

TITANITE CRYSTAL CHEMISTRY AND U-Pb ISOTOPIC DATA: A PETROGENETIC INDICATOR FOR PRECAMBRIAN GRANITOID PLUTONS OF THE EASTERN BRAZILIAN SHIELD

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Abstract

This paper presents crystal chemistry and U-Pb isotopic data for titanite (or sphene, CaTiSiO₆) from Precambrian granitoid plutons of distinct tectonic settings within the Eastern Brazilian shield. Despite the fact that most titanite ages are related to partial lead-loss, resetting or crystallization during metamorphic events, chemistry data reflect the magmatic history of the plutons, specially the Ti⁴⁺/Al+Fe³⁺ ratio. It is demonstrated that for plutons of different crystallization ages (Archean, Paleoproterozoic and Neoproterozoic) the measured Ti⁴⁺/Al+Fe³⁺ ratios of titanite grains are characteristic of the source region from which the magma was extracted, and the ratios remain unchanged during subsequent metamorphic events. Higher Ti⁴⁺/Al+Fe³⁺ values (> 9) are found in predominantly mantle-derived granitoid plutons whilst crust-derived granitoid rocks have lower ratios. Therefore, titanite crystal chemistry may be used to discriminate magma sources of granitoid rocks regardless their age and metamorphic history.

INTRODUCTION

Titanite can be an important petrogenetic indicator since it can incorporate by partial substitution a variety of chemical elements, such as REE, depending on the mineralogical and tectonometamorphic history of rocks. In addition, the phase relations between titanite and other Ti bearing phases (mostly ilmenite and rutile) are a function of bulk composition, pressure and/or temperature (Lambert & Holland 1974, Enami et al. 1993, Frost et al. 2000, Kazonovitz & Wolf 2002), and coexisting assemblage (Tropper et al. 2002). However, the incorporation mechanism in titanite of geochemically relevant elements is poorly known (Tiepolo et al. 2002), and also the existing relations between these substitutions and petrogenesis.

The chemical composition of titanite can be represented by the general formula CaTi(SiO₄)₂(O,OH,F), but it may deviate from its ideal composition through the substitution of Ti and O by Al and F (Frank & Spear 1985, Tropper et al. 2002). The Al + OH substitution produces the end-member vuagnatite - CaAlSiO₄(OH) - a typical low-temperature phase with a different structure than titanite (Enami et al. 1993). On the other hand, the Al + F substitution is isostructural and is common at high metamorphic temperatures and pressures (Frank & Spear 1985). The titanite structure is generally described in term of chains of corner-sharing octahedra, running parallel to the [100] axis and cross-linked by isolated tetrahedra. This configuration produces large cavities, where Ca ions in [7]-fold-coordinated sites lie (Deer et al. 1982).

In this paper, we discuss the crystal chemistry of titanite and how isomorphic substitutions may be related to its petrogenetic and metamorphic history.

The study is based on isotopic and crystal chemistry data of titanites from the São Francisco Craton and Araçuaí Orogen, in southeastern Brazil (figure 1). The analysed grains come from tonalitic- to granitic plutons of distinct tectonic settings and magmatic ages.

GEOLOGICAL SETTING AND SAMPLE DESCRIPTIONS

The granitoid bodies are found in two tectonic settings, the southern part of the São Francisco Craton and the Neoproterozoic Araçuaí Orogen developed during the Brasiliano-Pan African Orogeny. The cratonic basement consists of an Archean nuclei displaying a classical association of TTG gneiss complexes, greenstone belts and felsic plutons (e.g. Teixeira et al. 2000), that is partially surrounded by a Paleoproterozoic plutonic arc (e.g. Noce et al. 2000).

The Araçuaí Orogen developed at the southeastern margin of the São Francisco Craton. Both Archean and Paleoproterozoic rock associations can be traced into the orogenic domain making up strongly reworked basement units. The orogen also comprises the volcano-sedimentary record of basin/orogen evolution, ophiolitic remnants and a calc-alkaline magmatic arc. Geochronological data for pre-, syn- and late-collisional granitoids indicate that the orogenic stage lasted from 625 Ma to 560 Ma. A period of magmatic quiescence was followed by intrusion of postcollisional plutons at 535–500 Ma. (Pedrosa-Soares et al. 2001).

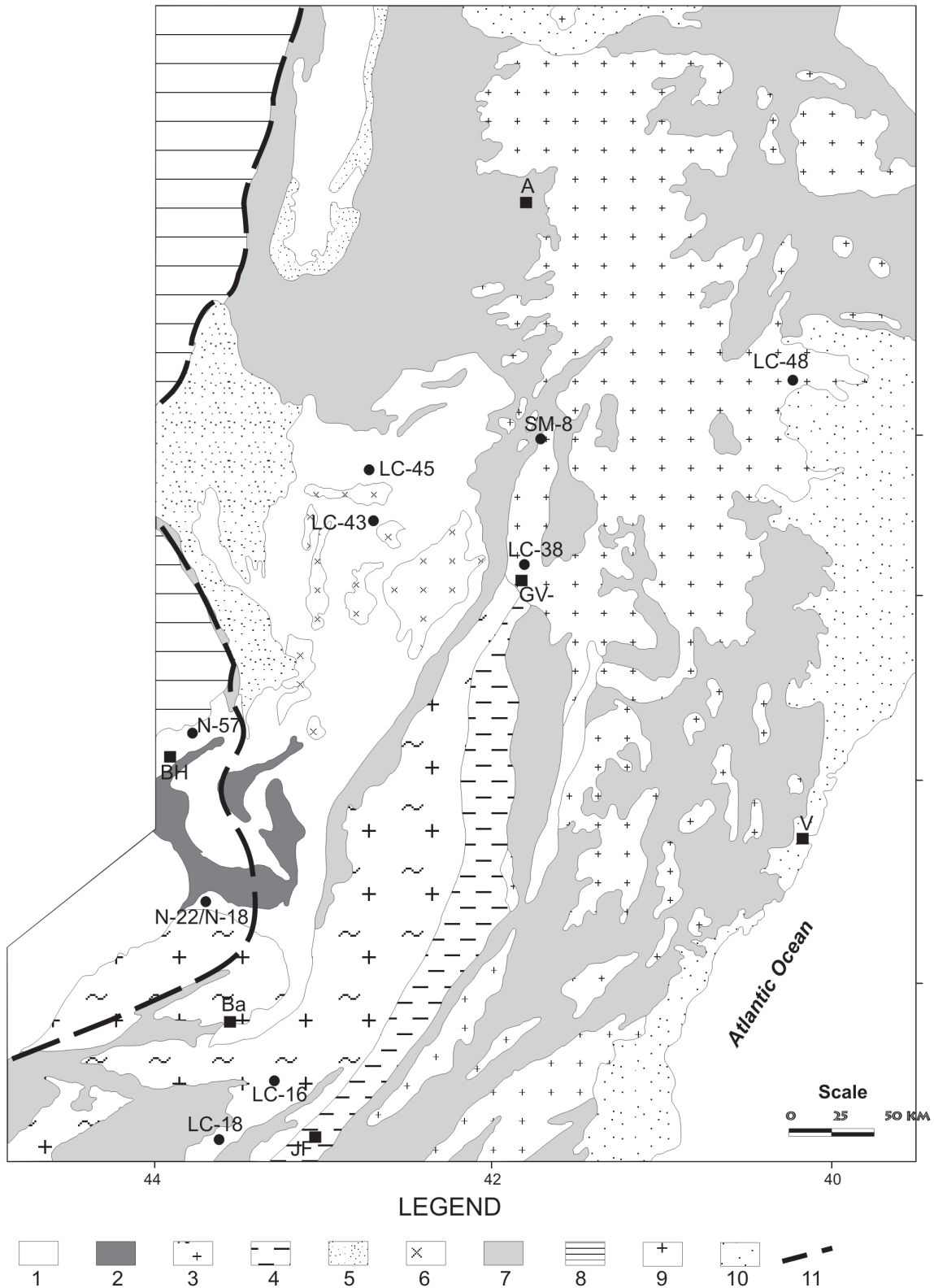
Titanite were extracted from eight samples of granitoid plutons, with magmatic ages ranging from Archean to Neoproterozoic.

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Distribution of Archean, Paleoproterozoic and Neoproterozoic studied plutons in the Brazilian Shield. Symbols: 1: Archean granitoid-gneiss-migmatitic rocks; 2 - greenstone belts and Minas Supergroup, 3 - Mantiqueira Complex 4 - Juiz de Fora Complex 5 -Espinhaço rift system (Paleo to Mesoproterozoic), 6 - Borracudos Suite 7 -Supracrustals units of Brasiliano Cycle , 8 - Bambuí Group (Neoproterozoic), 9 - granites from Araçuaí Belt (Neoproterozoic marginal belt), 10 - Fanerozoic covers, 11 - Limit of São Francisco Craton. Keys: A - Araçuaí, Ba - Barbacena, BH - Belo Horizonte, JF - Juiz de Fora, GV - Governador Valadares, V - Vitória.

Figure 1: Distribution of Archean, Paleoproterozoic and Neoproterozoic studied plutons in the Brazilian Shield (modified of Pedrosa-Soares et al. 2001 and Silva et al. 2002).

ARCHEAN GRANITOIDS

Sample N-57:

In the well-preserved Archean terrain within the cratonic domain it is possible to identify an important magmatic and tectonic event that took place at ca. 2790 to 2700 Ma, related to greenstone belt evolution and the intrusion of several tonalitic to granitic plutons (Machado & Carneiro 1992, Machado et al. 1992, Noce et al. 2005). Sample N-57 came from a small pluton dated at $2712 \pm 5/-4$ Ma (Noce et al. 1998), cutting across the much older TTG gneiss. It is a high K calc-alkaline and slightly peraluminous granite related to a late- to post-orogenic stage.

Samples LC-43 and LC-45:

The Guanhães Complex is a basement unit of the Araçuaí Orogen with a protracted geologic evolution that goes from Archean to Late Paleoproterozoic, strongly reworked during the Brasiliano Orogeny. Both samples are trondhjemitic-banded gneisses displaying migmatitic structures, and must represent the older TTG gneiss units within the complex. In spite of their similarity, these trondhjemite gneiss gave distinct crystallization ages of 2711 ± 11 Ma (sample LC-43) and 2867 ± 10 Ma (sample LC-45; Silva et al. 2002).

Sample LC-18:

This is a migmatitic banded gneiss with tonalitic composition, dated at 2777 ± 22 Ma (Silva et al. 2002). This sample belongs to another basement unit of the Araçuaí Orogen largely composed of Paleoproterozoic plutonic rocks (the Mantiqueira Complex), but including older inliers that cannot be distinguished in the field from the country rocks due to pervasive Neoproterozoic reworking.

PALEOPROTEROZOIC GRANITES

Samples N-18 and N-22:

Several Paleoproterozoic granitoid and mafic bodies crop out along the southern border of the São Francisco Craton, making up a magmatic arc partially preserved from the Neoproterozoic tectonism. The plutonic bodies display a wide range of composition, from gabbro-diorite, TTG (tonalite-trondhjemite-granodiorite), and granite (Quéméneur & Noce 2000, Noce et al. 2000). Both samples come from the Alto Maranhão pluton, a tonalite gneissic body that is interpreted as mantle-derived according to its chemical and isotopic signatures (Noce et al. 1997). Its crystallization age is given by a concordant zircon age at 2130 ± 2 Ma, whereas a titanite discordia line yields an upper intercept at 2124 ± 2 Ma (Noce et al. 1998). The difference between zircon and titanite ages may be ascribed to the intrusion-cooling rate, or to a metamorphic event contemporaneous to the magmatism.

Sample LC-16:

The Mantiqueira complex consists predominantly of banded biotite-amphibole gneiss. The thickness of the the alternating layers of felsic and more mafic composition varies from centimetric to metric, and concordant amphibolite boudins, lenses and layers are very common. The felsic layers are of granitic to tonalitic composition, and this unit is interpreted as the product of intense deformation of the Paleoproterozoic magmatic arc in the Araçuaí Orogen domain. Sample LC-16 represents a tonalite layer of a banded Mantiqueira gneiss displaying milonitic texture, and yielded a magmatic age of 2052 ± 26 Ma (Silva et al. 2002).

NEOPROTEROZOIC GRANITES

Sample SM-8:

The Brasilândia pluton is a pre-collisional intrusion of the Araçuaí Orogen, and consists of diorite, tonalite, and granodiorite. Dating through the Pb-Pb evaporation method yielded a minimum crystallization age of 595 ± 3 Ma (Noce et al. 2000). Nd and Sr isotopic data suggests a mixed magma-source involving a depleted lower crust and some mantle contribution (Martins et al. 2003). Sample SM-8c is a homogeneous foliated tonalite, fine- to medium-grained.

Sample LC-38:

This sample is granodioritic gneiss with a poorly constrained intrusion age of 565 ± 31 Ma (Silva et al. 2002). It contains tectonic lenses of garnet-sillimanite paragneisses and may represent a syncollisional intrusion of the Araçuaí Orogen.

ANALYTICAL TECHNIQUES

Titanite U-Pb analyses were carried out for this study at the Geochronology Laboratory of the University of Brasilia, with the exception of samples N-18/N-22 and N-57 that were analyzed previously and presented in Noce et al. 1998. Titanite concentrates were extracted from rock samples using conventional gravimetric and magnetic (Frantz isodynamic separator) techniques. Final separation was achieved by hand picking using a binocular microscope. Titanite grains were dissolved in concentrated HF and HNO₃ (HF:HNO₃ = 4:1), and a ²⁰⁵Pb–²³⁵U spike was used. Chemical extraction followed standard anion exchange technique using Teflon micro columns. Isotopic analyses were carried out on a Finnigan MAT-262 multi-collector mass spectrometer, and procedure blanks for Pb, at the time of analyses, were better than 15 pg. For data reduction and age calculation, PBDAT (Ludwig 1993) and ISOPLOT-Ex (Ludwig 2001) were used. Calculated ages are shown in table 1.

For crystal chemistry, fourteen single crystals were analyzed by electron microprobe on a JEOL JXA-8900RL spectrometer under the following

Table 1 – Synthesis of data from studied samples

Archean plutons					
Sample	Geotectonic Domain	Crystallization Age	Titanite age	Significance of titanite age	Nature of the rock
LC-45	Araçuaí Orogen	2867±10(a)	506±7 (*1)	Partial lead loss related to the late Brasiliano Orogeny (orogenic collapse)	TTG gneiss
LC-43	Araçuaí Orogen	2711±11(a)	528-434 (*2)	Resetting or crystallization during during the Brasiliano metamorphic peak followed by recent lead-loss	TTG gneiss
LC-18	Araçuaí Orogen	2777±22(a)	550-536 (*2)	Resetting or crystallization during during the Brasiliano metamorphic peak followed by recent lead-loss	TTG gneiss
N-57	São Francisco Craton	2712±5(c)	2328-2212 (*3)	Partial lead loss related to the Transamazonian Orogeny	High K granite
Paleoproterozoic plutons					
Sample	Geotectonic Domain	Crystallization Age	Titanite age	Significance of titanite age	Nature of the rock
N-18/N-22	São Francisco Craton	2130±2 Ma (c)	2124±2 (*4)	Magmatic age; fractions are concordant or display recent lead loss	Mantle-derived tonalite
LC-16	Araçuaí Orogen	2058±7(a)	636±89 (*4)	Resetting or crystallization during during the Brasiliano metamorphic peak followed by recent lead-loss	Tonalite gneiss
Neoproterozoic plutons					
Sample	Geotectonic Domain	Crystallization Age	Titanite age	Significance of titanite age	Nature of the rock
Sm-8	Araçuaí Orogen	595±3 (b)	564-534 (*2)	Partial lead loss and resetting related to Brasiliano metamorphic peak followed by recent lead-loss	Pre-collisional diorite- to tonalite pluton
LC-38	Araçuaí Orogen	565±31(a)	556±7 (*5)	Magmatic/metamorphic age	Sin- to late collisional granodiorite

*1 – lower-intercept age

*2 – range of $^{206}\text{Pb}/^{238}\text{U}$ ages, discordant and/or concordant analysis

*3 – range of $^{207}\text{Pb}/^{206}\text{Pb}$ ages, discordant analysis

*4 – upper intercept age *5 – mean $^{206}\text{Pb}/^{238}\text{U}$ age

(a) U-Pb SHRIMP isotopic data from Silva et al.

(2002); (b) $^{207}\text{Pb}/^{206}\text{Pb}$ in zircon crystals from Noce et

al. (2000); (c) Isotopic data from

Noce (1995)

operational conditions: 15 kV acceleration potential and 20 nA sample current. The crystals were analyzed using the following standards: jadeite (Na), asbestos (K), hortonolite (Si, Fe, Mg, Mn), anorthite (Ca, Al), chromite (Cr), synthetic glass (REE). Counting times

were 20s for REE and 16s for all other major elements. The chemical data for each crystal are averages of 3-7 analyses taken uniformly over each crystal. The lower limit of detection was 0.01 wt%. Calculation of the titanite unit formula is a very difficult task due to the

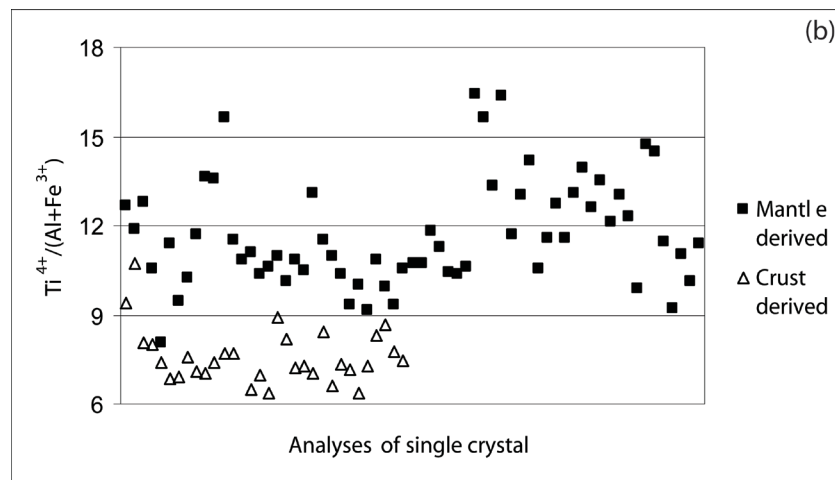
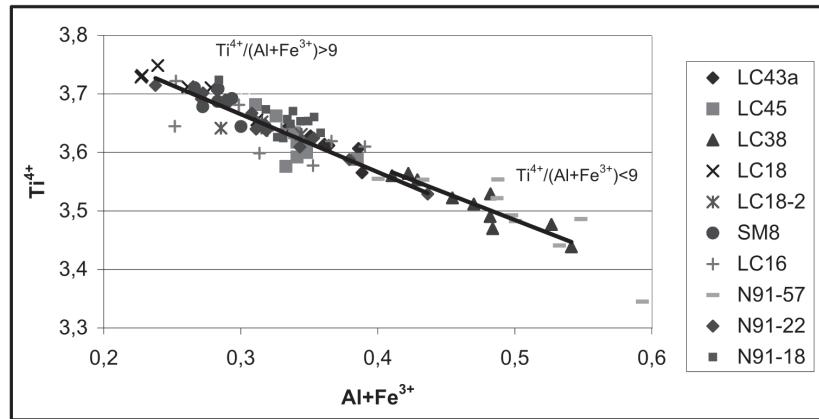


Figure 2 a, b - The relationship between Ti^{4+} apf and $Al+Fe^{3+}$ apf and the definition of two groups A and B, respectively.

lack of accurate estimates of H, F, REE and other minor elements. Iron is reported as Fe_2O_3 . In this work, the unit formula reported in Table 2 has been obtained based on five oxygen atoms. The OH apfu was calculated following Enami et al (1993).

RESULTS

ISOTOPIC DATA

Titanite crystals are near euhedral (N-57, LC43 and LC45) to subhedral (N-18, N-22, LC38, LC18, LC16, SM8), ranging in size from 50 to 200 μm , and no significant zoning was observed with the exception of grains from sample N-57. Crystal morphology, intragrain homogeneity and isotopic data are good evidences for titanite crystallization in equilibrium with the surrounding biotite and hornblende.

The wide titanite age spectrum is a consequence of distinct magmatic ages and metamorphic histories of studied plutons (Table 1). Granitoid plutons from the cratonic domain were not affected by the Neoproterozoic Brasiliano Orogeny, but record a Paleoproterozoic event dated at ca. 2120-2050 Ma (Noce et al. 1998). Titanite grains from the Archean granite (N-57) suffered partial

lead-loss due to this event, while titanite ages for the Paleoproterozoic pluton (N-18/N-22) are close to the intrusion age.

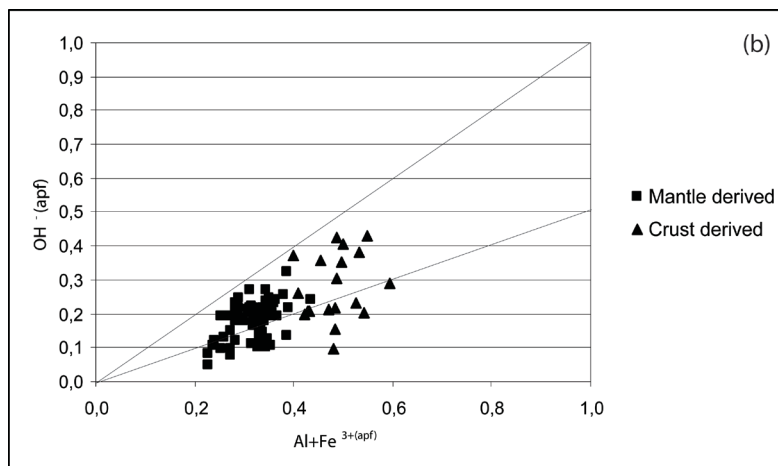
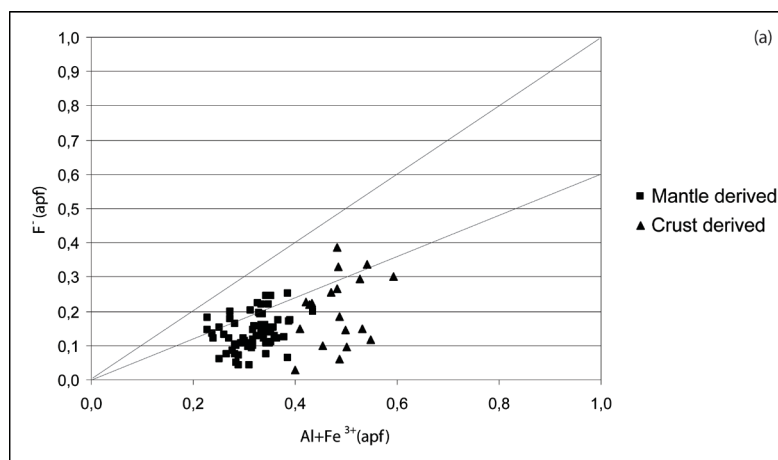
The Araçuaí Orogen records a syncollisional tectono-metamorphic event dated at 585-560 Ma, and a late orogenic thermal episode related to the gravitational collapse of the orogen, dated at 535-500 Ma (Noce et al. 2004). Titanite ages of the granitoid plutons located within the orogenic domain are all Neoproterozoic, regardless their magmatic age. For most samples, the combination of resetting and/or partial lead-loss during two thermal episodes resulted in a complex titanite age pattern.

MINERAL CHEMISTRY

A remarkable difference in titanite composition is disclosed by two distinct groups of granitoid plutons, especially concerning Ti^{4+} , Al^{3+} , Fe^{3+} and F^- contents. Titanite crystals from subduction-related plutons with an important mantelic contribution (and/or mafic lower crust) yield higher concentrations of Ti and lower concentrations of $Al+Fe^{3+}$, while opposite values are found in titanites from high fractionated crust-derived plutons (Table 2). The first group (Group A) comprises

Table 2 – Average chemical composition (wt%) and unit formula of titanite

	Mantle derived						Crust derived			
	LC 45	LC 43a	LC 18	LC 18-2	N-18	N-22	SM- 8	N-57	LC 16	LC 38
SiO ₂	30,08	29,73	30,17	29,98	29,68	30,40	29,86	29,43	30,37	29,98
TiO ₂	36,94	36,65	38,09	37,10	37,19	37,77	37,46	35,52	37,54	35,71
Al ₂ O ₃	1,70	1,60	1,38	1,64	1,30	1,89	1,37	1,70	1,93	2,38
Fe ₂ O ₃	0,92	1,32	0,57	0,71	1,51	0,36	0,82	1,85	0,31	1,16
MnO	0,11	0,11	0,07	0,07	0,00	0,00	0,11	0,00	0,06	0,12
CaO	28,06	26,79	27,92	27,68	27,80	28,70	27,59	26,62	28,51	27,34
Ce ₂ O ₃	0,00	0,24	0,01	0,03	0,33	0,01	0,31	0,56	0,01	0,16
Y ₂ O ₃	0,09	1,75	0,20	0,88	0,00	0,00	0,28	0,00	0,05	0,43
Nd ₂ O ₃	nd	nd	nd	nd	0,23	0,06	nd	0,37	nd	nd
Nb ₂ O ₅	nd	nd	nd	nd	0,14	0,15	nd	0,29	nd	nd
H ₂ O ⁻	0,21	0,28	0,15	0,26	0,96	1,03	0,21	0,87	0,19	0,25
F	0,39	0,29	0,32	0,22	0,39	0,29	0,25	0,53	0,38	0,62
O≡F	0,16	0,12	0,13	0,09	0,16	0,12	0,11	0,22	0,16	0,26
TOTAL	98,33	98,64	98,75	98,48	99,36	100,54	98,13	97,52	99,20	97,90
Si ⁴⁺	3,92	3,90	3,91	3,91	3,88	3,90	3,91	3,91	3,91	3,92
Ti ⁴⁺	3,62	3,61	3,71	3,64	3,66	3,65	3,69	3,55	3,64	3,51
Al ³⁺	0,26	0,25	0,21	0,25	0,20	0,29	0,21	0,27	0,29	0,37
Fe ³⁺	0,08	0,12	0,05	0,06	0,13	0,03	0,07	0,17	0,03	0,10
Mn ²⁺	0,02	0,02	0,01	0,01	0,00	0,00	0,02	0,00	0,01	0,02
Ca ²⁺	3,92	3,76	3,88	3,87	3,89	3,95	3,87	3,79	3,94	3,83
Ce ³⁺	0,00	0,01	0,00	0,00	0,02	0,00	0,01	0,03	0,00	0,01
Y ³⁺	0,01	0,12	0,01	0,06	0,00	0,00	0,02	0,00	0,00	0,03
Nd ³⁺	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,02	0,00	0,00
Nb ⁵⁺	0,00	0,00	0,00	0,00	0,01	0,01	0,00	0,02	0,00	0,00
F ⁻	0,16	0,12	0,13	0,09	0,16	0,12	0,10	0,22	0,16	0,26
OH ⁻	0,18	0,24	0,13	0,22	0,84	0,88	0,18	0,21	0,16	0,21

Figure 3 a, b - OH⁻ versus Al + Fe³⁺ and F⁻ versus Al + Fe³⁺ substitutions respectively

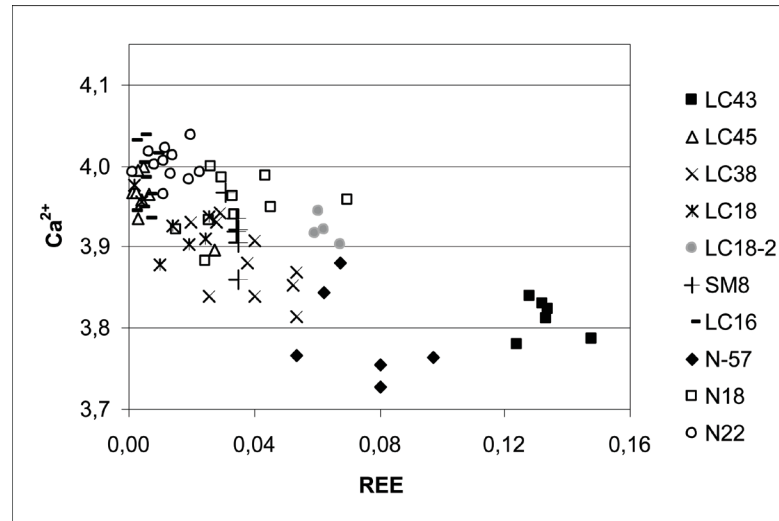


Figure 4: Ca ions versus REE contents to the studied samples

Archean TTG gneiss samples (LC45, LC43 and LC18), the Paleoproterozoic tonalite plutons (N-18/N-22 and LC16), and the pre-collisional Brasilândia tonalite of Neoproterozoic age (SM8). The second group (Group B) includes a high-K Archean granite (N-57) and two Neoproterozoic granitoid bodies related to the sincollisional stage of the Araçuaí Orogen (LC38 and MU56). The two groups of granitoids can be distinguished according to the titanite $Ti^{4+}/(Al+Fe^{3+})$ ratio values. Group A has $Ti^{4+}/(Al+Fe^{3+})$ ratio values > 9 , whereas Group B has lower values (< 9 ; Fig 2a,b).

It may be concluded that $Al+Fe^{3+}$ and Ti^{4+} substitutions involve the entrance of F^- and OH^- ions (Fig 3a,b). Titanite crystals from Group A plutons plot roughly close to the $Al-OH$ end-member $CaAlSiO_4(OH)$, while titanite crystals from Group B have a more variable composition. There is a negative correlation between $Al+Fe^{3+}$ and Ti^{4+} contents, and a positive correlation between F^- and OH^- ions, implying the substitutions can be coupled: $CaTiO \rightarrow Ca(AlFe^{3+})FTi$ and $Ca(AlFe^{3+})OHTi$. In this context, a greater fluid content seems to be present in crust-derived plutons (Group B) because of the positive correlation between F^- and OH^- contents and $Al + Fe^{3+}$ contents.

In Group B Neoproterozoic plutons (samples LC-38 and Mu-56a), a fraction of the iron must have oxidized during the generation of large volumes of fluids, and as a consequence $CaTiO \rightarrow Ca(AlFe^{3+})F$ substitution took place at the time of crystallization. The same hypothesis can be admitted concerning the Group B Archean pluton (sample N-57), but in this case the $CaTiO \rightarrow Ca(AlFe^{3+})OH$ substitution occurred preferentially. This significant fluid activity disclosed by crust-derived granitoids can be related to fractionated melting. According to Frank & Spear (1985), Carswell et al. (1996) and Markl & Piazzolo (1999), it is considered a petrogenetic indicator, according to studies developed on distinct tectonic domains.

According to the chemical data (Table 2) a negative correlation between $Al+Fe^{3+}$ and Mn contents may also

be inferred, since there is no other correlation between Mn^{2+} and Ca^{2+} ions. Si ions seem to be sufficient to nearly full the tetrahedron site. Ca contents are similar and invariable in all samples, ranging from 3.7 to 4.0 apfu, and no substitution can be established. There is only a slight negative correlation between REE contents and Ca ions. These evidences suggest that the entrance of $Al+Fe^{3+}$ at octahedral site can favor the incorporation of smaller cations and available fluid, what can be well identified by the nature of the rocks.

CONCLUSIONS

Titanite crystals from granitoid plutons with magmatic ages ranging from Archean to Neoproterozoic, and intruded into distinct tectonic domains, underwent a complex history of partial lead-loss to resetting during successive thermal events. Nevertheless, their original bulk composition has been preserved. Analytical techniques applied in this study show that Ti and Ca sites of titanite crystal are independent since the Ca-site is affected by tectonometamorphic events as evidenced by U-Pb isotopic data while Ti-octahedral site substitutions are directly related with the bulk composition or nature of the rocks.

The majority of titanite crystal chemical analyses for samples LC-38 and N-57, which are the most fractionated granites, yield $Ti^{4+}/Al+Fe^{3+} < 9$. On the other hand, TTG and tonalite samples presents $Ti^{4+}/Al+Fe^{3+} > 9$. Therefore, this ratio can be used as a petrogenetic pattern to distinguish mantle from crustal sources and/ or eventually mixing of sources.

ACKNOWLEDGMENTS

The authors are indebted to the Brazilian research-funding agencies: Conselho Nacional de Pesquisa (CNPq) (Danielle Piuçana – Grant 300121/02-4) and CAPES/PRODOC (Cristiane Castañeda).

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