosco Syncline and on the northeastern flank of the Mariana Anticline (Fig. 1), thus

demonstrating a structural and stratigraphic control of mineralizations (e.g., Gandini, 1994; Morteani et al., 2002; Rojas et al., 2009; Gauzzi et al. 2018).

All the rutile occurrences studied are related to the Southern Espinhaço Range and the southern portion of the Quadrilátero Ferrífero (Minas Gerais, SE Brazil) (Fig. 1).

The Espinhaço Range begins, in the south, in the Quadrilátero Ferrífero and extends northward for about 1200 km to the extreme north of the Bahia State, with widths varying from a few kilometers to almost 100 km. The main lithostratigraphic unit that crops out along this mountain range is the Espinhaço Supergroup, which was deposited during the Paleo-Mesoproterozoic (1.8-0.9 Ga; e.g., Santos et al., 2013; Guadagnin et al., 2015). It consists of quartzite with intercalations of phyllite and metaconglomerate, with rare units of metavolcanic rocks in its basal portion (e.g., Schöll and Fogaça, 1979; Machado et al., 1989; Dossin et al., 1990). The basement crops out in the central portion and in the eastern margin of the mountain range. In the Southern Espinhaço Range, the Espinhaço Supergroup is overlain by metasediments of the Neoproterozoic (0.85-0.6 Ga) São Francisco Supergroup (e.g., Babinski et al., 1999) and (0.93-0.6 Ga) Macaúbas Group (e.g., Kuchenbecker et al., 2015).

The Quadrilátero Ferrífero mining district occurs to the south of the Espinhaço Range. It is a granite-greenstone basement terrane characterised by multiple Archaean / Paleoproterozoic generations of TTG (tonalite-trondhjemite-granodiorite) and potassic granitoid plutonic rocks that surround polydeformed greenstone belt sequences (Rio das Velhas Supergroup) dated between 3.2 Ga and 2.6 Ga (e.g., Teixeira et al., 1996; Machado et al., 1996; Lana et al., 2013; Romano et al., 2013).

After the last magmatic event, the basement crust experienced extension and accumulation of a thick Paleoproterozoic succession (Alkmim and Marshak, 1998; Alkmim and Martins-Neto, 2012; Farina et al., 2016; Martinez-Dopico et al., 2017; Aguilar et al., 2017) of chemical and clastic strata constituting the Minas Supergroup and the Itacolomi Group.

In the Espinhaço Range, the Araçuaí Orogeny caused the development of large-scale, north-south trending, asymmetric folds with axial planes and associated foliations that dip steeply to the east (e.g., Uhlein, 1991; Chaves et al., 2003). On the eastern edge of the Quadrilátero Ferrífero, a well-developed stretching lineation, oriented from E-W to NW-SE, is associated with kinematic indicators that indicate NW vergence, and thrusting of the Minas Supergroup over the Archaean rocks (e.g., Marshak and Alkmim,

1989; Chemale Jr. et al., 1994; Chauvet et al., 2001). Regional metamorphic grade increases from greenschist to amphibolite facies, from west to east across the Espinhaço Range (e.g., Uhlein, 1991).

Fig. 1. Simplified geological map of the regions where the studied samples were taken. The regions are located in the Araçuaí belt, Southern margin of the São Francisco Craton (top). Samples and their localities: DB Dom Bosco; B Bocaina; SJ São João; AP Antônio Pereira; FB Fazenda Bandeirinha; D DR1 and DR2 from the Diamantina region; I Itamarandiba. Modified from Grossi-Sad et al. (1997), Lobato et al. (2005) and Alkmim and Martins-Neto (2012).

Rutile samples were obtained from both the Araçuaí Belt, geomorphologically represented by the Southern Espinhaço Range, and the southern portion of the São Francisco Craton, in the Quadrilátero Ferrífero (Fig. 1). The rutiles from the Araçuaí Belt are derived from quartz veins that cut greenschist facies metasedimentary rocks of the Espinhaço Supergroup and the Macaúbas Group, while the rutiles from the Quadrilátero Ferrífero were collected in quartz / carbonate veins. An additional three samples from the Quadrilátero Ferrífero are associated with deposits of Imperial Topaz.

The Fazenda Bandeirinha, DR1, DR2 and Itamarandiba rutile specimens (Fig. 1 and 2) came from the Southern Espinhaço Range and were obtained from vertical, discordant, metre-scale quartz veins that strike N30-40°E. In addition to quartz and rutile, the veins may also contain combinations of monazite, xenotime, specular hematite, ilmenite, kaolinite, kyanite, anatase, euclase, barite, tourmaline, almandine-rich garnet and/or gold (e.g., Chaves et al., 2010; Cabral et al., 2012; Gonçalves et al., 2018, 2019). The veins additionally locally contain fragments of the country rock that may show diffuse contacts with the quartz veins.

Antônio Pereira, Bocaina and Dom Bosco rutiles (Figs. 1 and 2) were collected from quartz or carbonate veins that contain the commercially important “Imperial” variety of topaz. These veins occur in the southern portion of the Quadrilátero Ferrífero. Dom Bosco and Bocaina rutiles come from veins that mainly cut altered phyllites from the Piracicaba Group and dolomitic marbles from the Gandarela Formation (Itabira Group). Antônio Pereira rutile comes from veins that mainly cut altered rocks of the Cauê and Gandarela Formations (Itabira Group) and the rocks of the Cercadinho Formation (Piracicaba Group) (e.g., Morteani et al., 2002; Rojas et al., 2009; Gauzzi et al., 2018). The topaz-bearing veins are discontinuous, subvertical and strike NW-SE. In addition to quartz and rutile, they also contain kaolinite, muscovite, hematite and euclase (Morteani et al., 2002). The country rocks to the Imperial Topaz veins are metamorphosed and quite altered, with rare outcrops of bedrocks (Gandini 1994). Bocaina rutile was the only one to be found in unaltered rock, being constituted by a dolomitic marble (Fig. 2b) belonging to the Fecho do Funil Formation (Piracicaba Group) (Ferreira 1991, Gandini 1994).

Additional rutile crystals (called São João – Figs. 1 and 2) were donated by miners. São João rutiles come from disaggregated material, associated with quartz veins that cut the meta-ultramafic rocks of the Nova Lima Group close to Ouro Preto. These veins are probably associated with the gold mineralization that occurs in the Mariana

Anticline, due to the contact between the rocks of the Nova Lima and Caraça Groups (Chauvet et al., 2001).

Rutile crystals from the different localities (Fig. 2) are predominantly euhedral, with short to elongated prisms, ranging in length from 2 mm to 3 cm. They are red/brown in colour and translucent.

Fig. 2. Rutile crystals analysed in this study – a) Prismatic crystals of Antônio Pereira rutile in a carbonate vein; b) Acicular crystals of Bocaina rutile in dolomitic marble; c) DR1 and DR2 rutile grains in quartz veins; d) Dom Bosco rutile crystals in aggregates with muscovite, biotite and quartz; e) Fazenda Bandeirinha rutile from a quartz vein that cuts hematitic phyllite; f) Itamarandiba rutile crystals in quartz vein with hematite; g) Prismatic crystals of São João rutile.

3. Analytical methods

The studied rutiles were obtained with the help of miners, who collected the samples directly from the quartz / carbonate veins. When necessary, the grains were broken and mounted on resin disks. The fragments were exposed and polished to provide a suitable surface for the subsequent analyses. The polished resin mounts were coated with carbon for BSE (backscattered-electron) imaging (Fig. 3) via the JEOL JSM-6010LA Scanning Electron Microscope, at the Laboratório de Microscopia e Microanálises of the Universidade Federal de Ouro Preto (UFOP), Minas Gerais (Brazil).

The chemical composition of the rutiles was determined by electron microprobe (EPMA) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at UFOP.

The mass fractions of major and minor elements were obtained in the Laboratório de Microscopia, Setor Microsonda Eletrônica at UFOP, using a JEOL Superprobe JXA-8230 EPMA, equipped with 5 WDS (Wavelength-Dispersive System) spectrometers. The operating conditions used for the analyses on the rutile crystals were: 15 kV acceleration voltage, 20 nA beam current and 10 μm beam diameter. The counting time for Na, Al, Mg, Zn, Fe, Ca, Cr, Sr, Ti, K and Mn was 10 s for the peak and 5 s for the background, and for Zr, V, Nb and Ta measurements were made for 30 s for the peak and 15 s for the background. For the calibration procedures, the following standards were used: Na (anorthoclase), Zr (zircon), Al (corundum), Mg (olivine), Zn (gahnite), Fe (magnetite), V (IR-W glass), Nb (Nb), Ta (Ta), Ca (F-apatite), Cr (chromite), Sr (strontianite), Ti (rutile), K (microcline) and Mn (MnO_2). Matrix corrections were performed automatically by JEOL software using the ZAF methodology (Goldstein et al., 2003).

Minor and trace element abundances were also determined by LA-ICP-MS in the Laboratório de Geoquímica Isotópica (LOPAG) at UFOP, using a single collector sector field (SF) ICP-MS of Thermo-Finnigan Element II, coupled to a CETAC UV NdYAG 213nm laser system. Table 1 shows the masses that were analysed, the acquisition parameters and the reference materials used. The average TiO_2 concentrations for individual rutile grain fragments determined by electron microprobe were used as internal reference in order to correct the differences in ablation yields between the samples analysed and the glass standards. The analyses were calibrated

using the NIST SRM 610 synthetic glass (Jochum et al., 2011). Elemental concentrations were calculated in time-resolved mode using the Glitter 4.4.3 software (Van Achterbergh et al., 2001).

Table 1: Summary of Laser ablation systems and analytical information.

Laboratory and Sample Preparation	Trace element determinations	LA-MC-ICP-MS (UFOP) U-Pb
Laboratory name	Laboratório de Geoquímica Isotópica, Departamento de Geologia, Universidade Federal de Ouro Preto (UFOP)	
Sample type / mineral	Hydrothermal rutile	
Sample preparation	Conventional mineral separation, 2.5 cm resin mount, 1 μm polish to finish	
Imaging	BSE, SEM JEOL JSM-6010LA, 20 nA, 20kV, 20 mm working distance	
Laser ablation system		
Make, Model and type	CETAC LSX-213 G2	Photon Machines G2 excimer laser
Ablation cell and volume	HelEx	Low volume HelEx
Laser wavelength (nm)	213 nm	193 nm
Pulse width (ns)	<5 ns	<4 ns
Fluence (J cm^{-2})	4 J cm^{-2}	2 J cm^{-2}
Repetition rate (Hz)	10 Hz	5 Hz
Ablation duration (s)	40 s	40 s
Ablation pit depth / ablation rate	~25 μm pit depth	~10 μm pit depth
Spot diameter (μm)	30 μm	85 μm
Sampling mode / pattern	Static spot ablation	Static spot ablation
Carrier gas	100% He in the cell, Ar make-up gas combined using a Y-piece 50% along the sample transport line to the torch.	100% He in the cell, Ar and N_2 make-up gas, combined using two Y-piece 50% along the sample transport line to the torch.
Cell carrier gas flow (l min^{-1})	0.8 l min^{-1}	1.2 l min^{-1}
ICP-MS		

Instrument		
Make, Model and type	ThermoFisher Scientific, Element II, SF-ICP-MS	ThermoFisher Scientific, Neptune Plus, MC-ICP-MS
Sample introduction	Ablation aerosol	Ablation aerosol
RF power (W)	1200 W	1300 W
Make-up gas flow (l min ⁻¹)	0.8 l min ⁻¹	0.7 l min ⁻¹
Detection system	SEM/discrete dynode detector system	SEM/compact discrete dynode ion counters/Faraday cups
Masses measured	¹¹ B, ²⁹ Si, ⁴⁵ Sc, ⁶⁶ Zn, ⁸⁸ Sr, ⁹⁰ Zr, ⁹³ Nb, ¹²¹ Sb, ¹⁸⁰ Hf, ¹⁸¹ Ta, ¹⁸⁴ W, ²⁰⁸ Pb, ²³² Th, ²³⁸ U	Faraday ²³² Th and ²³⁸ U and IC ²⁰² Hg, ²⁰⁴ Pb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb
Total integration time per output data point (s)	0.130 s	0.131 s
IC Dead time (ns)	18 ns	IC1-2: 20 ns; IC4-5: 70 ns and IC6: 5 ns.
Data Processing		
Gas blank	20 s	20 s
Calibration strategy	NIST SRM 610 used as primary reference material; NIST SRM 612, BCR-2G and BHVO-2G used as secondaries/ validation	Tanzania zircon used as primary reference material, Antonio Pereira and DR2 rutile used as secondaries/ validation
Reference Material info	NIST SRM 610 and NIST SRM 612 (Jochum et al., 2011) BCR-2G and BHVO-2G (Jochum et al., 2016)	Tanzania zircon (Santos et al., unpublished results) Antonio Pereira and DR2 (this study)
Data processing package used / Correction for LIEF	Glitter 4.4.3 software (Van Achterbergh et al., 2001). LIEF correction assumes that RM and sample behave identically	MATLAB in-house software. LIEF correction use the intercept method which independently corrects each ablation for downhole fractionation
Mass discrimination	External calibration	Corrected by normalization to the primary RM (Tanzania zircon)
Common-Pb correction, composition and		No common-Pb correction applied to the data.

uncertainty		
Uncertainty level and propagation	Quoted at 2s absolute, propagation by quadratic addition. Reproducibility and composition uncertainty of reference material were propagated where appropriate.	Ages are quoted at 2s absolute, propagation is by quadratic addition. Reproducibility and age uncertainty of reference material and common-Pb composition uncertainty are propagated where appropriate.
Quality control / Validation	NIST SRM 612 (Jochum et al., 2011) BCR-2G and BHVO-2G (Jochum et al., 2016)	Antônio Pereira rutile – Lower intercept age = 499.6 ± 2.4 Ma (2s, MSWD = 0.52, n = 18) Systematic uncertainty for propagation is 1% (2s).

U-Pb LA-ICP-MS geochronology was performed at LOPAG (UFOP) using a Thermo-Finnigan Neptune multi-collector (MC) sector field ICP-MS coupled to a Photon-Machines 193 nm laser system. Table 1 shows the reference materials and acquisition parameters used. Since the analysed rutiles had relatively low U concentrations ($3\text{--}81 \mu\text{g.g}^{-1}$; Table 4), Tanzania zircon, an in-house 601 ± 1 Ma, low-U (11 to $26 \mu\text{g.g}^{-1}$) reference material developed in LOPAG (UFOP), was used as the primary reference material (Santos et al., unpublished results; TIMS U-Pb data for Tanzania zircon can be found in supporting information). Non-matrix matched dating of a range of minerals using zircon as primary reference material is an approach that has been previously successfully used in a number of studies (e.g., Millonig et al., 2013; Avigad et al., 2017; Van Lichtenvelde et al., 2017; Be'eri-Shlevin et al., 2018; Ghobadi et al., 2018; Müller et al., 2018; Walter et al., 2018). In these studies, GJ-1 zircon was used as primary reference material for dating perovskite, monazite, apatite, baddeleyite, pyrochlore, titanite, xenotime, hematite, columbite, rutile, and secondary reference materials of the mineral of interest are used to establish a matrix offset to correct the age of these minerals (e.g., Avigad et al., 2017; Müller et al., 2018). For the quality control of the analyses, and in order to minimize the matrix effect caused by the use of zircon as

a reference material in the rutile analysis, an offset factor was applied based on newly acquired ID-TIMS U-Pb isotope data for Antônio Pereira rutile. Rutile from the Antônio Pereira hydrothermal deposit has previously been shown to have homogeneous U-Pb compositions at an intra- and intergrain scale, and thus could be considered a potential reference material for U-Pb geochronology (Gonçalves et al., 2019). In order to verify the efficiency of the offset applied, DR2 rutile was used as a quality control based on new ID-TIMS U-Pb data collected as part of this study. LA-ICP-MS U-Pb dating tests were performed on DR2 rutile (unpublished data) and it was isotopically homogeneous, which justifies TIMS analysis and the use of this mineral as a secondary reference material.

For data processing, we used a new MATLAB bundle, based on an in-house spreadsheet by Lana et al. (2017). The calculation of final ages and plots were performed in Isoplot 3.75 (Ludwig, 2012). A matrix offset of 3.5% between the Tanzania zircon and the Antônio Pereira rutile during the analysis session was used for calibration of the sample and the DR2 rutile U-Pb isotope data.

To characterise the Antônio Pereira and DR2 rutiles as quality control reference materials, U-Pb analysis were performed via ID-TIMS (Isotope Dilution-Thermal Ionisation Mass Spectrometry) at the Jack Satterly Geochronology Laboratory (JSGL, University of Toronto, Canada), and at TIMS U-Pb Laboratory (University of Oslo, Norway). The dissolution procedures, spike used, chemical concentration of U and Pb, mass spectrometer information and data processing are presented in Table 2. The uncertainties propagation was performed according to Schoene et al. (2006). The $^{207}\text{Pb}/^{235}\text{U}$ ratio and age were obtained from the $^{238}\text{U}/^{235}\text{U}$ ratio of 137.88 by Steiger and Jäger (1977).

Table 2: Summary of the U-Pb ID-TIMS methods.

Laboratory and Sample Preparation	U-Pb ID-TIMS (Toronto)	U-Pb ID-TIMS (Oslo)
Laboratory name	Jack Satterly Geochronology Laboratory at University of Toronto (Canada)	TIMS U-Pb Laboratory at University of Oslo (Norway)
Sample type/mineral	Hydrothermal rutile	Hydrothermal rutile
Sample preparation	Grains weighed prior to cleaning. Washed in dilute HNO ₃ at room temperature.	Fragments cleaned in hot HNO ₃ , water and acetone, dried and weighed
Dissolution	Teflon bombs, spiked, in HF (+HNO ₃) at 200°C for 4 days	Teflon bombs, spiked, in HF (+HNO ₃) at 195°C for 5 days
Spike information	²⁰⁵ Pb- ²³⁵ U	²⁰² Pb- ²⁰⁵ Pb- ²³⁵ U
Chemical concentration	Two stage HBr-HCl- HNO ₃ anion exchange resin	Two stage HBr-HCl- HNO ₃ anion exchange resin
Mass Spectrometer Instrument		
Make, Model and type	Micromass, VG354 Multi-Collector, TIMS	Finnigan, MAT262, TIMS
Sample introduction	Out-gassed rhenium filaments with silica gel and H ₃ PO ₄ (Gerstenberger and Haas, 1997)	Out-gassed rhenium filaments with silica gel and H ₃ PO ₄ (Gerstenberger and Haas, 1997)
Detection system	Faraday cups and Daly detector	Faraday cups and secondary electron multiplier
Masses measured	Faraday: 205, 206, 207, 235, 238 Daly: 204, 205, 206, 207, 208, 235, 238	Faraday: 202, 205, 206, 207, 208, 235, 238 SEM: 204
Data Processing		
Lab Blank	1 pg for Pb, 0.1 pg for U	2 pg for Pb, 0.1 pg for U

Initial common-Pb correction	Stacey and Kramers (1975)	Stacey and Kramers (1975)
Mass discrimination	Pb and U fractionation 0.10% per atomic mass unit	Pb fractionation $^{205}\text{Pb}/^{202}\text{Pb}$ ratio and U with 0.12%/amu using U500.
Multiplier discrimination	0.05% per atomic mass unit for Daly measurements	None
U isotopic composition	$^{238}\text{U}/^{235}\text{U} = 137.88$ (Steiger and Jäger, 1977)	$^{238}\text{U}/^{235}\text{U} = 137.88$ (Steiger and Jäger, 1977)
Decay constant	Jaffey et al. (1971)	Jaffey et al. (1971)
Uncertainty level and propagation	Ages are quoted at 95% c.l. absolute, uncertainty propagation is by quadratic addition. Spike and decay constant uncertainties were propagated where appropriate (Schoene et al., 2006)	Ages are quoted at 95% c.l. absolute, uncertainty propagation is by quadratic addition. Spike and decay constant uncertainties were propagated where appropriate (Schoene et al., 2006)

4. Results

4.1 Chemical composition

Antônio Pereira, Bocaina and São João rutile grains do not show compositional zoning in BSE images, whereas the BSE images of the DR1, DR2, Dom Bosco, Fazenda Bandeirinha and Itamarandiba rutiles show sector zoning (Fig. 3), indicating some compositional heterogeneity, as shown by the high standard deviation values in Tables 3 and 4. Complete chemical analysis data are available as supplementary material.

Fig. 3. BSE images of the studied rutiles: (a) Antônio Pereira; (b) Bocaina; (c) DR1 and DR2 from Diamantina region; (d) Dom Bosco; (e) Fazenda Bandeirinha; (f) Itamarandiba rutile grain fragment and detail of rutile (Rt), Ti-hematite (Ti-Hem) and ilmenite (Ilm) aggregate; (g) São João. Antônio Pereira, Bocaina and São João rutiles show no evidence of compositional zoning, whereas the DR1, DR2, Dom Bosco, Fazenda Bandeirinha and Itamarandiba rutiles show sector zoning.

Tables 3 and 4 present the chemical composition of the selected rutile crystals. The chemical composition of Bocaina rutile was obtained only by LA-SF-ICP-MS (Gonçalves et al., 2019) and can be seen in Table 4.

According to the EPMA results (Table 3), most of the rutiles are close to pure TiO_2 (~97-99 wt%) except for rutile from Fazenda Bandeirinha and Itamarandiba, which have much lower TiO_2 (92.6 to 97.5 wt% and 87.7 to 91.5 wt%, respectively), and correspondingly higher FeO (0.82 to 2.03 wt% for Fazenda Bandeirinha; 2.57 to 4.80 wt% for Itamarandiba rutile) and Nb_2O_5 (0.40 to 3.30 wt% for Fazenda Bandeirinha; 4.12 to 5.98 wt% for Itamarandiba rutile) contents.

According to the data obtained by LA-ICP-MS (Table 4), where the contents of minor and trace elements and Nb again were measured, Antônio Pereira, Bocaina, Dom Bosco and Itamarandiba rutiles have the highest U contents ($28\text{--}115\ \mu\text{g.g}^{-1}$), while DR1, DR2, Fazenda Bandeirinha and São João rutiles have low U contents ($2.0\text{--}7.7\ \mu\text{g.g}^{-1}$). Higher Nb contents in Fazenda Bandeirinha and Itamarandiba rutiles were confirmed by LA-ICP-MS analysis ($5674\text{--}42960\ \mu\text{g.g}^{-1}$). The Itamarandiba rutile also has greater Ta and W contents ($2047\text{--}3033\ \mu\text{g.g}^{-1}$ and $4168\text{--}8245\ \mu\text{g.g}^{-1}$, respectively).

Most of the Nb/Ta and Zr/Hf ratios are subchondritic, with mean values of: 4.8 and 15.2 for Antônio Pereira, 2.2 and 15.9 for Bocaina, 15.5 and 5.2 for DR1, 22.0 and 14.6 for DR2, 2.1 and 10.8 for Dom Bosco, 22.3 and 5.8 for Fazenda Bandeirinha, 15.3 and 3.2 for Itamarandiba, and 9.1 and 15.7 for São João. For comparison, $\text{Nb/Ta}_{\text{chondrite}} = 19.9$ (Münker et al., 2003) and $\text{Zr/Hf}_{\text{chondrite}} = 36.3$ (McDonough and Sun, 1995). These data show the existence of fractionation between Nb/Ta and Zr/Hf in hydrothermal systems and the preferential incorporation of Ta and Hf in relation to Nb and Zr by hydrothermal rutile (e.g., Green and Adam, 2003; Klemme et al., 2005; Pereira et al., 2019; Zeh et al. 2018).

The Cr vs Nb diagram (Fig. 4) was originally designed to separate pelitic from mafic protoliths (Zack et al., 2004) but Cr or Nb enrichments should also reflect the composition of the lithologies from which the hydrothermal fluids were derived (e.g., Pereira et al., 2019). Some of the studied rutiles (Antônio Pereira, Bocaina, DR1, DR2 and Dom Bosco) have intermediate contents of both elements, suggesting the mixing of both components, whereas the Fazenda Bandeirinha and Itamarandiba rutiles are rich in Nb and the São João rutile presents predominantly higher concentrations of Cr. This should reflect the nature of the fluids, as some rutiles incorporated more trace elements than others. As can be seen in the Cr vs Nb diagram, a predominantly mafic source was responsible for the precipitation of the Antônio Pereira, Bocaina, Dom Bosco and São João rutiles, a mixed source precipitated the DR1 and DR2 rutiles and a metapelitic source may have been responsible for the precipitation of the Fazenda Bandeirinha and Itamarandiba rutiles.

Table 3: EPMA results for the chemical composition of the studied rutiles.

Sample (wt%)	Antônio Pereira (n = 13)		DR1 (n = 17)		DR2 (n = 15)		Dom Bosco (n = 14)		Fazenda Bandeirinha (n = 21)		Itamarandiba (n = 27)		São João (n = 22)	
	Mean	1SD	Mean	1SD	Mean	1SD	Mean	1SD	Mean	1SD	Mean	1SD	Mean	1SD
Na ₂ O	0.008	0.006	0.019	0.012	0.016	0.013	0.035	0.016	0.027	0.021	0.015	0.010	0.018	0.013
MgO	0.013	0.008	0.013	0.006	0.012	0.004	0.013	0.009	0.016	0.012	0.015	0.008	0.013	0.013
Al ₂ O ₃	0.050	0.023	0.027	0.019	0.026	0.018	<d.l.		0.020	0.016	0.026	0.019	0.034	0.013
K ₂ O	0.003	0.002	0.004	0.002	0.003	0.002	0.007	0.005	0.008	0.007	0.005	0.003	0.006	0.005
CaO	0.037	0.060	0.012	0.007	0.009	0.006	0.022	0.016	0.017	0.009	0.015	0.014	0.044	0.125
TiO ₂	98.275	0.216	98.088	0.529	98.254	0.705	97.939	0.413	95.747	1.742	89.512	0.912	97.929	0.674
V ₂ O ₃	0.711	0.043	0.501	0.053	0.499	0.066	0.550	0.083	0.469	0.045	0.574	0.041	0.509	0.041
Cr ₂ O ₃	0.106	0.046	0.113	0.044	0.129	0.050	0.043	0.024	0.035	0.022	0.058	0.031	0.436	0.249
MnO	0.021	0.014	0.013	0.012	0.012	0.009	<d.l.		0.017	0.010	0.018	0.012	<d.l.	
FeO	0.122	0.036	0.271	0.085	0.324	0.139	0.916	0.062	1.295	0.466	3.182	0.474	0.236	0.026
ZnO	0.034	0.025	0.027	0.021	0.028	0.019	<d.l.		0.035	0.025	0.021	0.031	0.014	0.029
SrO	<d.l.		0.037	0.031	0.058	0.033	<d.l.		0.015	0.025	0.043	0.025	0.054	0.050
ZrO ₂	<d.l.		0.017	0.010	<d.l.		<d.l.		<d.l.		<d.l.		<d.l.	
Nb ₂ O ₅	0.044	0.020	0.112	0.053	0.085	0.060	0.054	0.036	1.506	1.162	4.891	0.481	0.100	0.043
Ta ₂ O ₅	<d.l.		0.028	0.022	0.028	0.028	0.255	0.160	0.199	0.118	0.251	0.168	0.185	0.136
TOTAL	99.4		99.2		99.4		99.7		99.3		98.5		99.4	
(a.p.f.u.)														
Na ⁺	0.000		0.000		0.000		0.000		0.000		0.000		0.000	
Mg ²⁺	0.000		0.000		0.000		0.000		0.000		0.000		0.000	
Al ³⁺	0.000		0.000		0.000		<d.l.		0.000		0.000		0.000	

K ⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca ²⁺	0.001	0.000	0.000	0.000	0.000	0.000	0.001
Ti ⁴⁺	0.991	0.991	0.991	0.988	0.975	0.936	0.988
V ³⁺	0.004	0.003	0.003	0.003	0.003	0.003	0.003
Cr ³⁺	0.001	0.001	0.001	0.000	0.000	0.000	0.002
Mn ²⁺	0.000	0.000	0.000	<d.l.	0.000	0.000	<d.l.
Fe ²⁺	0.001	0.003	0.004	0.010	0.015	0.037	0.003
Zn ²⁺	0.000	0.000	0.000	<d.l.	0.000	0.000	0.000
Sr ²⁺	<d.l.	0.000	0.000	<d.l.	0.000	0.000	0.000
Zr ⁴⁺	<d.l.	0.000	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
Nb ⁵⁺	0.000	0.000	0.000	0.000	0.005	0.015	0.000
Ta ⁵⁺	<d.l.	0.000	0.000	0.000	0.000	0.000	0.000
TOTAL	1.00	1.00	1.00	1.00	1.00	0.99	1.00
O ²⁻	2	2	2	2	2	2	2

<d.l. = below detection limit; n = number of analyses. Structural formulas based on two oxygens.

Table 4: Mean of the minor and trace elements mass fractions ($\mu\text{g}\cdot\text{g}^{-1}$) of the studied rutiles determined by LA-SF-ICP-MS.

Element (μg g ⁻¹)	Rutiles																
	Antônio Pereira (n = 15)		DR1 (n = 5)		DR2 (n = 10)		Dom Bosco (n = 5)		Fazenda Bandeirinha (n = 5)		Itamarandiba (n = 5)		São João (n = 15)		Bocaina ^a (n = 22)		
	Mean	2SD	Mean	2SD	Mean	2SD	Mean	2SD	Mean	2SD	Mean	2SD	Mean	2SD	Element (μg g ⁻¹)	Mean	2SD
¹¹ B	3.1	0.4	3.1	0.2	3.2	0.2	4.4	0.8	4.6	0.5	5.3	0.3	3.2	0.3	²⁷ Al	423	443
²⁹ Si	3857	1292	3507	2235	3925	1511	2574	833	2894	1094	2562	282	2975	1459	⁴⁵ Sc	9.7	5.4
⁴⁵ Sc	3.4	2.3	72.6	38.9	83.2	13.8	3.4	1.1	16.1	4.0	41.9	9.9	12.7	5.8	⁵¹ V	2308	1067
⁶⁶ Zn	43	8	41	5	44	7	34	3	28	1	33	4	43	19	⁵² Cr	723	129
⁸⁸ Sr	1.2	0.5	1.1	0.4	1.1	0.4	3.8	0.2	3.4	0.3	3.4	0.3	1.3	0.3	⁹⁰ Zr	70	72
⁹⁰ Zr	50	5	78	55	73	8	70	39	33	16	93	5	47	15	⁹³ Nb	340	253
⁹³ Nb	516	91	1817	1503	977	145	350	181	16231	19417	39814	5553	996	243	⁹⁷ Mo	0.44	0.33
¹²¹ Sb	171	33	0.8	0.1	0.7	0.2	275	137	5.9	0.5	107	26	257	72	¹¹⁹ Sn	101	73
¹⁸⁰ Hf	3.3	0.7	15.1	19.0	5.0	0.9	5.8	3.1	5.9	4.2	30.1	15.4	3.0	1.1	¹²¹ Sb	437	142
¹⁸¹ Ta	108	17	205	350	45	16	177	119	674	602	2632	766	110	22	¹⁸⁰ Hf	4.4	6.6
¹⁸⁴ W	117	20	2372	4206	103	74	424	837	280	52	5411	3397	24	48	¹⁸¹ Ta	160	137
²⁰⁸ Pb	3.5	3.2	1.3	3.8	3.4	4.0	0.2	0.2	0.3	0.4	6.9	23.4	3.1	5.6	¹⁸⁴ W	248	575
²³² Th	0.18	0.26	0.05	0.01	0.05	0.01	0.06	0.14	<d.l.		0.02	0.02	<d.l.		²⁰⁸ Pb	3.8	4.1
²³⁸ U	45	6	4.8	3.8	3.1	0.7	81	63	5.7	2.1	30	3	3.2	1.8	²³² Th	4.6	10
Nb/Ta	4.8	0.9	15	20	22	6	2.1	0.8	22	11	15	3	9.1	3.0	²³⁸ U	56	72
															Nb/Ta	2.2	0.67

<d.l. = below detection limit; n = number of analyses; ^a Data from Gonçalves et al. (2019).

Fig. 4. Cr vs Nb diagram for rutile after Zack et al. (2004) and later modified by Meinhold et al. (2008). Note how the Fazenda Bandeirinha and Itamarandiba rutiles are highly enriched in Nb. The results plotted are derived from the EPMA analyses, except for Bocaina rutile, whose data are from LA-SF-ICP-MS, published by Gonçalves et al. (2019).

4.2 U-Pb dating by ID-TIMS

Antônio Pereira and DR2 rutiles were dated by U-Pb ID-TIMS, because these were presented as potential reference materials for U-Pb geochronology via LA-ICP-MS. Three aliquots of Antônio Pereira fragments were analysed in JSGL, while DR2 rutile had an aliquot analysed in JSGL and one in Oslo. The analyses showed the following U mass fractions: 39 to 57 $\mu\text{g.g}^{-1}$ for Antônio Pereira, 3 $\mu\text{g.g}^{-1}$ (JSGL) and 2 $\mu\text{g.g}^{-1}$ (Oslo) for DR2. The Th/U ratio in Antônio Pereira varied from 0.002 to 0.010 and in the case of the DR2 the Th values were below the detection limits. The samples have a considerable common Pb content, as can be observed by the $^{206}\text{Pb}/^{204}\text{Pb}$ values of 4553–7035 for Antônio Pereira and 617–989 for DR2, and total common Pb levels (blank + initial) of 0.6–5.6 pg.

U-Pb results are shown in Table 5 and Fig. 5. The analytical uncertainties were propagated according to Schoene et al. (2006). The three aliquots of Antônio Pereira analysed at the JSGL are concordant and yielded a $^{206}\text{Pb}/^{238}\text{U}$ weighted average age of $499.4 \pm 0.5/0.6/1.1$ Ma (MSWD = 0.40; n = 3). For DR2, the individual aliquots analysed provided a $^{206}\text{Pb}/^{238}\text{U}$ age of $527.8 \pm 1.1/1.2/1.8$ Ma and $531.3 \pm 1.8/1.9/2.5$ Ma in JSGL and Oslo respectively. The age discrepancy for DR2 may be due to the fact that two different grain fragments were analyzed, but the small difference between ages

is only perceived by the TIMS technique, and the $^{206}\text{Pb}/^{238}\text{U}$ simple average of 529 Ma is suggested as the accepted age for the DR2 rutile.

Isotopic ratios and the U-Pb ages presented in Table 5 were considered when using the Antônio Pereira and DR2 rutiles as secondary reference materials in the LA-ICP-MS analyses.

4.3 U-Pb dating by LA-ICP-MS

As most of the analysed rutiles have a spread in their common Pb composition, no common Pb correction was applied, and the data are presented in Tera-Wasserburg diagrams. Dom Bosco was the only rutile that showed no variation in its common Pb composition and, therefore, its data are plotted on the Concordia diagram. The uncertainties (2s) are presented at the 95% confidence level and were propagated according to Horstwood et al. (2016). The U-Pb results for the studied rutiles are listed in Table 6 and illustrated in Fig. 6. The Th/U ratios, as reflected by the radiogenic ^{208}Pb mass fractions (Table 4), are generally low.

Thirty-three analytical points performed in Antônio Pereira rutile generated a lower intercept age of $500.2 \pm 1.9/5.4$ Ma (2s; MSWD = 0.63; n = 33), using the 529 Ma DR2 rutile as secondary reference material. Twenty-one points were performed on the DR1 rutile, providing a lower intercept age of $503.4 \pm 3.3/6.0$ Ma (2s; MSWD = 0.94; n = 21). Thirty-four spots in DR2 rutile produced a lower intercept age of $526.7 \pm 2.3/5.8$ Ma (2s; MSWD = 0.44; n = 34). Thirty-four points in the Dom Bosco rutile generated a concordia age of $497.7 \pm 0.8/5.1$ Ma (2s; MSWD_{c+e} = 0.90; n = 34). The Fazenda Bandeirinha rutile produced a lower intercept age of $506.4 \pm 4.0/6.5$ Ma (2s; MSWD = 1.0; n = 11). The U-Pb results of the Itamarandiba rutile yielded a lower intercept age of $493.7 \pm 0.8/5.0$ Ma (2s; MSWD = 1.7; n = 13). Twenty-eight points in the São João rutile gave a lower intercept age of $487.2 \pm 1.6/5.1$ Ma (2s; MSWD = 1.3; n = 28). And, finally, five points made in the Bocaina rutile by Gonçalves et al. (2019) provided a concordia age of $493 \pm 3/9$ Ma (2s; MSWD_{c+e} = 1.8; n = 5). The upper intercepts on the Tera-Wasserburg diagrams were freely calculated as part of regression, which correspond to an initial common Pb composition of approximately $^{207}\text{Pb}/^{206}\text{Pb} = 0.875$, consistent with the expected composition of common Pb at the ages obtained in this study according to the crustal Pb evolution model of Stacey and Kramers (1975).

The U-Pb analytical data from the rutile samples are available as supplementary material.

Table 5: U-Pb results obtained via ID-TIMS for the studied rutile crystals.

Sample	U-Pb results				Atomic ratios						Apparent Ages (Ma)						
	U ($\mu\text{g g}^{-1}$)	$\frac{\text{Th}}{\text{U}}$	Pbc (pg)	$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	2s abs	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	2s abs	Error corr	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	2s abs	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	2s abs	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	2s abs	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	2s abs
Antônio Pereira JSGL	57	0.010	0.6	4553	0.63612	0.00257	0.08059	0.00015	0.63	0.05725	0.00018	499.7	0.9	499.9	1.6	501.0	7.1
	52	0.002	1.9	7035	0.63402	0.00164	0.08056	0.00014	0.83	0.05708	0.00008	499.5	0.8	498.6	1.0	494.6	3.2
	39	0.004	5.6	5709	0.63537	0.00226	0.08047	0.00022	0.84	0.05726	0.00011	499.0	1.3	499.4	1.4	501.6	4.3
DR2 JSGL	3	na	2.6	989	0.67658	0.00635	0.08532	0.00019	0.37	0.05751	0.00051	527.8	1.1	524.7	3.8	511.3	19.4
DR2 Oslo	2	0.000	2.6	617	0.68094	0.01031	0.08591	0.00030	0.46	0.05749	0.00080	531.3	1.8	527.3	6.2	510.3	30.2

Notes:

Th/U calculated from radiogenic $^{208}\text{Pb}/^{206}\text{Pb}$ ratio and $^{207}\text{Pb}/^{206}\text{Pb}$ age (na is not available).

Correction for ^{230}Th disequilibrium in $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ assuming Th/U of 4.2 in the magma (for JSGL data only).

Pbc is total amount of common Pb.

Pb/Pb corrected for fractionation and common Pb in the spike.

Pb/U corrected for fractionation, common Pb in spike, blank, and initial common Pb (Stacey and Kramers 1975).

(laboratory Pb isotopic composition $^{206}\text{Pb}/^{204}\text{Pb}$: 18.221; 2s errors of 1%).

Error Corr is correlation coefficients of X-Y errors on the concordia plot.

Fig. 5. U-Pb ages obtained by ID-TIMS for the studied rutilite (Antônio Pereira and DR2). The yellow ellipse refers to the JSGL result and the pink one is the result of Oslo. The red area is the Concordia curve including the uncertainty of the decay constant of Jaffey et al. (1971).

Table 6: Summary of the U-Pb data obtained by laser ablation MC-ICP-MS for the studied rutiles.

Rutile	U-Pb results			Data for plotting					Apparent Ages (Ma)								
	$^{207}\text{Pb}^a$ (cps)	U^b ($\mu\text{g g}^{-1}$)	$\frac{\text{Th}^b}{\text{U}}$	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$2s^c$ (%)	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$2s^c$ (%)	ρ^e	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$2s^c$ abs	$2s_{\text{sys}}^d$ abs	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$2s^c$ abs	$2s_{\text{sys}}^d$ abs	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	$2s^c$ abs	$2s_{\text{sys}}^d$ abs
Antônio Pereira (n = 33)	1897	45	0.005	1.4947	9.3067	0.0879	1.0962	0.06	543	6	11	911	58	59	1883	58	71
DR1 (n = 21)	2744	5	0.010	1.8026	8.0280	0.0909	1.0728	0.05	561	6	12	1030	53	55	2163	53	68
DR2 (n = 34)	2072	2	0.026	1.3511	10.2025	0.0909	0.9422	0.07	561	5	11	859	61	62	1682	62	73
Dom Bosco (n = 34)	31418	81	0.001	0.6300	5.4906	0.0806	2.4724	0.13	500	12	17	496	22	23	481	25	31
Faz. Bandeirinha (n = 11)	3207	3	0.004	1.2712	7.3478	0.0875	0.9229	0.07	541	5	10	825	42	43	1649	42	53
Itamarandiba (n = 13)	20656	53	0.000	1.3387	1.7802	0.0847	0.6126	0.08	524	3	8	804	11	15	1526	12	23
São João (n = 28)	2605	5	0.122	2.0014	6.6468	0.0891	1.0399	0.05	550	6	12	1050	45	48	2201	46	61

Note

The results are presented in this table as simple averages. The complete data set can be found in supporting information.

^a Within run background-corrected mean ^{207}Pb signal in cps (counts per second).

^b U and Pb content and Th/U ratio were calculated relative to Tanzania zircon (Santos et al., unpublished results).

^c $2s$ is the within session uncertainty (at 95% confidence level).

^d $2s_{\text{sys}}$ is the within session uncertainty plus systematic uncertainties (primary reference material uncertainty and long-term variance of validation materials).

^e ρ is the $^{206}\text{Pb}/^{238}\text{U}/^{207}\text{Pb}/^{235}\text{U}$ error correlation coefficient.

Fig. 6. U-Pb ages of the studied rutiles. MSWD of the concordia diagram of Dom Bosco rutile refers to concordance plus equivalence (c + e). The results are reported in 2s with the respective measurement and systematic uncertainties.

5. Discussion

5.1 Implications of rutile chemical composition

The occurrence of large rutile crystals in fluid-rich systems, such as hydrothermal veins, indicates that either there must be a very large fluid flow through the system with trace amounts of Ti, or that Ti is more soluble in some aqueous fluids as a function of the fluid chemistry (Rapp et al., 2010). Rapp et al. (2010) showed that rutile solubility increases significantly in F-rich fluids. This compositional dependence on Ti solubility also has implications for HFSE (high field strength elements) mobility, since hydrothermal rutile is characterised by relatively high concentrations of these elements, compared to those of igneous and metamorphic rocks (e.g., Meinhold, 2010). If an F-enriched (and thus Ti-enriched) fluid becomes depleted in F rutile precipitation should occur since the solubility of Ti depends on the concentration of F in the fluid. Such a model of F-loss has been invoked to explain the association of hydrothermal rutile with Imperial Topaz in the Quadrilátero Ferrífero, where early crystallization of the topaz depleted the hydrothermal fluid in F, and thus favoured precipitation of rutile (Morteani et al., 2002).

Putnis (1978) and Putnis and Wilson (1978) observed that rutile formed at low temperatures (below 450 °C, hydrothermally) contains remarkable concentrations of Fe, as is the case in some of the rutiles in this study. It is also important to note that the evidence that rutile and hematite are stable (as can be seen in Fig. 3f) and precipitated from hydrothermal fluids indicates oxidized conditions in these fluids (Buddington and Lindsley, 1964; Rečnik et al., 2015).

The presence of HFSE in hydrothermal rutiles helps, for example, in the identification of the fluid sources responsible for the precipitation of the studied rutiles. The Cr vs Nb diagram in Fig. 4 and the rocks that occur in the regions the samples were collected allow us to suggest that: a predominantly mafic source was responsible for the precipitation of the Antônio Pereira, Bocaina, Dom Bosco and São João rutiles, probably associated with a progressive dehydration of the greenstone belt rocks in the Quadrilátero Ferrífero; the mixed source that precipitated the DR1 and DR2 rutiles may be associated with the progressive dehydration of the metasedimentary rocks with subordinate greenschist occurring in the São João da Chapada Formation, Espinhaço Supergroup; the metamorphic fluid responsible for precipitation of Fazenda Bandeirinha

rutile may be derived from the Espinhaço Supergroup metasediments, while Itamarandiba rutiles may have been precipitated from a metamorphic fluid derived from dehydration of the Macaúbas Group metasedimentary sequences.

5.2 Comparison with published data along the Araçuaí Belt

A large number of isotopic dating methods have already been applied along the Araçuaí Belt to obtain ages for various events such as magmatism, metamorphism, cooling histories, hydrothermal processes and mineralizations. Gonçalves et al. (2018, 2019) and Vasconcelos et al. (2018) determined U-Pb crystallization ages of hydrothermal monazite, rutile and xenotime, which indicated fluid circulation throughout the Araçuaí Orogen between 515 and ca. 495 Ma, largely coincident with the U-Pb ages of hydrothermal systems and mineralized zones in the adjacent São Francisco craton (e.g., Cabral et al., 2013b, 2015b, Cabral and Zeh, 2015a).

Schmiedel (2015) applied EPMA Th-U-Pb chemical dating to monazite from mica schists in the transition zone between the São Francisco Craton and the Araçuaí Belt (Quadrilátero Ferrífero), obtaining ages between 505 and 440 Ma. Queiroga et al. (2016) also dated monazite from garnet-mica schists in the studied region (Serra do Espinhaço Meridional), finding Th-U-Pb recrystallization ages between 490 and 480 Ma. These dates were interpreted to give the age of the tectono-thermal event associated with the gravitational collapse of the Araçuaí Orogen.

Au-Pd mineralizations occurring in the Southern Espinhaço Range and in the Quadrilátero Ferrífero (PGP - platiniferous gold-palladium - belt), following approximately the north-south trend of the Brasiliano thrust faults (e.g., Cabral et al., 2009), were also dated. Chauvet et al. (2001) found an $^{40}\text{Ar}/^{39}\text{Ar}$ age of ca. 485 to 490 Ma for hydrothermal biotite and muscovite, demonstrating that the gold deposits of Ouro Preto (Quadrilátero Ferrífero) were formed synchronously with the collapse of the Araçuaí Orogen. Cabral and Zeh (2015a) dated xenotime at the Passagem de Mariana deposit (Quadrilátero Ferrífero) and obtained a U-Pb age of 496.3 ± 2.0 Ma. Cabral and Zeh (2015b) obtained a U-Pb age of 500.6 ± 4.3 Ma from metamorphic zircon and 499.2 ± 2.9 Ma from rutile in the Sítio Largo amphibolite (southern portion of the PGP belt) and interpreted these ages to date the metamorphic overprint caused by the Brasiliano event. In the Itabira district, Cabral et al. (2015b) determined a U-Pb age of 495.6 ± 2.2 Ma from hydrothermal monazite in auriferous quartz-hematite veins. In the

northern portion of the PGP belt, Cabral et al. (2013a) obtained a U-Pb age of 524 ± 16 Ma from hydrothermal rutile in an auriferous vein, and, lastly, Pb-Pb ages of 464 ± 7 Ma and 444 ± 4 Ma were obtained from monazites in quartz veins by Chaves et al. (2010).

The wide range of ages found both in this work and in previous studies indicates that either episodic hydrothermal events or prolonged hydrothermal activity affected both the Araçuaí Belt units and the adjacent margin of the São Francisco craton (e.g., Cabral et al., 2017; Gonçalves et al., 2019).

5.3 Rutile samples associated with Imperial Topaz mineralization

Rutile samples from the Quadrilátero Ferrífero (Antônio Pereira, Bocaina and Dom Bosco) were taken from deposits containing Imperial Topaz mineralization. Several studies had already associated this mineralization with a tectono-metamorphic event of broadly Brasiliano age. Based on fluid inclusion studies, Morteani et al. (2002) considered the topaz crystallization to be related to F-rich metamorphic fluids that originated during the Brasiliano Orogeny, a relative timing also suggested by Almeida et al. (2007). The structural relations characterised and recognized by Endo (1988), Chemale Jr. et al. (1994) and Rojas et al. (2009) showed that the Imperial Topaz-bearing veins are associated with a system of extension fractures related to folds of N-S and E-W axial directions, as well as boudins. Both structural patterns originated during the Brasiliano Orogeny that affected the Quadrilátero Ferrífero.

Gonçalves et al. (2019) stated that U-Pb ages of 493 ± 3 Ma and 496 ± 2 Ma obtained from rutile in the same region represent the first age constraints for Imperial Topaz deposit formation. In principle, it may be argued that this age estimate, and the 500-498 Ma rutile ages (this work) associated with Imperial Topaz mineralization are cooling ages, if the rutiles had formed before 500-498 Ma above the blocking temperature for the U-Pb system ($> 500 - 550$ °C; Cherniak, 2000). Morteani et al. (2002), based on fluid inclusion data, oxygen isotope geothermometry and considerations on the stability fields of minerals included in the topaz (kaolinite, pyrophyllite and carbonates), indicated that this mineral crystallized under T-P conditions around 360 °C and 3.5 kbar. In addition, Gonçalves et al. (2019) performed Ti-in-quartz thermometry on rutile-bearing quartz veins from the Southern Espinhaço Range and coeval with Imperial Topaz deposits. These authors found temperatures

ranging from 341 °C to 410 °C to 3.4 kbar. These data allow us to conclude that the ages of 500-498 Ma of the studied rutiles correspond to the age range of Imperial Topaz mineralizations.

6. Conclusions

U-Pb ages between 527 Ma and 487 Ma of both hydrothermal quartz veins and Imperial Topaz mineralization were found in hydrothermal rutile occurring along the southeastern portion of the Araçuaí Belt, indicating that different regions and rocks were affected by a similar style of fluid-rock interaction under oxidizing conditions. The reported age variation may be associated with prolonged or episodic events of hydrothermal activity that affected the Araçuaí Belt region.

The U-Pb dating of rutile associated with Imperial Topaz mineralization, together with considerations on the temperature of formation of these rutiles, allows us to say that the age of these deposits is 500-498 Ma.

The chemical composition of the studied rutiles makes it possible to state, corroborating previous studies, that an extensive fluid production was generated from multiple sources, due to the collapse of the Araçuaí Orogen.

The results of this study clearly demonstrate that U-Pb dating of rutile via LA-ICP-MS is a robust tool for the geochronological study of hydrothermal deposits containing hydrothermal rutile. The applied methodology, using zircon as primary reference material, and rutile, to minimize the matrix effect between the reference material and the analyzed samples, as well as data processing with a new MATLAB bundle, proved to be effective in obtaining U-Pb ages similar to those of studies already performed in the region.

This work, through TIMS U-Pb analysis, also proposed the Antônio Pereira and DR2 rutiles as potential primary and/or secondary reference materials for U-Pb geochronology via LA-ICP-MS, with $^{206}\text{Pb}/^{238}\text{U}$ weighted average of $499.4 \pm 0.5/0.6/1.1$ Ma (Antônio Pereira) and $527.8 \pm 1.1/1.2/1.8$ Ma and $531.3 \pm 1.8/1.9/2.5$ Ma (DR2 - variation detected by the TIMS technique only). It is noteworthy that, for validation of these potential reference materials, additional analyses are required.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at ...

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Journal Pre-proof

Highlights

- Hydrothermal rutile dating showed episodic fluid flow affecting the Araçuaí Belt area;
- Fluids from multiple sources formed hydrothermal deposits in the Araçuaí Belt area;
- The Imperial Topaz deposits age in the Quadrilátero Ferrífero is 500-498Ma;
- Two rutiles were proposed as potential reference materials for LA-ICP-MS U-Pb dating.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: