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ARTICLE

Age of the emerald mineralization from the Itabira-Nova Era District, Minas Gerais, Brazil, based on LA-ICP-MS geochronology of cogenetic titanite

Idade da mineralização de esmeralda do distrito de Itabira-Nova Era, Minas Gerais, Brasil, com base em geocronologia LA-ICP-MS de titanita cogenética

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ABSTRACT: In the Itabira-Nova Era Emerald District, southeast Brazil, gemological emerald is extracted from underground mines found in schist-type deposits at the contact zone of the Archean Metavolcanosedimentary Sequence of the Guanhães Complex and Paleoproterozoic anorogenic granites of the Borrachudos Suite. Schist-type deposits are commonly generated by reactions enhanced by deformation and heat during regional metamorphism. The age of the mineralization in the region has been a matter of debate for decades: Ages ranging from the Archean to the Neoproterozoic are mentioned in the literature. In the mineralized zone from the Piteiras mine fluorine-aluminum-bearing titanite is found in metamafic rocks. The fluorine content was probably derived from the Borrachudos granites and pegmatites like the beryllium for emerald, thus both minerals could have been generated during the same event. U-Pb titanite geochronology via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was performed on a thin section of a phlogopite-plagioclase-hornblende schist from the Piteiras mine. The determined age of 576 ± 7 Ma is also the probable age for emerald generation during the Brasiliano cycle, which was the only tectonometamorphic event postdating the intrusion of the granites. This event provided heat and fluids necessary for reactions between the Be- and the Cr-bearing rocks, thus enabling the formation of emeralds.

KEYWORDS: Titanite, U/Pb geochronology, Neoproterozoic, Emerald, Brazil.

RESUMO: *No Distrito Esmeraldífero de Itabira-Nova Era, sudeste do Brasil, esmeralda gemológica é extraída em minas subterrâneas em depósitos do Tipo Xisto na zona de contato da sequência metavulcanossedimentar arqueana do Complexo Guanhães com granitos anorogênicos paleoproterozoicos da Suite Borrachudos. Depósitos do Tipo Xisto são comumente gerados por reações promovidas por deformação e calor durante metamorfismo regional. A idade da mineralização na região tem sido motivo de debates por décadas: idades variando do Arqueano ao Neoproterozoico são mencionadas na literatura. Na zona mineralizada da mina Piteiras, titanita portadora de alumínio e flúor é encontrada em rochas metamáficas. O conteúdo de flúor foi provavelmente derivado dos granitos e pegmatitos Borrachudos, tal como o berílio para a esmeralda, portanto ambos minerais podem ter sido gerados durante o mesmo evento. Geocronologia U-Pb via ablação a laser associada a espectrometria de massa por plasma acoplado indutivamente laser (LA-ICP-MS) em titanita foi realizada em uma seção delgada de um flogopita-plagioclásio-hornblenda xisto da mina Piteiras. A idade determinada de 576 ± 7 Ma é também a provável idade de geração da esmeralda durante o ciclo Brasiliano, que foi o único evento tectonometamórfico posterior à intrusão dos granitos. Este evento forneceu calor e fluidos necessários para reações entre as rochas portadoras de berílio e de cromo, possibilitando assim a formação de esmeralda.*

PALAVRAS CHAVE: *Titanita, geocronologia U/Pb, Neoproterozoico, Esmeralda, Brazil.*

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INTRODUCTION

The formation of emeralds requires the uncommon interaction of beryllium and chromium, the latter being the usual chromophore element responsible for the typical green color. Be and Cr are incompatible elements found in quite distinct geochemical environments; while Be is concentrated in granitic rocks and their pegmatites, higher amounts of Cr are mostly found in mafic, and especially ultramafic igneous rocks. In order to enable the formation of emerald, reactions between these two contrasting lithotypes are usually enhanced by deformation. Among the emerald deposits found worldwide, the schist type is one of the most important. The reactions involved in the formation of this type of deposit usually happen during a tectonometamorphic event since the simple intrusion of granites or pegmatites in ultramafic rocks is not able to supply enough energy and fluids to produce important reaction zones (Franz *et al.* 1996, Franz & Morteani 2002). As suggested by Grundmann and Morteani (1989), most if not all schist-type emerald deposits in metamorphic rocks may be the product of a deformational event accompanied or followed by regional metamorphism which provided heat and the abundant fluids necessary for the reactions of Be- and Cr-rich rocks. In addition, the transformation of the original ultramafic rock (peridotites and/or their volcanic equivalents such as komatiites) into the typical emerald-bearing phlogopite schists is due to the percolation of K-rich fluids derived from pegmatites under the influence of deformation.

The Itabira-Nova Era Emerald District (Fig. 1), located ca. 120 km northeast of Belo Horizonte, state of Minas Gerais, Brazil, is known worldwide for the production of high-quality emerald gems. The two main mines, Belmont and Capoeirana, besides the temporarily closed mines Piteiras and Rocha, are found at the contact zone of metaultramafic phlogopite schists of the Metavolcanosedimentary Sequence correlative of the Archean Guanhães Complex (Padilha *et al.* 2000) and the Paleoproterozoic anorogenic Borrachudos granites (Dorr and Barbosa 1963, Grossi-Sad *et al.* 1990, Dossin *et al.* 1993, Chemale Jr. *et al.* 1997, Silva *et al.* 2002). Souza (1988), Giuliani *et al.* (1990), Souza *et al.* (1992), Machado (1998), Schwarz and Giuliani (2001), Schwarz

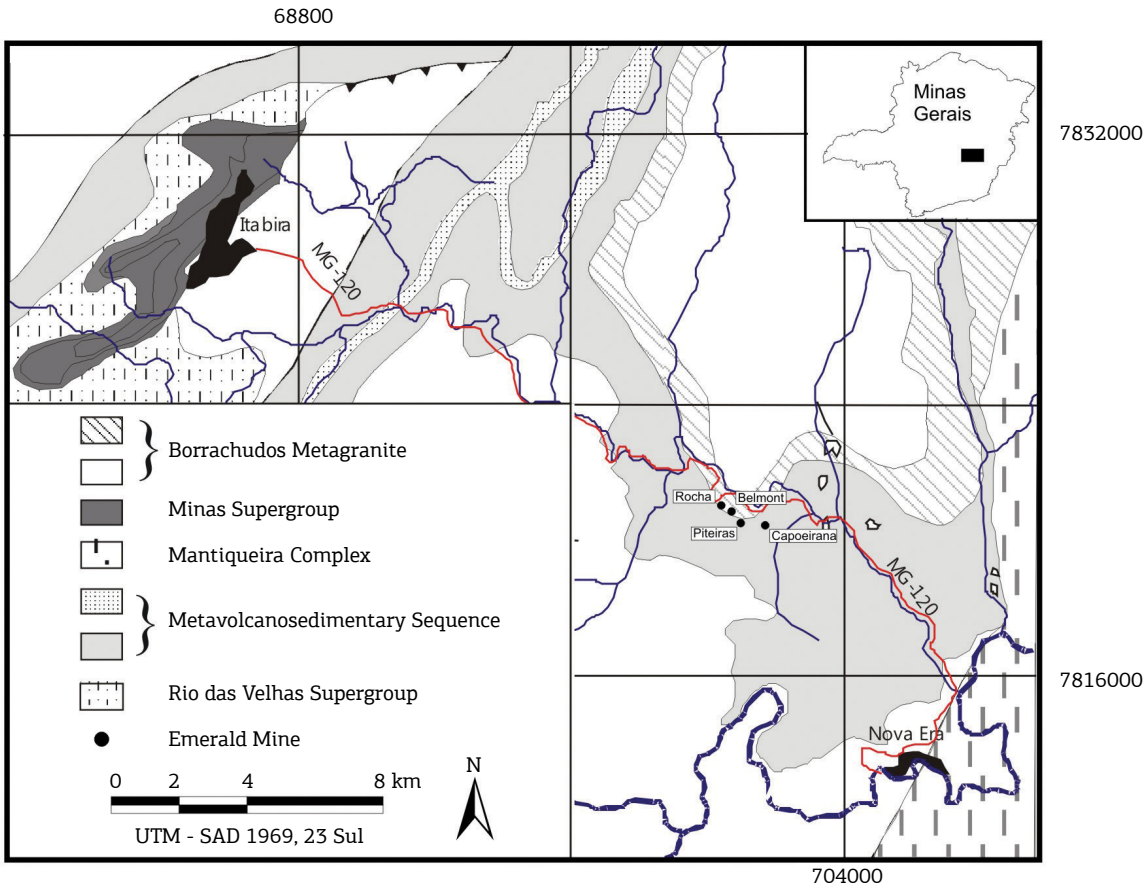

Figure 1. Simplified geological map of the area of the Itabira-Nova Era Emerald District (modified from Machado 1998) and the location of the emerald mines Piteiras, Belmont, Rocha, and Capoeirana.

et al. (2002), and Franz and Morteani (2002) have classified the deposits of Belmont and Capoeirana as belonging to the schist type. Similar studies by Viana (2004), Viana *et al.* (2006), and Delgado (2007) in the mines Piteiras and Rocha led to the conclusion that also in these mines the emerald deposit is of identical origin.

The age of the schist-type mineralization in the Itabira-Nova Era Emerald District remains debatable. More than one phase of mineralization was described by some authors based on the observation of two types of emeralds: one strongly deformed and therefore considered as older, and another undeformed and therefore postulated as being younger (Machado 1994, 1998, Ribeiro-Althoff *et al.* 1997, Morteani *et al.* 2000, Preinfalk *et al.* 2002, Ribeiro 2006). Schorscher (1991), Machado (1994, 1998), and Ribeiro (2006) interpreted the strongly deformed generation as of Archean age and the underformed generation as being Proterozoic. However, if the growth of emeralds lasts during the whole time span of a tectonometamorphic event, the early-formed crystals would be deformed while the late crystals remain undeformed. Considering that the mineralization is controlled by the spatial association of the Archean Metavolcanosedimentary Sequence with the Paleoproterozoic Borrachudos granite plutons and their pegmatites, the mineralization cannot be Archean. A Paleoproterozoic age for the mineralization was postulated by Preinfalk *et al.* (2002) based on Rb-Sr dating of pegmatites associated with the Borrachudos anorogenic metagranitoids. If, as discussed earlier, the generation of schist-type mineralization is associated with a tectonometamorphic event, the emerald formation in the region of Itabira-Nova Era cannot be of the same age as the 1.7 Ga Borrachudos magmatism because at that time the Transamazonian (~2.0 Ga) tectonometamorphic event had already ceased. The only major tectonometamorphic event in the region postdating the intrusion of the Borrachudos granites is the Brasiliano event (~0.7 – 0.5 Ga) that could therefore be responsible for the emerald generation.

In order to check if the Brasiliano tectonometamorphic event played a role during the generation of the schist-type emerald mineralization, this paper presents the results of in situ laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U-Pb age determination on metamorphic fluorine-aluminum-bearing titanite belonging to a metamafic schist found in the mineralized zone from the Piteiras mine. The generation of both titanite and emerald was probably synchronous, therefore the age of the titanite is relevant to establish the age of the mineralization.

Geological Setting

The Itabira-Nova Era emerald deposits belong to the Santa Maria de Itabira Pegmatite District (Netto *et al.* 1998), in the southern portion of the Eastern Brazilian Pegmatite Province (Paiva 1946, Correia Neves *et al.* 1986). The deposits are located near the northeastern border of the Quadrilátero Ferrífero (QF), which is an important province for gold and iron deposits (Dorr 1969).

The oldest rocks of Archean age of this region record the influence of two younger orogenic events, the Transamazonian (~2 Ga) and the Brasiliano (0.7 – 0.5 Ga; Brito Neves & Cordani 1991, Alkmim and Marshak 1998). The strong influence of the Brasiliano event in the region of Itabira-Nova Era is recorded in the regional structures described by Peres *et al.* (2004) and Padilha *et al.* (2000) as well as in geochronological data by Ribeiro-Althoff *et al.* (1997), Fernandes *et al.* (2000), and Preinfalk *et al.* (2002).

The geological outline in the Itabira-Nova Era region (Fig. 1) is defined by the envelopment of metagranitic plutons of the Paleoproterozoic Borrachudos Suite (Grossi-Sad *et al.* 1990) by rocks of the Metavolcanosedimentary Sequence correlative of the Archean Guanhães Complex (Padilha *et al.* 2000). The emerald mineralization is found mainly at this contact zone. Rocks belonging to the Archean Rio das Velhas greenstone belt, and to the Paleoproterozoic Minas Supergroup and Mantiqueira Complex are found locally. Additional lithotypes are younger metamafic bodies and the pegmatites associated with the emerald mineralization.

Although gneisses and metagranitoids are prevalent in the area, there is no consensus about their spatial arrangement and stratigraphic relationship; thereby the crystalline basement has been recorded in the literature as belonging to the Guanhães or to the Mantiqueira complexes. Souza (1988) and Schorscher (1991) named the rocks of the crystalline basement as Archean TTG Complex. The lithotypes of the Metavolcanosedimentary Sequence are metaultramafic, metamafic, and metasedimentary rocks that occur as meter-sized intercalations within TTG gneisses and migmatites dated at 2.9 – 2.7 Ga (U/Pb SHRIMP age, Silva *et al.* 2002). In the area of the emerald mines, the metaultramafic rocks host the emerald mineralization.

The main lithotypes of the Mantiqueira Complex are banded and locally migmatized ortognaisses of granitic, granodioritic, and tonalitic composition. Lenses of amphibolites are relatively common. U-Pb SHRIMP age determinations resulted in Paleoproterozoic magmatic crystallization ages of 2.21 – 2.05 Ga and metamorphic ages of 2.05 Ga and of 560 Ma (Silva *et al.* 2002).

Sericitic and ferruginous quartzite and phyllite, banded iron formations, and marble are the rock types of the Minas Supergroup in the Itabira-Nova Era region.

Metagranitic bodies of the Borrachudos Suite make up most of the area in Figure 1. They are composed of anorogenic alkaline metagranites related to the opening of the

Espinhaço rift (Chemale Jr. 1987, Fernandes *et al.* 1995, Chemale Jr. *et al.* 1997, Dussin *et al.* 1997, Silva *et al.* 2002). Shear zones leading to variable degrees of gneissification are common (Peres *et al.* 2004). Quartz, microcline, plagioclase (commonly nearly pure albite, Jordt-Evangelista *et al.* 2000) and biotite are the main minerals. Additionally, there are subordinated amounts of hornblende, titanite, apatite, garnet, zircon, ilmenite, and fluorite. Fluorite is a diagnostic mineral for the Borrachudos granitoids, enabling its distinction from the quartz-feldspar-rich rocks belonging to other geological units. Single-zircon dating by stepwise Pb evaporation yielded a Paleoproterozoic crystallization age of 1.7 Ga for the Borrachudos granite (Dossin *et al.* 1993) corroborated by the 1.74 Ga U-Pb SHRIMP age by Silva *et al.* (2002). Neoproterozoic U/Pb ages of 620 Ma on zircon were obtained by Fernandes *et al.* (2000) for the metamorphism and anatexis of the Borrachudos Suite.

Pegmatites occur as veins, dykes, and pods within all rock units of the region. They are mostly composed of albite, less common are quartz, micas, and microcline. Accessory minerals not found in all pegmatites are beryl, apatite, molybdenite, chrysoberyl, monazite, and titanite. Preinfalk *et al.* (2002) dated the pegmatites by the Rb-Sr method and found an older, 1.9 Ga generation, and a younger, dated 480 Ma that is associated with the migmatization of the Borrachudos granite. $^{40}Ar/^{39}Ar$ age of 508 ± 2 Ma was determined by Ribeiro-Althoff *et al.* (1997) on biotite from the emerald-bearing biotitites at Capoeirana, which was considered as the emerald forming event. However, this Brasiliano age was considered by Preinfalk *et al.* (2002) as the rejuvenation rather than the crystallization age. The formation of a second emerald generation during the Brasiliano event is not excluded by Preinfalk *et al.* (2002).

Piteiras Mine

The country rocks in the Piteiras Mine where the dated titanite sample was collected are centimeter to decimeter thick banded gneisses belonging to the Metavolcanosedimentary Sequence correlative of the Guanhães Complex. They are made up of quartz, plagioclase, biotite, and garnet, less commonly also staurolite, kyanite, and fibrolitic sillimanite. These paragneisses show gradational contacts with biotite gneisses of tonalitic to granodioritic composition. Less commonly layers of quartz-plagioclase-anthophyllite granofels can be found. PT-conditions of the amphibolite facies are indicated by the presence of staurolite. These conditions were corroborated by geothermobarometric calculations which resulted in T = 610°C and P = 5.2 kbar (Viana *et al.* 2006). The emerald mineralization occurs in a 2 – 4 m thick and hundreds of meters long phlogopite-rich horizon. Due to folding, the thickness may locally reach 12 m. The mineralized metamafic/metaultramafic horizon comprises amphibole-biotite schists enclosing centimeter to meter thick lenses of gneisses similar to the above described country rocks, of amphibole schists (also named ultramafic amphibolites), of amphibolite, and of phlogopite schist. Pegmatites occur as irregular bodies up to 8 m long which may be concordant or discordant in relation to the metamorphic foliation and the compositional banding of the schists and gneisses. Most usually they are decimeter to meter sized, rounded to elongated, and fractured bodies involved by the foliation. The major mineral is albite, more seldom graphic quartz, microcline, beryl, and pockets of muscovite and clinochlore can be found. The association of phlogopitization with the pegmatites is indicated by the observation that phlogopite schists are nearly monomineralic near the pegmatites while farther away they are hornblende bearing (Fig. 2). The amount of phlogopite increases and that of amphibole decreases towards the pegmatites. The emerald-bearing phlogopite schist constitutes coarse grained, strongly foliated and easily disaggregated decimeter to meter thick layers and pods enclosing quartz ± feldspar veins. Talc appears along fault surfaces oriented parallel to the metamorphic foliation. Quartz and fluorite are secondary minerals that were introduced into the phlogopitite during the metassomatic transformation. It is worthwhile to note that quartz is absent in samples that contain Mg-hornblende besides phlogopite, possibly because this rock type was less transformed during metasomatism than the phlogopitite, as is also indicated by relics of Al-rich chromite preserved from the original ultramafic rock.

Emerald occurs in the phlogopitite and in the quartz veins as porphyroblasts which are sometimes bent or fractured. Centimeter to decimeter thick veins composed of quartz, feldspar, or quartz plus feldspar are found in the phlogopite schist. The quartz veins appear farther away from the pegmatites and contain the best-colored emerald crystals. In the feldspathic veins the emerald crystals are less well formed, commonly showing corroded outlines.

MATERIAL AND METHODS

The studied rock sample (Sample PI-5) is a phlogopite-plagioclase-hornblende schist belonging to the subterraneous emerald mineralized zone in the Piteiras mine. The sample was chosen for geochronology due to two characteristics:

1. the presence of abundant metamorphic titanite surrounding ilmenite relics (Fig. 3), suggesting that titanite was formed during the same tectonometamorphic event responsible for the generation of the schist; and

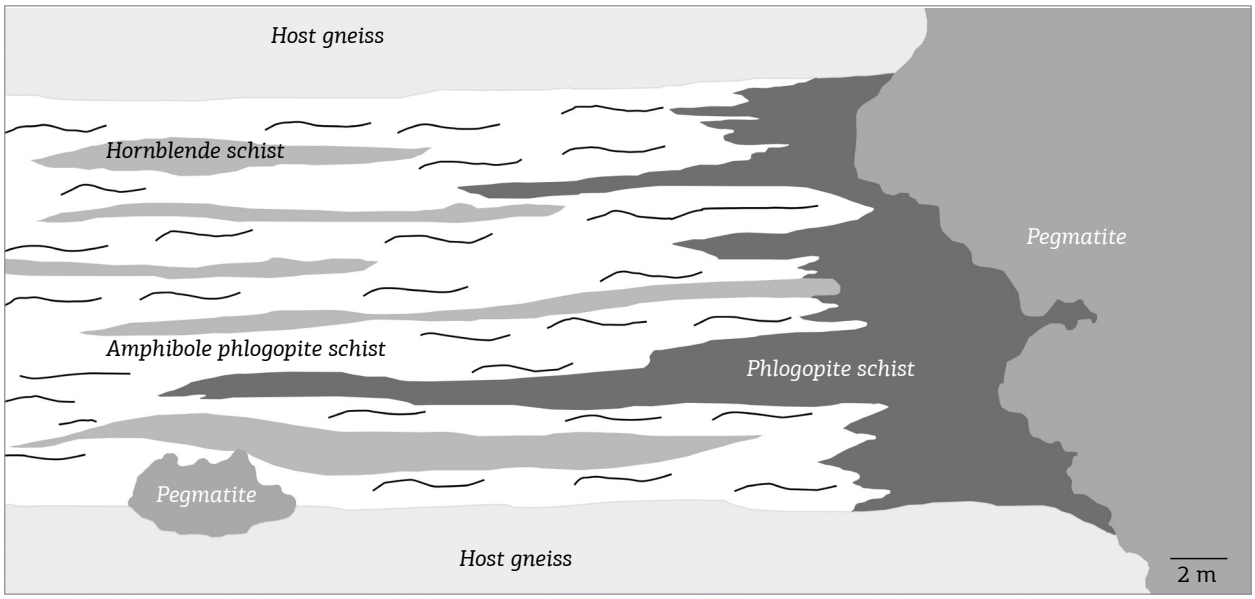

Figure 2. Schematic illustration showing the location of an emerald-bearing phlogopite schist adjacent to a pegmatite body in the Piteiras Mine (Viana 2004).

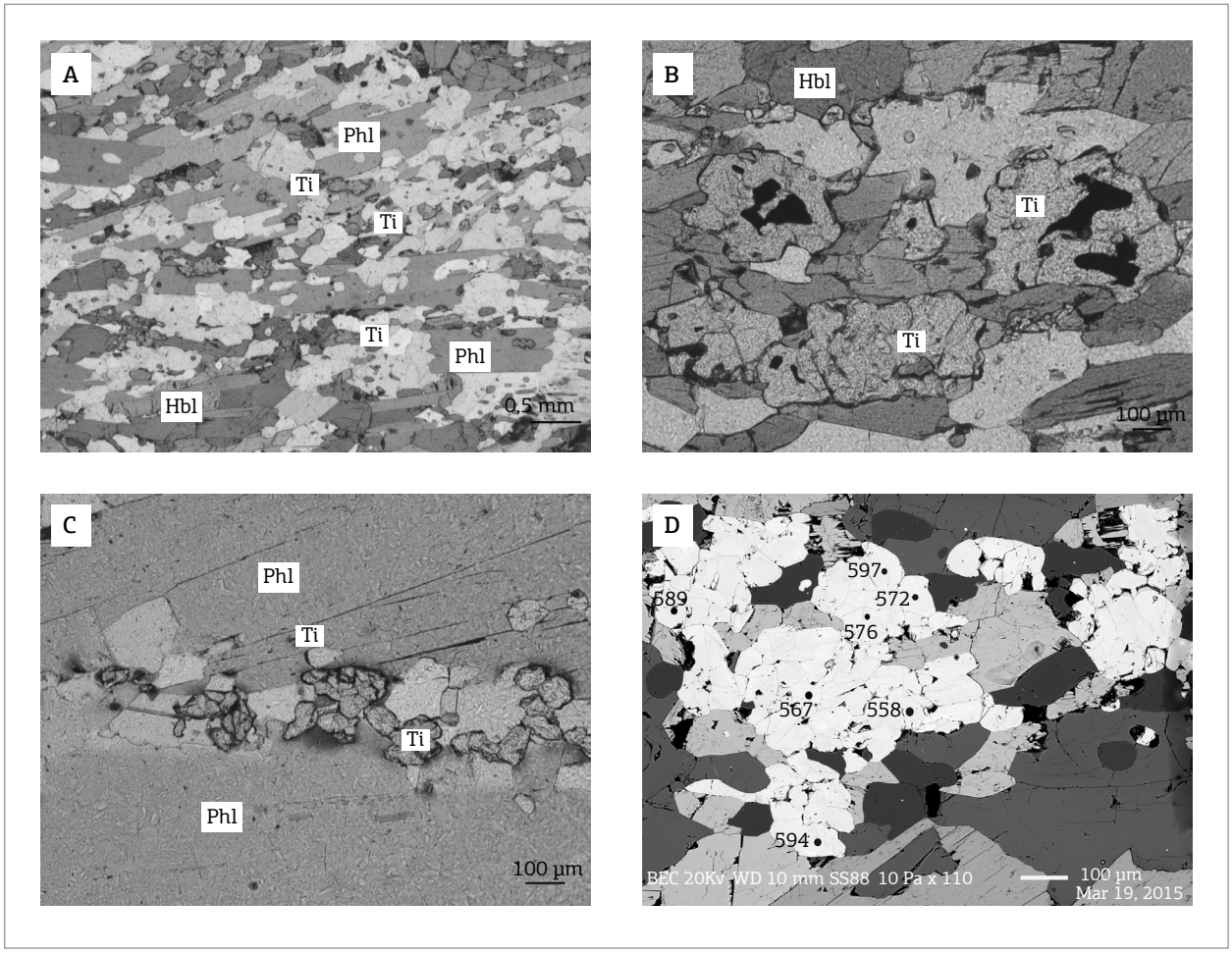

Figure 3. Photomicrographs (A – C) of thin section of the dated metamafic schist under plane polarized light. (A) General view showing titanite (grains with high relief), phlogopite, Mg-hornblende, plagioclase, and quartz (both colorless). (B) Ilmenite (black) surrounded by titanite. (C) Titanite grains surrounded by pleochroic haloes in phlogopite. (D) Ages (in million years) of titanite grains plotted on BSE-image. Ti = titanite; Phl = phlogopite; Hbl = Mg-hornblende.

2. the unusual high fluorine content (Table 1) in the titanite that was probably derived from the Borrachudos granites that were also the source of the Be for the emerald generation.

Thin sections were described on a Leica DM EP microscope at the Departamento de Geologia (DEGEO), Universidade Federal de Ouro Preto. Microprobe analyses on the titanite were performed on a JEOL microprobe JXA 8900 RL, at the Laboratório de Microanálises of the Universidade Federal de Minas Gerais, Belo Horizonte, Brazil. Operating conditions were 20 kV, 10 µm beam, and counting time of 100 s. The LA-ICP-MS analyses were performed using a Thermo Scientific Element II and a 213 nm CETAC laser at the isotope/geochemistry laboratory of the Department of Geology, Universidade Federal de Ouro Preto. The analyses were performed on a conventional polished (30 µm-thick) thin section. Sample contamination is excluded because the thin section was as clean as any other epoxy mount and 100% free of common Pb. In addition, the analyzed titanite grains were mostly larger than 200 µm whereas the laser holes were narrow (20 µm-wide) and substantially shallow (less than 5 µm-deep). Acquisitions consisted of 20 s measurement of the gas blank, followed by 20 s measurement of U, Th, and Pb signals during ablation, and 20 s washout. Laser conditions were 20 µm beam at 10 Hz and 0.02 J energy, giving a fluency of 8 J/mm. Common Pb corrected isotopic ratios were reduced using an Excel spreadsheet (Gerdes & Zeh 2006). Apparent age calculations and concordia diagrams were produced using Isoplot 4 (Ludwig 2012). Two standards were used during runs: the primary standard BLR (1049.9 ± 1.3 Ma; Aleinikoff *et al.* 2007) and the secondary standard Khan titanite (522.2 ± 2.2 Ma, Heaman 2009). Twenty-five within-run analyses of the secondary standard gave a concordia age of 524 ± 2.6 Ma whereas six analyses of BLR (as secondary standard) gave a concordia age of 1053 ± 10 Ma (Table 2).

RESULTS

Petrography

Sample PI-5 comes from an amphibolite facies metamafic schist (Fig. 3A) of the mineralized zone at the Piteiras mine. It is composed of Mg-hornblende (40 vol.%), phlogopite (25 vol.%), plagioclase (23 vol.%), quartz (7 vol.%), and titanite (5 vol.%). There is a mineralogical layering with hornblende-rich layers alternating with phlogopite-rich ones. Titanite (Fig. 3A – C) is more abundant in the phlogopite-rich layers, where it may reach about 10 vol.%. Ilmenite is a relictic accessory mineral being always surrounded by titanite (Fig. 3B).

Fluorine-aluminum-bearing titanite

In metamafic rocks of the mineralized zone from the Piteiras mine, Al-rich titanite commonly constitutes 0.5 – 1 mm large clusters that may surround ilmenite relics (Fig. 3B). Titanite is characterized by relatively low interference colors of upper second to lower third order and for

Table 1. Chemical composition (wt.%) by microprobe analyses of fluorine-aluminum-bearing titanite from the Piteiras mine.

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	CaO	F	Sum
PI5-Ca-Tit-1	31.48	28.76	8.01	0.75	0.08	28.60	2.39	100.07
PI5-Ca-Tit-2	31.42	27.59	8.96	0.55	0.13	29.13	2.86	100.64
PI5-Ca-Tit-3	31.32	31.14	6.45	0.69	0.11	29.02	2.38	101.11
PI5-Ca-Tit-4	31.18	28.28	8.35	0.67	0.11	29.06	2.84	100.49
PI5-Ca-Tit-5	31.21	29.64	7.45	0.82	0.15	28.80	2.21	100.28
PI5-Ca-Tit-6	30.86	29.27	7.47	0.72	0.15	28.53	2.64	99.64
PI5-Ca-Tit-7	30.68	27.87	8.38	0.56	0.11	28.69	2.09	98.38
PI5Ca-C1-Tit-8	30.34	27.80	8.34	0.63	0.05	28.30	1.84	97.30
PI5Ca-C1-Tit-9	30.67	28.93	7.47	0.71	0.15	28.11	2.16	98.20
PI5Ca-C1-Tit-10	31.15	28.16	7.89	0.68	0.09	28.35	2.49	98.81
PI5Ca-C1-Tit-11	30.87	29.10	7.26	0.70	0.10	28.37	2.66	99.06
PI5Ca-C1-Tit-12	30.56	29.95	7.19	0.66	0.06	28.54	1.67	98.63

Table 2. Results of U-Pb LA-ICP–MS dating of titanite from the Piteiras mine in the Itabira-Nova Era Emerald District.

Spot	[a]207 Pb (cps)	[b]U (ppm)	[b]Pb (ppm)	[b]Th / U	[c]206 Pb (%)	[d]207 Pb 235U	±2s (%)	[d]206 Pb 238U	±2s (%)	rhoe	[d]207 Pb 206 Pb	±2s (%)	206 Pb 238 U	±2s (Ma)	207 Pb 235 U	±2s (Ma)	207 Pb 206 Pb	±2s (Ma)	Conc %
Sample PI-5																			
4.sSMPABC056	4910	19.00	1.96	0.06	0.255	0.731	2.770	0.091	2.279	0.823	0.059	1.574	559	12	557	12	550	34	101.65
4.sSMPABC055	4893	19.62	2.06	0.06	0.074	0.746	3.036	0.092	2.520	0.830	0.059	1.693	568	14	566	13	558	37	101.85
4.sSMPABC030	466	2.50	0.26	0.01	0.954	0.844	6.658	0.104	4.507	0.677	0.059	4.901	637	27	621	31	566	107	112.59
4.sSMPABC016	486	3.41	0.31	0.01	1.128	0.730	6.987	0.090	4.776	0.684	0.059	5.099	554	25	556	30	568	111	97.56
4.sSMPABC078	883	2.20	0.20	0.01	2.045	0.740	5.216	0.090	3.363	0.645	0.060	3.988	556	18	562	23	587	87	94.84
4.sSMPABC026	500	2.26	0.21	0.01	1.553	0.749	6.495	0.091	4.019	0.619	0.060	5.102	562	22	568	29	591	111	95.19
4.sSMPABC013	496	4.29	0.41	0.01	0.118	0.801	6.101	0.097	3.760	0.616	0.060	4.805	598	22	597	28	595	104	100.42
4.sSMPABC082	849	1.84	0.17	0.01	0.572	0.754	4.551	0.091	3.209	0.705	0.060	3.226	563	17	570	20	598	70	94.15
4.sSMPABC034	707	2.82	0.26	0.01	0.797	0.783	4.908	0.095	3.205	0.653	0.060	3.717	583	18	587	22	605	80	96.35
4.sSMPABC032	463	1.96	0.19	0.01	1.986	0.794	6.064	0.096	3.506	0.578	0.060	4.948	590	20	593	28	605	107	97.55
4.sSMPABC011	723	5.88	0.56	0.01	1.524	0.778	5.175	0.094	3.600	0.696	0.060	3.718	579	20	584	23	606	80	95.48
4.sSMPABC070	1198	2.92	0.26	0.01	2.526	0.745	4.427	0.090	2.660	0.601	0.060	3.539	555	14	565	19	607	77	91.52
4.sSMPABC081	675	1.30	0.12	0.01	1.940	0.753	6.115	0.091	3.547	0.580	0.060	4.981	560	19	570	27	608	108	92.20
4.sSMPABC084	27029	35.25	3.77	0.03	1.995	0.751	3.559	0.091	2.849	0.801	0.060	2.133	559	15	569	16	608	46	92.01
4.sSMPABC017	687	3.89	0.36	0.01	2.403	0.767	5.206	0.092	3.012	0.579	0.060	4.246	570	16	578	23	611	92	93.35
4.sSMPABC079	617	1.12	0.10	0.01	2.846	0.746	6.715	0.090	4.664	0.695	0.060	4.831	555	25	566	30	611	104	90.71
4.sSMPABC053	27553	63.13	6.82	0.03	2.105	0.772	3.328	0.093	2.469	0.742	0.060	2.231	572	14	581	15	615	48	93.10
4.sSMPABC075	1037	2.63	0.25	0.01	1.591	0.787	4.639	0.095	2.680	0.578	0.060	3.786	583	15	590	21	615	82	94.81
4.sSMPABC033	653	2.08	0.20	0.01	3.521	0.760	6.130	0.091	3.272	0.534	0.060	5.184	563	18	574	27	615	112	91.60
4.sSMPABC052	27073	61.98	6.78	0.03	2.123	0.779	3.568	0.094	2.757	0.773	0.060	2.266	577	15	585	16	616	49	93.67
4.sSMPABC083	801	1.41	0.13	0.01	2.043	0.751	5.885	0.090	3.782	0.643	0.060	4.509	557	20	569	26	618	97	90.16
4.sSMPABC022	760	3.77	0.36	0.01	1.282	0.780	4.898	0.094	3.430	0.700	0.060	3.496	577	19	586	22	620	75	93.05
4.sSMPABC031	703	2.59	0.24	0.01	2.487	0.786	5.089	0.094	2.895	0.569	0.060	4.186	581	16	589	23	607	90	95.71
4.sSMPABC080	684	1.29	0.12	0.01	0.707	0.775	5.325	0.093	4.081	0.566	0.058	3.421	572	22	583	24	532	74	107.46
4.sSMPABC054	28288	63.08	6.96	0.03	2.034	0.802	3.624	0.096	2.912	0.803	0.060	2.158	589	16	598	17	594	46	99.20
4.sSMPABC050	27572	64.55	7.33	0.03	2.180	0.809	3.541	0.096	2.684	0.758	0.059	2.310	594	15	602	16	556	50	106.73
4.sSMPABC096	710	0.89	0.08	0.01	3.097	0.765	5.942	0.091	3.491	0.588	0.061	4.808	562	19	577	26	633	104	88.84
4.sSMPABC051	27430	62.79	7.13	0.03	1.972	0.814	3.412	0.097	2.679	0.585	0.060	2.112	596	15	605	16	607	45	98.25
4.sSMPABC014	632	3.87	0.37	0.01	2.482	0.800	6.095	0.095	4.238	0.695	0.061	4.381	586	24	597	28	638	94	91.85
4.sSMPABC025	632	2.58	0.25	0.01	2.469	0.802	6.090	0.095	4.238	0.696	0.060	4.374	586	24	598	28	607	94	96.49
4.sSMPABC095	608	0.66	0.06	0.01	3.756	0.762	6.166	0.090	3.783	0.583	0.059	4.869	557	20	575	27	578	105	96.26
4.sSMPABC015	510	2.49	0.26	0.01	3.866	0.804	6.671	0.095	4.615	0.592	0.060	4.818	584	26	599	31	588	103	99.31
4.sSMPABC029	510	1.61	0.17	0.01	3.853	0.806	6.666	0.095	4.615	0.692	0.059	4.810	584	26	600	31	556	103	104.92
4.sSMPABC073	583	0.95	0.10	0.01	4.340	0.788	5.845	0.092	4.257	0.728	0.058	4.005	567	23	590	26	534	86	106.24
4.sSMPABC012	529	2.77	0.29	0.01	4.408	0.834	6.198	0.097	4.484	0.723	0.059	4.279	595	26	616	29	550	91	108.35
4.sSMPABC097	32324	36.12	4.34	0.03	2.601	0.897	3.431	0.104	2.382	0.694	0.060	2.470	636	14	650	17	593	53	107.26

Continue...

Table 2. Continuation.

Spot	[a]207 Pb (cps)	[b]U (ppm)	[b]Pb (ppm)	[b]Th U	[c]206 Pb (%)	[d]207 Pb 235U	±2s (%)	[d]206 Pb 238U	±2s (%)	rhoe	[d]207 Pb 206 Pb	±2s (%)	206 Pb 238 U	±2s (Ma)	207 Pb 235 U	±2s (Ma)	207 Pb 206 Pb	±2s (Ma)	Conc %
Khan Accepted age 522 Ma																			
Within run standard points normalized with BLR 1																			
4.sSMPABC094	4852	10.38	1.00	0.06	0.000	0.668	2.986	0.084	2.512	0.841	0.058	1.614	521	13	520	12	516	35	100.90
4.sSMPABC093	4891	9.93	0.96	0.06	0.410	0.674	2.784	0.084	2.318	0.833	0.058	1.542	522	12	523	11	529	34	98.60
4.sSMPABC092	4827	10.47	1.03	0.06	0.000	0.689	2.649	0.086	2.252	0.850	0.058	1.395	532	12	532	11	535	31	99.32
4.sSMPABC091	4933	10.56	1.03	0.06	0.352	0.684	2.985	0.085	2.487	0.833	0.058	1.652	527	13	529	12	539	36	97.70
4.sSMPABC090	4950	10.74	1.04	0.06	0.000	0.668	2.499	0.084	2.047	0.819	0.058	1.435	518	10	519	10	523	31	99.13
4.sSMPABC089	25842	28.78	2.88	0.03	2.114	0.688	3.652	0.084	2.862	0.784	0.059	2.269	519	14	531	15	585	49	88.74
4.sSMPABC086	30209	35.11	3.61	0.03	2.875	0.700	3.862	0.085	2.684	0.695	0.060	2.777	526	14	539	16	594	60	88.57
4.sSMPABC084	799	1.21	0.11	0.01	3.453	0.678	5.969	0.082	3.855	0.646	0.060	4.557	510	19	525	25	593	99	86.06
4.sSMPABC067	989	1.60	0.14	0.01	4.463	0.705	6.089	0.084	3.603	0.592	0.061	4.909	522	18	542	26	629	106	82.98
4.sSMPABC066	934	2.02	0.18	0.01	1.712	0.684	5.093	0.084	2.945	0.578	0.059	4.154	517	15	529	21	582	90	88.85
4.sSMPABC062	738	1.78	0.16	0.01	2.813	0.691	6.186	0.085	4.156	0.672	0.059	4.582	525	21	533	26	570	100	92.00
4.sSMPABC068	5148	16.60	1.54	0.06	0.000	0.660	2.486	0.081	2.089	0.840	0.059	1.348	505	10	515	10	560	29	90.14
4.sSMPABC067	5439	20.51	2.03	0.06	0.000	0.690	2.726	0.086	2.353	0.863	0.058	1.376	534	12	533	11	527	30	101.27
4.sSMPABC021	6311	43.67	4.33	0.06	0.000	0.685	3.212	0.086	2.865	0.892	0.058	1.452	531	15	530	13	525	32	101.21
4.sSMPABC020	6258	45.30	4.48	0.06	0.764	0.680	3.091	0.085	2.486	0.804	0.058	1.837	529	13	527	13	518	40	102.04
4.sSMPABC019	6036	45.36	4.53	0.06	0.000	0.680	3.094	0.086	2.745	0.887	0.058	1.428	529	14	527	13	518	31	102.10
4.sSMPABC018	6737	52.01	5.12	0.06	0.000	0.681	3.430	0.085	3.190	0.930	0.058	1.260	528	16	527	14	524	28	100.72
4.sSMPABC010	6244	73.33	7.35	0.06	0.000	0.696	3.228	0.087	2.872	0.890	0.058	1.473	537	15	536	14	531	32	101.25
4.sSMPABC009	6258	78.25	7.74	0.06	0.764	0.680	3.091	0.085	2.486	0.804	0.058	1.837	529	13	527	13	518	40	102.04
4.sSMPABC008	6092	80.12	7.94	0.06	0.000	0.673	3.075	0.085	2.728	0.887	0.058	1.421	524	14	522	13	514	31	101.99
4.sSMPABC007	6737	92.46	9.11	0.06	0.000	0.681	3.430	0.085	3.190	0.930	0.058	1.260	528	16	527	14	524	28	100.69
4.sSMPABC006	6406	94.36	9.38	0.06	0.000	0.687	3.437	0.086	3.143	0.914	0.058	1.391	532	16	531	14	524	31	101.52
4.sSMPABC004	6418	107.70	10.67	0.06	0.000	0.676	3.037	0.085	2.772	0.913	0.058	1.241	526	14	524	13	517	27	101.83
4.sSMPABC003	6216	114.69	11.20	0.06	0.000	0.665	3.270	0.084	2.989	0.914	0.057	1.325	519	15	518	13	510	29	101.93
BLR 1 Accepted age 1049 Ma																			
Within run standard points normalized with BLR 1																			
4.sSMPABC001	44702	382.30	75.32	0.03	1.012062	1.868	2.405	0.180	2.001	0.832	0.075	1.334	1065	20	1070	16	1080	27	98.66
4.sSMPABC002	41961	514.18	99.92	0.03	0.756406	1.839	2.048	0.178	1.804	0.881	0.075	0.969	1057	18	1059	14	1064	19	99.35
4.sSMPABC003	42130	409.02	79.60	0.03	0.694349	1.837	2.051	0.178	1.809	0.882	0.075	0.968	1057	18	1059	14	1062	19	99.52
4.sSMPABC004	42274	446.58	86.57	0.03	0.722678	1.810	2.112	0.177	1.815	0.860	0.074	1.079	1053	18	1049	14	1040	22	101.24
4.sSMPABC005	42275	474.94	90.49	0.03	0.675464	1.769	2.004	0.174	1.759	0.878	0.074	0.961	1032	17	1034	13	1039	19	99.35

[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 BLR reference STD; [c]percentage of the common Pb on the ^{206}Pb. b.d. = below dectection limit;[d]corrected for background. within-run Pb/U fractionation (in case of 206Pb/238U) and common Pb using Stacy and Kramers (1975) model Pb composition and subsequently normalised to GJ-1 (ID-TIMS value/measured value); $^{207}Pb/^{235}U$ calculated using $^{207}Pb/^{206}Pb/(^{238}U/^{206}Pb*1/137.88)$; [e]rho is the $^{206}Pb/^{238}U/^{207}Pb/^{235}U$ error correlation coefficient.

being surrounded by strong pleochroic haloes when included in phlogopite (Fig. 3C). Chemical analyses by electron microprobe show relatively high contents of Al2O3 (7.19 – 8.96 wt.%, Table 1) and fluorine (around 2 wt.%). Due to the high Al content, this titanite was classified as grothite (Gaines *et al.* 1997) by Delgado *et al.* (2005).

Geochronology

Figure 3D is a BSE image of the sample PI-5, showing bright white titanite clusters with the location of some dated points. The mineral with light gray color is Mg-hornblende and the dark gray ones are plagioclase and quartz. The sample consists of Mg-hornblende, phlogopite, plagioclase, quartz, and titanite and is marked by a strong foliation defined by hornblende and phlogopite. Note that titanite is part of this fabric indicating growth during the metamorphic event.

Thirty-six analyses were performed on center and rims of the titanite grains (Table 2). No age difference could be detected between center and rim of titanite grains. Pooling of all data points did not yield a concordia age (Fig. 4). The points scatter about a mean $^{206}Pb/^{238}U$ age of 576 ± 7 Ma which is considered the age of titanite growth during medium-grade metamorphism.

DISCUSSION AND CONCLUSIONS

The substitution of Ti by Al in titanite, as found in the dated fluorine-aluminum-bearing titanite, can be the result of the high activity of fluorine that causes the simultaneous substitution of O by (F, OH) (Černý & Povondra 1972). Thereafter, the discussions regarding the formation of the titanite must take into consideration the source of fluorine, which is a scarce element in mafic igneous rocks but relatively abundant in granitic rocks. The metamafic schist belongs to the Archean Metavolcanosedimentary Sequence that surrounds the 1.7 Ga anorogenic Borrachudos metagranites. The Borrachudos metagranites postdate the main deformation phases of the 2.2 – 2.0 Paleoproterozoic Transamazonian tectonothermal event. The origin of fluorine must be linked to these granitic intrusions and their pegmatites which were also the source of beryllium for the emerald found in the associated phlogopite schists. The generation of emerald as well

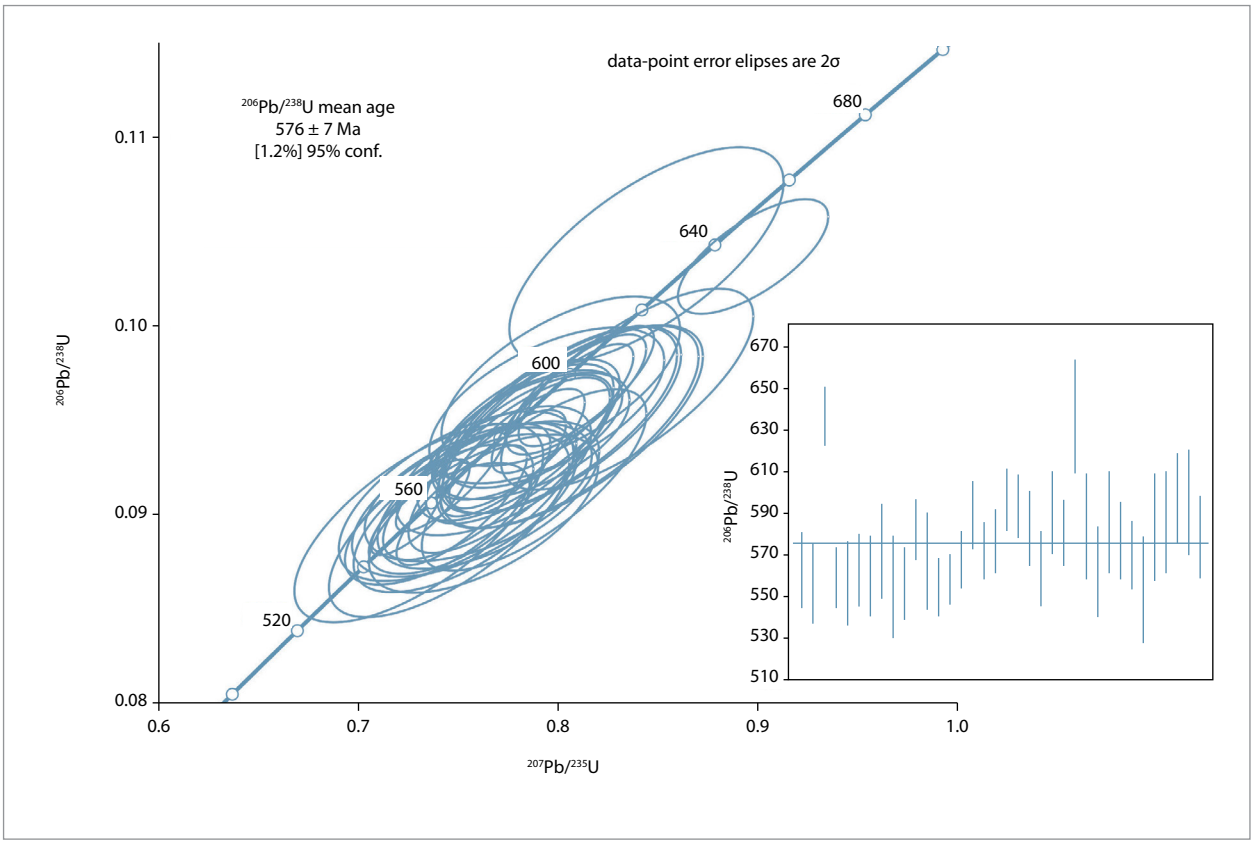

Figure 4. U-Pb concordia and weighed mean diagrams of LA-ICP-MS analyses of fluorine-aluminum-bearing titanite from a metamafic schist of the Piteiras mine.

as the titanite was possibly due to the metassomatic introduction of, respectively, Be and F into the metaultramafic and metamafic rocks. The discussions on the age of titanite and emerald must also take into consideration the nature of the rocks where the two minerals are found: These rocks are strongly deformed and completely metamorphosed and transformed by metassomatic reactions. As discussed in the literature (Grundmann & Morteani 1989, Franz *et al.* 1996, Franz & Morteani 2002), the formation of schist-type emerald deposits such as that of the Piteiras mine involves a tectonometamorphic event that supplies the necessary heat and fluids to enhance the metassomatic reactions between the granitic and the ultramafic rocks. Since the plausible source of beryllium and fluorine are the postorogenic Borrachudos metagranites and pegmatites, the only younger tectonometamorphic event that could have been responsible for the deformation, metamorphism, and metassomatic reactions between the Be/F-bearing and the Cr-bearing rocks was the 0.7 – 0.5 Ga Neoproterozoic Brasiliano event, which is the last tectonothermal event registered in the region. The obtained 576 ± 7 Ma age of the dated titanite corroborates the interpretation that the Brasiliano event was indeed responsible for its generation.

We conclude thereafter that the 576 ± 7 Ma age of the fluorine-aluminum-bearing titanite of the metamafic rock associated with the emerald-mineralized phlogopite schists in the Piteiras mine from the Itabira-Nova Era Emerald District could also be the age of the emerald generation during the Neoproterozoic tectonometamorphic Brasiliano event. We suggest that the following geological processes were involved in the generation of the emerald deposits from the Itabira-Nova Era region:

1. Formation of the Volcanosedimentary Sequence (including Cr-bearing ultramafic rocks) of the Guanhães Complex during the Archean (~2.8 Ga).
2. Generation and metamorphism of the gneisses of the Mantiqueira Complex during the Paleoproterozoic Transamazonian event (2.2 – 2.0 Ga) and intrusion of the late 1.7 Ga anorogenic Borrachudos granite and their pegmatites.
3. Regional metamorphism during the Neoproterozoic and generation of the schist-type emerald mineralization by reactions between Be-bearing granites and pegmatites and Cr-rich metaultramafic rocks was enhanced by deformation and heat supplied by the tectonometamorphic Brasiliano event (~0.7–0.5 Ga). The participation of hydrothermal fluids was crucial for the growth of emerald as well as for the phlogopitization of the ultramafic rock.

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