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In Situ Isotopic Analyses of U and Pb in Zircon by Remotely Operated SHRIMP II, and Hf by LA-ICP-MS: an Example of Dating and Genetic Evolution of Zircon by $^{176}Hf/^{177}Hf$ from the Ita Quarry in the Atuba Complex, SE Brazil

Análises in situ de U e Pb em Zircão por SHRIMP II por Controle Remoto e de Hf por LA-ICP-MS: um Exemplo de Datação e da Evolução Genética de Zircão Através da Razão $^{176}Hf/^{177}Hf$ em amostra da Pedreira Ita no Complexo Atuba, SE Brasil

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ABSTRACT

Remotely-operated SHRIMP dating of zircon is an interesting alternative for dating of zircon crystals. Although it does not represent any technical progress of the geochronological method using the U-Pb system in zircon it is a very useful and cheap facility. The procedure was first used for mass spectrometric analyses involving two international laboratories in São Paulo, Brazil and Beijing, China. It was applied to samples of three gneiss-migmatitic rocks from the Ita quarry in the Atuba Complex (located between the Luis Alves and the Apiaí Domain) to test previous controversial hypotheses about its evolution. The presence of important archean and paleoproterozoic components in the complex is confirmed by analyses of zircon found in probably neoproterozoic leucosomes. Diorite intrusion also occurred during the neoproterozoic, associated with the 0.6Ga continental collisions involved in the assembly of Gondwana. The determination of Hf isotope ratios by LA-ICP/MS represents a new option for checking the relative importance of mantle ($\varepsilon_{Hf} > 0$) and crustal contributions ($\varepsilon_{Hf} < 0$) during the growth of the zircon crystals. While the archean component in the complex was derived from the mantle (ε_{Hf} +1.5 to +8.7) the paleoproterozoic component had a crustal contribution (ε_{Hf}-9.1 to -10.1).

Keywords: Remotely-controlled SHRIMP II; Zircon dating; LA-ICP-MS; Hf isotopic composition; Atuba Complex; SE Brazil.

RESUMO

Operar o espectrômetro de massa SHRIMP à distância, remotamente via Internet, é sem dúvida uma técnica alternativa de grande interesse para a datação de cristais de zircão. Embora não represente avanço no método geocronológico U-Pb em zircão, a técnica de operação remota traz, além de facilidade, grande economia nesse tipo de análise. Foi executada pela primeira vez em análises espectrométicas envolvendo dois laboratoratórios internacionais (São Paulo, Brasil - Beijing, China) possibilitando a obtenção de resultados em tempo real. O procedimento foi aplicado em três amostras de rochas gnáissico-migmatíticas da pedreira Ita (próxima à cidade de Curitiba - Paraná - Brasil) pertencentes ao Complexo Atuba. Tais rochas, quando analisadas através do método U-Pb (TIMS) demonstraram uma evolução complexa, com idades bastante imprecisas. A presença de importantes heranças arqueanas e paleoproterozoicas, neste complexo, foram confirmadas nas zonas internas de cristais de zircão obtidas em leucossomas neoproterozoicos. Análises adicionais realizadas em rochas dioríticas indicaram ser intrusivas, e não encaixantes, e apresentaram idades relacionadas às colisões continentais (0.6 Ga) envolvidas durante a assembléia de Gondwana, no Neoproterozoico. A determinação das razões de isótopos de Hf em cristais de zircão, por meio de LA-ICP-MS, representa uma nova opção para checar a importância relativa da contribuição de material do manto ($\varepsilon_{Hf} > 0$) e crosta ($\varepsilon_{Hf} < 0$). No Complexo Atuba, o componente arqueano sugere derivação de material oriundo do manto (ε_{Hf} +1,5 a +8,7), enquanto o componente paleoproterozoico indica contribuição crustal (ε_{Hf} -9,1 a -10,1).

Palavras-chave: SHRIMP II controlado remotamente; Datação de zircão; LA-ICP-MS; Composição isotópica de Hf; Complexo Atuba; SE Brasil.

INTRODUCTION

In this article we describe an experience with the use of the Remotely Operated SHRIMP System (ROSS) installed at Beijing, China, and operated from the Geochronology Research Centre (CPGeo) at the University of São Paulo, Brazil. Results of U-Pb dating of zircon of three samples from the Ita quarry (near Curitiba city, Paraná State, Figure 1) in the Atuba Complex are presented in order to test a controversial hypothesis about its evolution, obtained by conventional methods of dating single and multi-grain fractions, as well as by preliminary analyses by SHRIMP I and II. This complex is located between the Luis Alves microplate and the Apiaí Domain (Figure1).

The use of Hf isotopes in zircon to evaluate of the contributions of sources of different origins and ages is also a novel tool. Hf isotopic ratios were obtained from Laser Ablation Inductively Coupled Plasma Source Mass Spectrometry (LA-ICP-MS) at the TITech laboratories in Japan.

The present paper has objective to confirm previous data (Sato et al., 2003; Silva, 2005; Siga Jr., 1995) that demonstrate that different parts of the Atuba Complex underwent different evolutionary paths and additional Hf isotope analysis to complements and enhances the previous inferences using the Sm-Nd system in identifying the sources that contributed to the evolution of the rocks and their zircon grains.

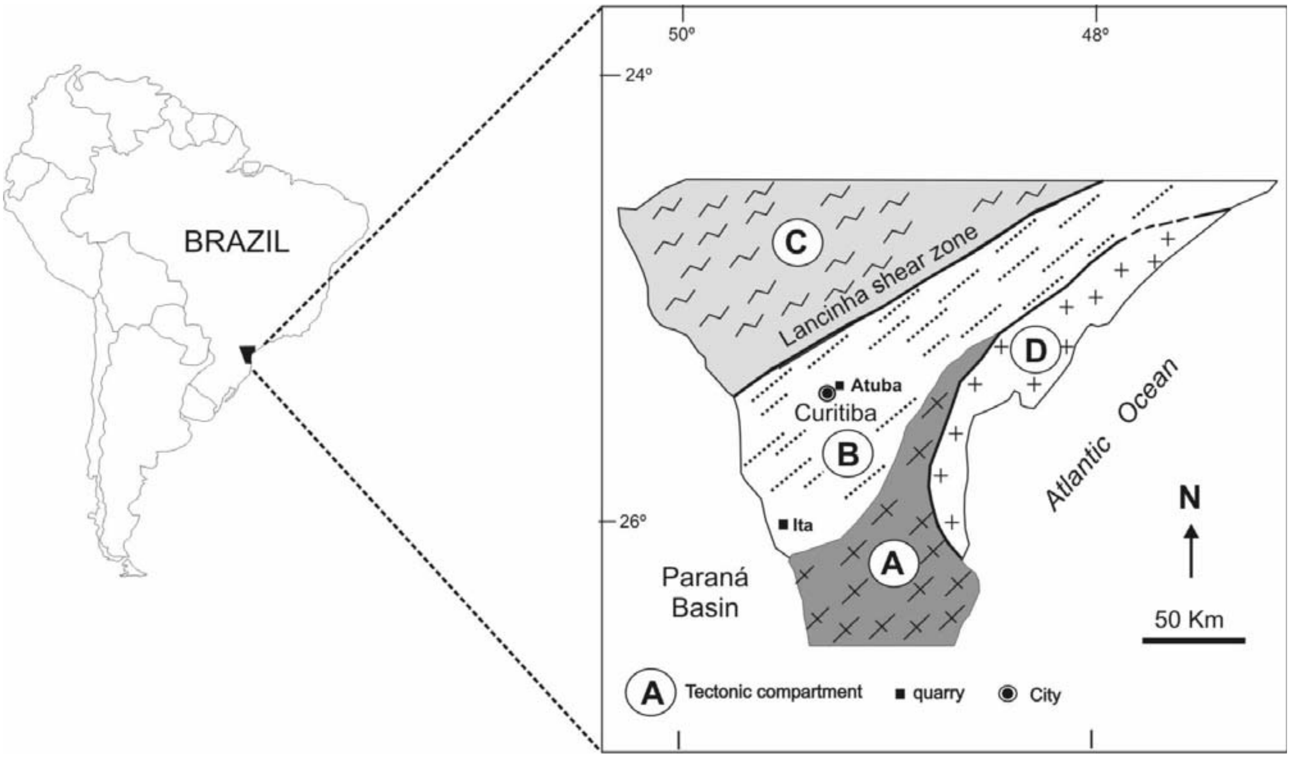

Figure 1. Simplified tectonic compartments of south - southeast Brazil and quarry locations (Basei et al., 2000; Siga Jr. et al., 2003): **A.** Luis Alves Microplate; **B.** Atuba Complex; **C.** Apiaí Domain; **D.** Paranaguá Batholith.

ANALYTICAL METHODS

Sample preparation

After conventional crushing, grinding and sieving, selected size fractions of heavy minerals were concentrated by tabling and heavy liquid separation at the CPGeo. Zircon grains were hand-picked from these fractions. The grains were mounted in epoxy resin at Beijing, and the mounts were ground down to expose the internal structures of the zircon grains after removal of about one-half their volume. After polishing the mounts were gold-coated. Cathodoluminescence (CL) images were transmitted to São Paulo to orient the selection of the points to be analyzed.

The selected samples for analysis of Hf isotope ratios were mounted in epoxy resin discs, and ground down to expose internal textures at the TITech Laboratories, Japan. For obtaining the CL images the discs were coated with a thin graphite film that was removed by abrasion before LA-ICP-MS measurements that do not need conductive surface.

U and Pb isotopic compositions by Beijing SHRIMP II

The ROSS is operated using two microcomputers installed at the Geochronology Research Centre (CPGeo) of the University of São Paulo, Brazil, connected to the computer-controlled operating system of the SHRIMP II equipment installed at Beijing, China. One of the two CPGeo computers is used to control the instrument and to obtain images while the other acquires the data and communicates partial and final results. The software used in Beijing was developed by local engineers. Problem-solving during analysis uses webcams and microphones, or exchange of instantaneous e-mails.

Normalization standards for U-Pb analysis were Temora (TEM) and Sri Lanka (SL13). After the installation of zircon sample disc inside the ion source chamber of SHRIMP II, ROSS can be positioned at a chosen analytical point in a chosen grain directly from CPGeo, São Paulo, Brazil in real time. Besides displacement in the X, Y directions, focus adjustment (Z direction) is also possible. Amongst other commands, the coordinates of each point are recorded, the primary beam is connected or disconnected, and an analysis can be aborted. The analytic results are sent through internet, by on line system and in real time, from Beijing to São Paulo. Analysis conditions were: spot size = 30 μm, 5 scans, dead time = 25 ηs, auto center ON. About 11 min 36 s is required for each analysis.

Determination of Hf isotopic ratios by LA-ICP-MS

The laser system MICROLAS 200 CQ (Göttingen, Germany) uses a Lambda Physik Compex 102 source. To produce the 193 nm emission the laser uses ArF gas. The final irradiation energy is < 10 mJ cm^{-2}, while the range of spot diameter is between 4 and 100 μm (30 μm to this experiment). He gas is used to transport the abraded particles into the plasma source.

The NU-PLASMA ICP-MS equipment was operated at 27.12 MHz with a power of 1.15 KW. Gas flows were: cooling 13 L min^{-1}; auxiliary 0.7 L min^{-1}; carrier Ar 0.8 L min^{-1}; carrier N_2 4.0 m L min^{-1}. The ion energy voltage was 3990 V, and the extraction voltage was 2200V. The 7 Faraday collectors (Axial = Ax, Low = L and High = H) were configured as follows: L_3 (^{171}Yb), L_2 (^{173}Yb), A_x (^{175}Lu), H_1 [^{176}(Hf+Yb+Lu)], H_2 (^{177}Hf), H_3 (^{178}Hf), e H_4 (^{179}Hf). Standards used were NIST 610SRM and international zircon standard 91500. Other informations on the procedures used can be found in Iizuka e Hirata (2005).

Determination of U-Pb isotopic compostions by TIMS

The analytical procedure to U-Pb geochronological method using Thermal Ionization Mass Spectrometer (TIMS) was based by Sato et al. (2008).

THE ATUBA COMPLEX

Previous geochronological and isotopic geochemical studies of crustal evolution of the Atuba Complex

The Atuba Complex (Figure 1) is mainly composed of migmatitic banded gneiss, banded granitic gneiss, leucogranite, and minor amphibolite, mafic to ultramafic gneiss or schist, and diorite. It occurs between the Luiz Alves microplate and Apiaí Domain (Figure1). The regional structure trends NE and follows the usually steep dip of the banding. Deformation was predominantly ductile shearing which led to rotation of feldspar megacrystals and the development of strong mineral stretching lineation.

Sm-Nd model T_{DM} ages for whole rocks indicate that mostly juvenile material were added to the crust during the Archean, between 3.1 and 2.7 Ga. Analyses using SHRIMP I and II, single crystal Pb evaporation, and isotope dilution TIMS determinations of zircon from mesosomes of the Atuba Complex at Ita quarry confirm the formation of crustal rocks during same time interval (Sato et al., 2003). The archean ages are more frequently found in cores and their surrounding igneous zones, and in internal overgrowths. A few of the grains have paleoproterozoic overgrowths.

During the Paleoproterozoic (between 2.2 and 1.9 Ga) an intense migmatization (U-Pb and Rb-Sr; Siga Jr., 1995) with some juvenile crustal addition, is registered by Sm-Nd model, T_{DM} ages (Siga Jr., 1995; Sato et al., 2003). SHRIMP I analyses of zircon grains from a granodioritic to tonalitic mesosome from the Atuba quarry (northern of Ita quarry and close Curitiba city, Figure 1) shows that the paleoproterozoic event was very important, since many zircon core ages fall in this time interval. On the other hand the archean component at this is limited to the core of one single analyzed grain. It is important to note that no sign of granulite facies rocks was found in rocks from this quarry, though field and petrographic evidence for the action of partial melting is more convincing (Silva, 2005).

The Neoproterozoic is registered by SHRIMP I analyses in only 1 zircon rim from mesosomes (Sato et al., 2003), as well as by Rb-Sr whole rock and mineral isochrons, and also by K-Ar ages in hornblende and biotite (Siga Jr., 1995).

Geology, petrology and geochemistry of the Ita quarry

The samples used in this study were collected from the active Ita quarry. The outcrop show white, sometimes pinkish, mobilizates of granitic to granodioritic composition that occur as centimeter to meter-thick bands concordant with the regional gneissic banding. Mesosomes are mostly tonalitic or dioritic while leucosomes are granodioritic or tonalitic (Siga Jr., 1995; Siga Jr. et al., 2003). A biotite-rich gabbroic melanosome is oversaturated and ultrapotassic. Descriptions presented by Silva (2005) showed that alkali feldspar contents are low or very low. One granodioritic leucosome is TiO_2, P_2O_5 and Zr-poor, it has a feldspar-like REE pattern with low ΣREE, a prominent positive Eu anomaly, and strong LREE-enrichment relative to HREE. Taking into account the small scale of banding in the gneiss from which this leucosome was extracted, it is possible that it is a product of metamorphic differentiation. Another wider granodioritic leucosome has a REE pattern with higher ΣREE, less LREE enrichment relative to HREE, and an insignificant Eu anomaly. This type may be a product of partial melting. Petrographic evidence for the operation of this process on a wide scale, however, is unconvincing. A few rocks collected from earlier active fronts of the Ita quarry contain rare garnet, augite and hypersthene. Both the latter minerals are present as cores to amphibole grains or in amphibole-biotite agglomerates. While most of the rocks from the more recent sample collections are upper amphibolite facies, the pyroxene-bearing rocks preserve evidence of an earlier granulite facies assemblage.

In a new sample collection made for the present study, a reddish leucosome with monzogranitic to syenogranitic composition, different from examples studied by Silva (2005), was found. This probably has low ΣREE contents judging by the low concentrations of Nd and Sm encountered. The other analyzed leucosome is macroscopically similar to the wider granodioritic leucosome analyzed by Silva (2005). Also conspicuous is the consistent presence of mafic-ultramafic rocks and magnesian schist that occur intercalated among the migmatitic gneisses. The dioritic rocks show granoblastic texture with mineralogy composed of amphibole, biotite, plagioclase and quartz and until present moment without U-Pb dating.

STUDIED SAMPLES AND GEOCHRONOLOGICAL RESULTS

Results of U-Pb dating of zircon obtained from Remotely Operated SHRIMP II and by TIMS

Emphasis was given to three critical samples from the Ita quarry in order to confirm the previously determined age pattern. Zircon from white and reddish leucosomes and from a diorite samples were analyzed through ROSS. Cathode-luminescence images showing the positions of the analyzed points are presented in Figures 2 and 4, while the analytical results are given in Tables 1 and 2.

When the results for the 7 zircon grains from the white leucosome (OM1233C) are plotted in the concordia diagram (Figure 3), two age groups are defined: one with an archean age of 3025 ± 25 Ma from the inner parts of the grains, which corresponds to about 60% of their volume. The other age is paleoproterozoic (1998 ± 28 Ma), and is found in the outer parts, representing about 40% of their volume. Mostly the neighbour mesosome rock indicated archean age (U-Pb zircon ages, Sato et al, 2003) which correspond to about 95% (core) of their volume and paleoproterozoic is only 5% (rim). Very thin overgrowths are observed on practically all the grains, but only one grain from the sixty grains in the mount was sufficiently wide in relation to the spot diameter to be useful for analysis. Even so the age of 1050 Ma (Figure 3) obtained is very discordant and may not have geological significance since a small quantity of older material was probably present in the analyzed grain. It does suggest that the old zircon grains were slightly affected by late mesoproterozoic or neoproterozoic phenomena.

The reddish leucosome sample (Ita 18) presents a different age pattern. From 8 zircons analyzed (10 spots, Figure 4) only one core in one grain yielded an age of 3.0 Ga (Figure 5). Most of the nuclei that represent about

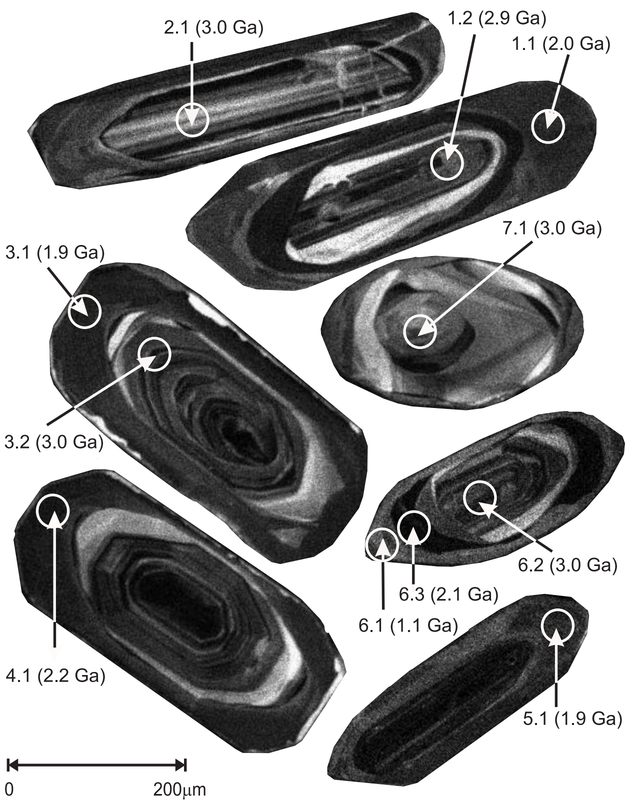

Figure 2. Zircon CL images from white leucosome sample from Ita quarry, Atuba Complex. *Legend*: 1.1 (2.0 Ga) represent respectively zircon spot number and age.

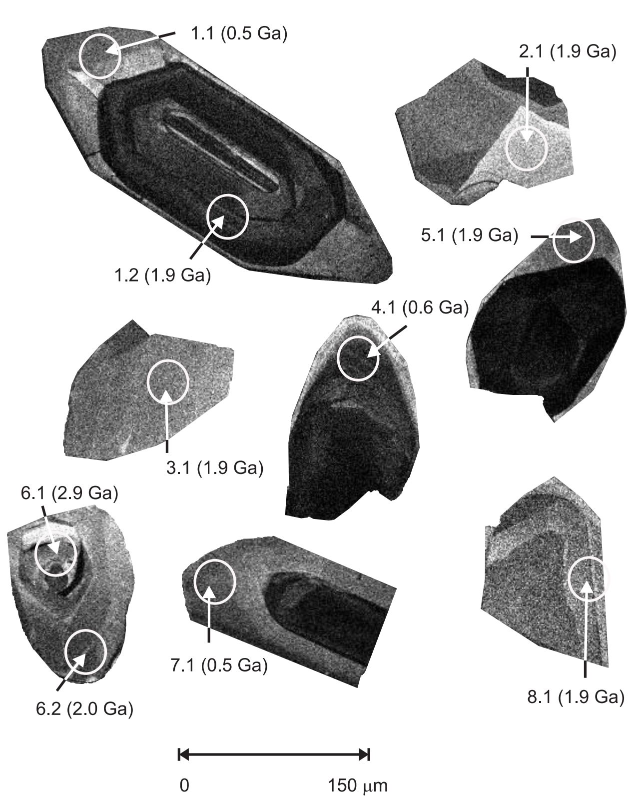

Figure 4. Zircon CL images from reddish leucosome (sample Ita 18) from Ita quarry, Atuba Complex (Legend as Figure 2).

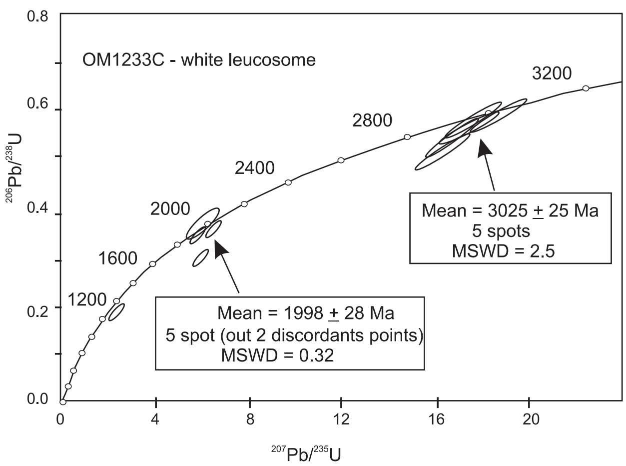

Figure 3. Concordia diagam for the zircon grains from the white leucosome (sample OM 1233C). Zircon cores are archean, and rims are paleoproterozoic, but one rim has a discordant mesoproterozoic age. The U-Pb isotopic data were obtained by ROSS (Table 1).

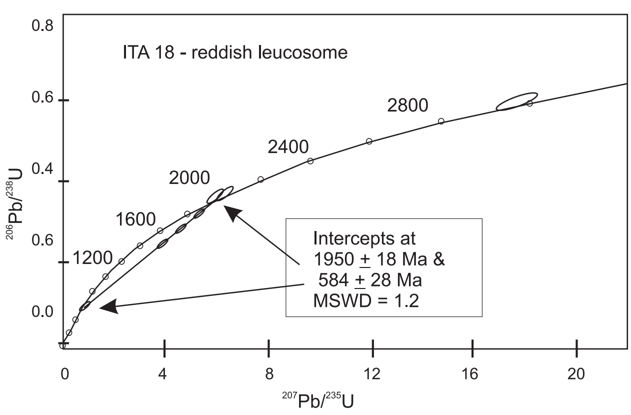

Figure 5. Concordia diagram for the reddish leucosome (sample ITA-18). At the upper intercept there are three concordant points around 1950 ± 18 Ma. U-Pb isotopic data were obtained by ROSS (Table 1).

Table 1. U-Pb zircon data from white and reddish leucosome samples of Ita quarry, Atuba Complex obtained by ROSS – SHRIMP, Beijing. *Legend*: **comm** = common, **corr** = correlation, **abs** = absolute, **disc** = discordance. *Notes*: Errors are 1-sigma and in Standard calibration was 0.32% (not included in above errors but required when comparing data from different mounts; Common Pb corrected using measured ^{204}Pb).

Spot	U ppm	Th ppm	^{232}Th/^{238}U ratio	^{206}Pb$_{comm}$ %	^{207}Pb/^{235}U ratio	error %	^{206}Pb/^{238}U ratio	error %	^{207}Pb/^{206}Pb ratio	error %	error corr	^{207}Pb/^{206}Pb age (Ma)	error abs	disc %
sample OM1233C - white leucosome														
1.1	145	55	0.390	0.08	5.790	2.6	0.3430	2.4	0.1225	1.2	0.89	1992	21	5
1.2	147	71	0.499	0.00	16.528	2.5	0.5362	2.4	0.2235	0.7	0.96	3006	11	8
2.1	103	48	0.481	0.04	18.665	2.5	0.5898	2.4	0.2295	0.8	0.95	3049	13	2
3.1	173	91	0.544	0.04	5.768	2.6	0.3405	2.4	0.1229	1.2	0.90	1998	20	5
3.2	194	79	0.420	0.02	15.942	2.4	0.5068	2.3	0.2281	0.7	0.95	3039	12	13
4.1	94	23	0.253	0.00	5.913	3.1	0.2980	2.7	0.1439	1.5	0.87	2275	26	26
5.1	162	60	0.379	0.22	6.028	4.8	0.3662	3.4	0.1194	3.4	0.71	1947	61	-3
6.1	133	33	0.258	0.62	2.295	4.4	0.1822	2.5	0.0914	3.7	0.56	1454	70	26
6.2	171	83	0.500	0.00	16.984	2.5	0.5458	2.3	0.2257	0.8	0.95	3022	13	7
6.3	647	28	0.046	0.05	6.426	2.3	0.3521	2.3	0.1324	0.6	0.97	2130	11	9
7.1	50	25	0.514	0.00	17.651	2.8	0.5773	2.6	0.2218	1.2	0.90	2993	20	2
sample ITA 18A - reddish leucosome														
1.1	173	64.9	0.386	0.37	0.809	5.05	0.1025	1.8	0.0573	4.7	0.35	502	104	-25
1.1	938	86.9	0.096	0.03	5.319	1.43	0.3273	1.3	0.1179	0.5	0.93	1924	10	5.1
2.1	75.9	35.1	0.478	0.16	5.845	2.66	0.3646	1.9	0.1163	1.8	0.73	1900	33	-6
3.1	163	77.4	0.491	0.09	5.959	2.01	0.3633	1.6	0.1189	1.2	0.80	1940	21	-3
4.1	467	27.7	0.061	0.16	0.791	2.69	0.0956	1.5	0.0600	2.3	0.55	604	49	2.5
5.1	518	37.7	0.075	0.03	4.607	1.58	0.2899	1.4	0.1152	0.8	0.88	1884	14	13
6.1	121	32.6	0.278	0.03	17.678	2.02	0.5944	1.8	0.2157	0.9	0.89	2949	15	-2
6.2	142	63.5	0.462	0.05	6.236	2.11	0.3741	1.7	0.1209	1.3	0.79	1969	23	-4
7.1	147	57.4	0.403	0.39	0.759	7.12	0.0957	1.8	0.0575	6.9	0.25	511	151	-15
8.1	140	40.7	0.301	0.00	3.920	2.27	0.2507	1.7	0.1134	1.5	0.74	1855	28	22

80% of the volume of the grains have paleoproterozoic concordia intercept ages at 1950 ± 18Ma. The results for two analyzed points fall on the upper intercept, three analyzed points lie on the lower intercept, while two results are slight discordant and other two are strongly discordant with lower intercept at 584 ± 29 Ma (Figure 5). This leucosome records a history (Sato et al., 2003) similar to that found for mesosomes from the Atuba quarry (northern Ita quarry).

The mesosome, white leucosome and reddish leucosome occurs at centimeter band but predominance of old U-Pb ages in these mesosome and leucosome rocks are surprising since K-Ar ages are all neoproterozoic.

ROSS analysis of zircon grains from the diorite (OM1233B) proved difficult due to the small grain size (30 - 40 μm), their very low radiogenic Pb contents (1 - 8 ppm), and to metamictization of one of the grains. The Concordia ages obtained have large errors, and we attempted analyses of multigrain fractions by TIMS. The Tera-Wasserburg diagram yields an imprecise age of 596 ± 63 Ma (Figure 6, Table 2), but this confirms the previously suspected neoproterozoic age of this rock.

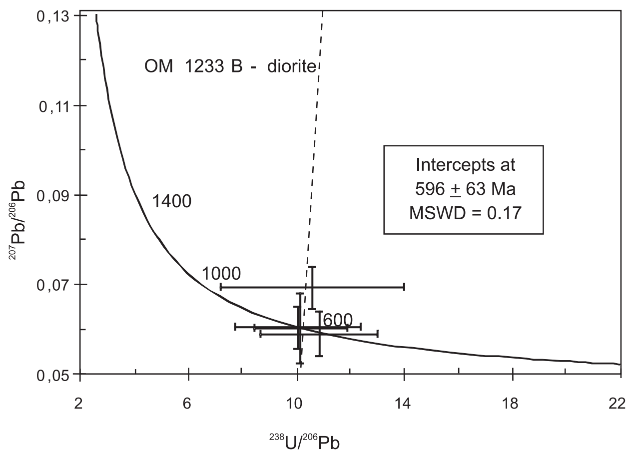

Figure 6. Tera-Wasserburg diagram for zircon from the diorite (OM 1233B). U-Pb isotopic data were obtained in zircon multi grains and measured by TIMS. Figure show three points on Concordia line (596 ± 63 Ma). The large error is due the very low Pb concentrations (Table 2).

Hf isotopic compositions of the zircon grains by LA-ICP-MS

When possible, the Hf isotopic compositions were determined either on the same spot analyzed for U-Pb dating, or in similar geometrical position (cores, internal parts of borders) within the grains. The results of the analyses are presented in Tables 3 and 4, and are plotted on the Hf evolution diagram (Figure 7). The evolution of CHUR and DM mantle types are also shown (Vervoort and Blichert-Toft, 1999). Since the concentrations of the radioactive element Lu are extremely low in relation to those of the daughter element Hf the present-day ratios are practically equal to the initial ratios.

The $^{176}Hf/^{177}Hf$ ratios found at 4 cores of ca. 3 Ga zircon grains separated from the white leucosome (OM1233C, ε_{Hf} between 1.5 and 8.8, Table 3) lie above the CHUR reference line, showing that the mantle source the was main contribution to the magmas formed at that time. The paleoproterozoic at 2 rims of the grains from the white leucosome have Hf isotopic ratios which fall below the CHUR reference (ε_{Hf} between -9 and -10, Table 3), and this suggests that crustal rocks contribute to the genesis of the magmas with which the zircon equilibrated at that time.

The much younger diorite (OM1233B) has zircon grains whose Hf isotopic compositions are equal, or close to below that of CHUR at the model age of 590 Ma (ε_{Hf} between +0.1 and -5, Table 4). A mainly juvenile contribution at 590 Ma with a small older crustal contribution is one of the possible interpretations of these data.

Unfortunately Hf isotopic ratios not was analyzed to reddish leucosome because it not carried out to TITech laboratory, but we suggest negative ε_{Hf} values at paleoproterozoic and neoproterozoic rims, and positive ε_{Hf} values to archean core.

Table 2. U-Pb zircon data from diorite sample (OM1233B) of Ita quarry, Atuba Complex.

SPU	207/235 ratio	error %	206/238 ratio	error %	coef.	238/206 ratio	error %	207/206 ratio	error %	206/204 ratio	Pb ppm	U ppm	206/238 age (Ma)	207/235 age (Ma)	207/206 age (Ma)
3425a	0.8187	17	0.0986	10.7	0.66	10.139	17	0.06020	13.0	32.3	2.45	6.2	606	607	611
3424a	0.8298	25.0	0.0996	23.0	0.94	10.042	23.0	0.06043	8.00	33.37	1.01	3.7	612	614	619
3458a	0.7512	20.0	0.0924	18.0	0.91	10.826	20.0	0.05903	8.30	31.5	7.5	22.0	-	-	568
3459a	0.7646	34.0	0.0931	32.0	0.90	10.738	34.0	0.05955	8.10	31.1	3.2	12.7	574	576	587

Table 3. Hf and Lu isotopic data of white leucosome (sample OM1233C) obtained by LA-ICP-MS (TITech - Tokyo - Japan).

Spot	U-Pb age (Ma)	$^{176}Hf/^{177}Hf$	2se	$^{176}Lu/^{177}Hf$	2se	$^{176}Hf/^{177}Hf$ initial	2se	εHf(T)	Obs.
1	3000	0.281149	0.000024	0.000501	0,000015	0.281120	0.000024	8.7	core
2	3000	0.281157	0.000023	0.000588	0,000003	0.281123	0.000023	8.8	core
3	3000	0.281016	0.000044	0.001046	0,000043	0.280957	0.000044	2.9	core
4	2200	0.281142	0.000044	0.000376	0,000008	0.281127	0.000044	-10.1	rim
5	3000	0.280996	0.000046	0.001375	0,000021	0.280916	0.000046	1.5	core
6	2200	0.281181	0.000029	0.000400	0,000005	0.281154	0.000028	-9.1	rim

Table 4. Hf and Lu isotopic data of diorite (sample OM1233B) obtained by LA-ICP-MS (TITech – Tokyo - Japan). Lu e Hf data: $^{176}Hf/^{177}Hf$ (DM) = 0.28323; $^{176}Hf/^{177}Hf$ (CHUR) = 0.282772 and $^{176}Hf/^{177}Hf$ (CHUR) = 0.0332. Ref.: Blichert-Toft and Albarede (1997), Vervoort and Blichert-Toft (1999).

Spot	U-Pb age (Ma)	$^{176}Hf/^{177}Hf$	2se	$^{176}Lu/^{177}Hf$	2se	$^{176}Hf/^{177}Hf$ initial	2se	εHf(T)
1	590	0.282345	0.000048	0.000096	0.000003	0.282344	0.000048	-2.1
2	590	0.282404	0.000063	0.000120	0.000002	0.282403	0.000063	-0.1
3	590	0.282357	0.000042	0.000171	0.000011	0.282356	0.000042	-1.7
4	590	0.282407	0.000043	0.000092	0.000005	0.282406	0.000043	+0.1
5	590	0.282260	0.000052	0.000090	0.000008	0.282259	0.000052	-5.2
6	590	0.282343	0.000046	0.000141	0.000009	0.282342	0.000046	-2.2

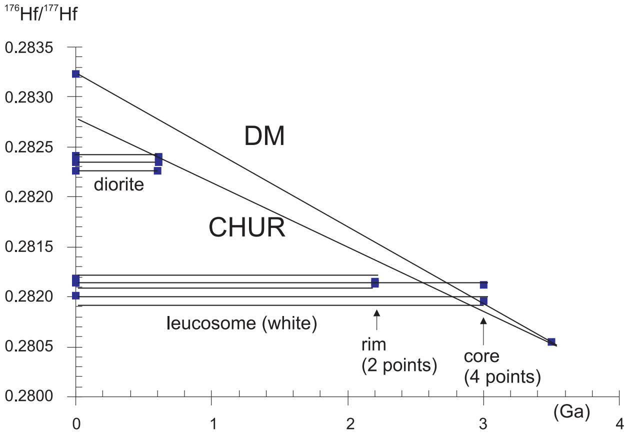

Figure 7. Hf isotopic evolution diagram. Figure show CHUR, DM (Vervoort and Blichert-Toft, 1999) and zircon sample evolutions curves. The archean zircon cores have positive ε_{Hf} suggesting a mantle source, but in the paleoproterozoic zircon rims the ε_{Hf} are negative, therefore suggesting a crustal source (Table 3). The neoproterozoic zircon grains from the diorite present ε_{Hf} very close to zero suggesting mantle source mixed with small crustal material contribution (Table 4). Hf isotopic data were obtained by LA-ICP-MS from TITech, Tokyo, Japan.

DISCUSSION AND CONCLUSIONS

Since no SHRIMP facility was available in Brazil at the time of writing this contribution, the ROSS facility offered an option for obtaining point age analyses of complex zircon crystals. The results obtained in this study confirm the previously proposed history of the rocks of the Ita quarry. Zircon grains from a granodioritic leucosome, which may have been slightly modified during the Gondwana formation (Neoproterozoic), register the presence of an early ca. 3.0 Ga component, and a younger ca. 2.1 Ga overgrowth. Hf isotope ratios show that the early component was mantle-derived, while the second includes a crustal contribution. Both age events are also registered in the mesosomes (SHRIMP U-Pb ages, Sato et al., 2003), though no complementary Hf data on these rocks are available to identify sources. A monzo to syenogranitic leucosome presents a contrasting age pattern, with very limited evidence for the presence of the older mantle-derived component, and predominance of ca. 2.0 Ga material with a crustal component which was re-equilibrated during the Neoproterozoic. Dioritic rocks were intruded at this time.

Previous work has shown that the Atuba quarry has many similar field relationships, and petrographical and geochemical features with Ita quarry, but some important differences (Silva, 2005) suggest a different evolution. No evidence for a previous granulite-facies metamorphism has been encountered at Atuba quarry, and geochronological evidence for an archean component in the mesosomes is limited.

In view of the complex evolution revealed by the few detailed SHRIMP studies undertaken up to now, it is clear that further investigations are necessary, especially of the quarries at the NW border of the Atuba Complex in which granulites are more prominent.

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