



Article On the Morphology and Geochemistry of Hydrothermal Cryptoand Microcrystalline Zircon Aggregates in a Peralkaline Granite

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Abstract: Singular crypto- and microcrystalline hydrothermal zircon aggregates occur in peralkaline granites from the Corupá Pluton of "A-type" granites and syenites in Graciosa Province, Southern Brazil, and are herein characterized for their morphological, textural and geochemical (major, minor and trace elements, and Lu-Hf isotopes) properties. The aggregates were found to present a variety of habits, such as dendritic, oolitic, botryoidal and spherulitic, and they are associated with typical hydrothermal minerals (alkali-feldspars, quartz, fluorite, epidote-group minerals, phyllosilicates and Fe oxides) in micro-fractures and small miarolitic cavities in the host rock. They precipitated directly from a hydrothermal fluid and, compared to magmatic zircon crystals from the host, were found to contain relatively high abundances of the "non-formula" elements (e.g., Fe, Al, and Ca) and HFSEs (High-Field-Strength Elements), particularly the L- and MREEs (Light and Medium Rare Earth Elements), features most typical of hydrothermal zircon, as well as high Th/U ratios, whereas the Lu-Hf isotopic signatures were found to be similar. The formation of the zircon aggregates and the associated epidote-groups minerals was probably due to the interaction between an orthomagmatic, Fbearing, aqueous fluid transporting the HFSEs with the host-rock and/or with an external meteoritic fluid from the country rocks. The preservation of an amorphous-like Zr-silicate compound and crypto-to-microcrystalline zircon varieties is arguably related to the inefficient fluid flux and/or elemental diffusion in a low-temperature oxidizing environment.

Keywords: hydrothermal zircon; crypto- and microcrystalline aggregates; zircon geochemistry and Lu-Hf isotopes; peralkaline granite

1. Introduction

Zircon, ideally ZrSiO₄, is an accessory mineral highly stable under most crustal environments and hence widely distributed in rocks and sediments of the Earth's crust. The elemental and isotopic compositions of zircon provide critical insights into the geochronology and petrology of igneous and metamorphic rocks, provenance studies of sedimentary rocks and sediments, and (therefore) the Earth's geodynamic evolution in general [1–7]. In magmatic systems, zircon saturation in melts, Ti-in-zircon thermometry, and oxibarometry based on the Ce and Eu oxidation states and/or anomalies allow for the determination of intensive crystallization parameters [8–13], while its elemental—particularly the HFSEs (High-Field-Strength Elements, including the REEs, Rare Earth Elements)—and O and Hf isotopic compositions provide invaluable information on magma sources and evolution [14–17]. Zircon is also the main source of zirconium oxide (ZrO_2), an important refractory material, and Zr alloys have multiple applications in modern technology; furthermore, zircon also provides beautiful gemstones [18]. Hence, this mineral has become one of the most studied accessory minerals from the Earth's crust.

Relatively low-temperature hydrothermal zircon occurs in a variety of geological environments. It may precipitate directly from a fluid phase as isolated crystals or crystalline aggregates (1), form overgrowths on primary zircon crystals of magmatic or metamorphic origin (2), substitute other mineral phases (3), or be the product of dissolution-reprecipitation or diffusion–reaction processes (4) resulting from reactions involving previous

zircon crystals and late (generally aqueous and acid) fluid phases [1,19–22]. Contrasting primary with hydrothermal zircon in magmatic and metamorphic rocks is crucial for accurate U-Pb dating and the determination and modeling of crystallization conditions and primary geochemical signatures [14,19,23–25]. On the other hand, hydrothermal zircon allows for U-Pb dating and provides information on the evolution of hydrothermal systems and related ore-forming processes [12,26,27].

Zircon U-Pb dating is one of the most powerful available geochronological methods, so a significant number of studies on hydrothermal zircon have dealt with the effects of hydrothermal processes on the U-Pb systematics of igneous and metamorphic rocks and their implications. Some features, such as the "spongy" texture caused by the abundance of minute "inclusions" and micro- or nano-cavities imprinting a general porous aspect to the crystals [1,19,23], the lobate texture, crystal overgrowths truncating original primary micro-structures, and the relative high contents of so-called "non-formula" elements (such as Fe, Al and Ca) and the LREEs are most typically associated with hydrothermal varieties [20,28]. However, distinguishing primary from hydrothermal zircon is not straightforward in several cases, and the most reliable criterion is the associated mineral assemblage [19,23,29].

In this study, the relatively rare occurrence of crypto- and microcrystalline zircon aggregates in close association with hydrothermal mineral phases in a peralkaline granite from Graciosa Province, South-Southeastern Brazil [30] is described. Morphological, textural, geochemical (major-, minor-, and trace element) and Lu-Hf isotope data are presented. Mineral paragenesis, unusual morphology, textures and microstructures suggest that they precipitated directly from a fluid phase at relatively low temperatures, which—along with inefficient elemental diffusion—prevented the development of larger euhedral crystals.

2. Materials and Methods

2.1. Sample Characterization

The studied rock came from the Corupá Pluton (Figure 1), a Neoproterozoic (ca. 580 Ma, [25,31]) occurrence of the alkaline petrographic association of "A-type" granites and syenites in Graciosa Province, South-Southeastern Brazil [30]. The pluton has a crescent outline and intrudes Archaean granulitic rocks from the Luis Alves microplate. It is a shallow intrusion largely comprising dominant metaluminous, leucocratic, SiO₂-oversaturated alkali-feldspar syenites and alkali-feldspar quartz syenites, with subordinate peralkaline alkali-feldspar granites. The granites occur as minor bodies in the central areas of the pluton and represent late products, probably originating from magmatic fractionation and filter-pressing processes acting on previous trachytic-like melts [32,33].

Hydrothermal zircon aggregates were found in a unique granite sample from the northern area of the pluton (sample CO-2A). The rock is homogenous and slightly pinkish, with a massive structure and a medium-grained hypidiomorphic texture. It is leucocratic and composed of mesoperthitic alkali-feldspar, quartz and some interstitial sodic-calcic and sodic amphiboles. Ilmenite, chevkinite, zircon, and minor titanite, apatite, and sphalerite are the main primary accessories, while albite, K-feldspar, quartz, Fe-rich biotite and chlorite, fluorite, epidote-group minerals (allanite-(Ce), ferriallanite-(Ce), epidote and ferriepidote), zircon, and minute magnetite, hematite, and galena are the main hydrothermal minerals [34]. From the geochemical standpoint, the rock comprises SiO₂ = 74.63 wt.%, Na₂O + K₂O = 9.08 wt.%, FeO^T / (FeO^T + MgO) (wt.%) = 0.98 and is moderately peralkaline, with a peralkaline or agpaitic index ((Na₂O + K₂O)/Al₂O₃ molar) of 1.06 [33].



Figure 1. Simplified geological context (**a**) and map of the Corupá Pluton (**b**), Southern Brazil [25,32–34]. (**a**): I: Volcano-sedimentary basins; II: "A-type" granitic and syenitic plutons and complexes from the Graciosa Province; III: "A-type" granitic plutons from the Itu Province; IV. A: Ribeira fold belt; b: Curitiba microplate; c: Luiz Alves microplate; d: Coastal granitoid belt. V: Piên-Mandirutuba Granite batholith; VI: Undifferentiated late- to post-collisional granites; VII: Três Córregos batholith. LCSZ: Lancinha Shear Zone; RPSRSZ: Rio Palmital-Serrinha Shear Zone. (**b**): 1: Sedimentary and volcanic rocks from Guaratubinha Basin (above) and Corupá Graben (below); 2: Alkali-feldspar granites, 3: Alkali-feldspar syenites, 4: Gabbro-diorites and related hybrid rocks, 5: Basic volcanics, 6: Archaean granulitic rocks from the Luis Alves microplate. The location of the studied CO-2A sample is indicated.

2.2. Analytical Techniques

Qualitative and quantitative chemical and isotopic data and imagery for primary and hydrothermal zircon crystals and crypto- and microcrystalline aggregates were obtained in polished thin (30 and 80 μ m) sections at the GeoAnalitica and Geochronological Research Center facilities of the University of São Paulo. After conventional optical analysis under a petrographic microscope, cathodoluminescence (CL), electron probe micro-analyzer (EPMA) and laser ablation inductively coupled mass spectrometry (quadrupole, LA-ICPMS and multi-channel LA-MC-ICPMS) analyses were carried out as follows.

Conventional Cl images of hydrothermal aggregates were obtained with a Nuclide ELM-3R luminoscope (Nuclide Corporation, Acton, MA, USA) operating with a 15 kV accelerating voltage and a 0.5μ A beam current.

The EPMA work was carried out with the JXA-8600S and JXA-FE-8530 instruments (JEOL Ltd., Tokio, Japan) and included backscattered electron (BSE, compositional mode), imaging, qualitative and quantitative spot analysis by energy- and wavelength-dispersive spectrometry (EDS and WDS, respectively), and WDS x-ray dot mapping. Quantitative WDS spot analysis was conducted under analytical conditions of 20 kV, 50 nA, and 5 μ m for the column accelerating voltage, beam current, and diameter, respectively.

elements, spectral lines and standards, from the Smithsonian and the laboratory internal collections, were as follows: Si (K α , zircon), Th (M α , ThSiO₄*), U (M β , UO₂*), Zr (L α , zircon), Hf (L α , HfSiO₄*), Ti (K α , rutile), Al (K α , Yal-garnet*), Y (L α , YPO₄*), La (L α , LaPO₄*), Ce (L α , CePO₄*), Nd(L β , NdPO₄*), Sm (L β , SmPO₄*), Gd (L β , GdPO₄*), Dy (L β , DyPO₄*), Er (L α , ErPO₄*), Yb (L α , YbPO₄*), Fe (K α , hematite), Mn (K α , Mn-olivine), Mg (K α , diopside), Ca (K α , diopside), Na (K α , jadeite), K (K α , microcline), P (K α , CePO₄*) and Nb (L α , met Nb*), where (*) stands for synthetic phases. The total counting times, equally distributed between peak and background, varied from 10 to 50s; matrix effects were corrected with the PROZA software [35]. Spectral interferences over U, Er and Yb lines were better than 2% for Si and Zr, better than 10% for minor elements, and higher than 10% for the trace elements.

Trace-element LA-ICPMS spot and raster analysis was carried on with the Elan 6100DRC equipment (Perkin-Elmer Inc., Waltham, MA, USA) provided with an UP-213 laser ablation system (New Wave Research Inc., Fremont, CA, USA) using a 213 nm Nddoped YAG laser. The analytical routine used in the laboratory was described in detail by Andrade [37]. The raster sampling followed aggregate zoning patterns as observed in BSE images. The energy density and the beam diameter over the samples surface were about 8.5 J/cm² and 40 (spot) or 30 (raster) μ m, respectively, with a 4 Hz repetition rate. Besides ²⁹Si and ⁹¹Zr, the isotopes ³¹P, ⁴⁹Ti, ⁵⁵Mn, ⁸⁸Sr, ⁸⁹Y, ⁹¹Zr, ⁹³Nb, ⁹⁵Mo, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁵Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷³Yb, ¹⁷⁵Lu, ¹⁷⁹Hf, ¹⁸¹Ta, ²⁰⁸Pb, ²³²Th, and ²³⁸U were measured using a signal integration and dwell time of 8.3 and 1.66 ms, respectively. The isotopic interferences of oxide and hydroxide compounds over the selected isotopes (e.g., ¹³⁵Ba¹⁵O⁺ on ¹⁵¹Eu) are relatively limited in dry plasmas without hydroxyl and oxygen [37]. The daily rate of generation of oxide was controlled holding ThO⁺ formation lower than 1%. The total acquisition time was set to 120 s, equally distributed between blank and ion signal measures. However, given the higher susceptibility of the hydrothermal aggregates to the laser beam and their dimensions, point and even raster analysis were interrupted earlier to prevent contamination, which resulted in somewhat larger analytical errors. The Glitter software [38] was used for data acquisition, treatment and conversions to elemental concentrations. The synthetic NIST glass SRM-612 and the SiO₂ contents previously measured by WDS were used as the external and internal standards, respectively. Analytical errors are quoted along with the presented results. Supplementary Table S1 provides analytical results for the 91500 and GJ-1 zircon references obtained in the laboratory with the applied analytical routine, which showed relatively good agreement with the recommended values (e.g., GeoRem Database [39] and [40,41]).

Lu-Hf LA-MC-ICPMS spot analysis was conducted with the Thermo-Finnigan Neptune Spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled with an Excimer ArF Laser (λ = 193 nm) system, according to the procedures described by Sato et al. [42], using a laser spot of 40 µm diameter and 50 s (1 cycle/s) for the ablation time under a frequency of 7 Hz and an energy fluency of 60 mJ (90% of the nominal laser energy: 7.70 J/cm²). ¹⁷¹Yb, ¹⁷³Yb, ¹⁷⁴Yb, ¹⁷⁵Lu, ¹⁷⁶(Hf + Yb + Lu), ¹⁷⁷Hf and ¹⁷⁹Hf masses were simultaneously quantified. ¹⁷⁶Lu/¹⁷⁷Hf ratios were calculated considering ¹⁷⁶Lu/¹⁷⁵Lu = 0.02669. The GJ-1 zircon standard gave ¹⁷⁶Hf/¹⁷⁷Hf = 0.282021 ± 0.000008 (2 σ , n = 10) during our analysis, which approached the results presented by Liu et al. [41]. Initial ¹⁷⁶Hf/¹⁷⁷Hf ratios were computed considering $\lambda_{(176Lu)} = 1.867 \times 10^{-11} \text{ yr}^{-1}$ [43].

3. Results

3.1. Textural and Micro-Structural Patterns

The zircon aggregates occur in close association with hydrothermal mineral phases, particularly albite, epidote-group minerals, phyllosilicates, fluorite and Fe oxides. They appear filing in rock micro-fractures, interstices, and small miarolitic cavities, and they have variable dimensions (from ca. 2 to 80 μ m; see Figures 2 and 3). Among the hydrothermal

HFSE mineral hosts, zircon is subordinated in relation to the epidote-group minerals, and they both occur in small volumes (<0.1%). The zircon aggregates are morphologically and micro-structurally diverse and present singular and variable habits, such as dendritic, rosette, oolitic, lenticular or semi-lenticular fibro-radiated, spherulitic, and botryoidal, with distinct zoning patterns. Some of these habits resemble those described for hydrothermal zircon in some peralkaline granites and related pegmatites, such as the Ambohimirahavavy (Madagascar), Strange Lake (Canada), and Khan Bogd (Mongolia) complexes [22,44,45]. Idiomorphic or typical "spongy"-textured crystals were not found.



Figure 2. BSE images of hydrothermal zircon aggregates in peralkaline granite from the Corupá Pluton. (a): Dendritic, rosette, oolitic, and other zircon (Zrn) aggregates included in and probably co-precipitated with hydrothermal albite (Ab); note the zoning patterns with gravish or darker core areas and whitish rims. (b): Botryoidal and oolitic hydrothermal zircon, accompanied by minor phyllosilicates (Ph) and fluorite (Flr), filling in fractures in primary quartz (Qz) and protruding a K-feldspar (Kfs) substrate, along with hydrothermal albite. (c): Zoned zircon aggregates with a variety of morphologies, associated with phyllosilicates, fluorite, and allanite-(Ce) (Aln-Ce), filling in a small miarolitic cavity; note the shell-shaped crypto-crystalline aggregate with a concentric zoning pattern in the center of the image. (d): Botryoidal zircon aggregates, with subrounded globules mainly composed of Zr and Si (gZrSi) packed together and enveloped by microcrystalline zircon overgrowths (mZrn); note the dark cores in some globules (gZrSi1) and dark spots in-between globules and overgrowths. (e): Botryoidal aggregate with better-developed microcrystalline aggregates over globular nuclei; note the concentric zoning pattern and Fe-oxide (Fe-ox) "inclusions" and other unidentified dark spots accompanying this pattern. (f): Spherulitic, crypto-to-microcrystalline, fibroradiated zircon aggregate with concentric zoning pattern, associated with allanite-(Ce) and brighter ferriallanite-(Ce) and epidote (Ep) fibro-radiated aggregate, filling in a miarolitic cavity. White bars measure 10 μ m (**a**–**c**) and 50 μ m (**d**–**f**). Mineral abbreviations as recommended by the IMA [46]. See text for discussion.



Figure 3. Images and compositional maps of hydrothermal zircon aggregates in peralkaline granite from the Corupá Pluton. Botryoidal zircon aggregate associated with fibro-radiated allanite-(Ce) and ferriallanite-(Ce) (Aln-Ce, dark brown) + epidote (Ep, green) aggregates between K-feldspar (Kfs) crystals. (**a**): Transmitted light image emphasizing the brown nuclei and the colorless better-crystallized zircon overgrowths; (**b**): Cathodoluminescence image displaying zonal and concentric arrangement of light blue, slightly violet, and red colors in zircon. Allanite-(Ce), ferriallanite-(Ce) and epidote are represented in black. (**c**): BSE image of spherulitic, crypto-to-microcrystalline fibro-radiated zircon aggregate with concentric zoning pattern and minute dark spots (Fe-oxide inclusions and/or micro-pores) accompanying the zoning and crystal fibers arrangements; note the idiomorphic pyramidal termination of the fibers. (**d**): BSE image of lenticular and semi-lenticular cryptocrystalline aggregates with concentric zoning pattern. (**e**,**f**): X-ray dot maps for Fe (**e**) and Zr (**f**) of the aggregates shown in (**d**); note the Fe-rich and Zr-poor irregular nuclei surrounded by a more regular and less Fe-rich, Zr-poor zone and then by a relatively Fe-poor and Zr-rich external zone. White bars measure 50 μm. See text for discussion.

The aggregates present variable crystallization degrees to the extent that could be inferred from optical and BSE images (Figures 2 and 3). Under the optical microscope, the aggregates with relatively smaller dimensions (Figure 2a–c) show variable dark-to-pale brownish colors and undetectable birefringence that suggest an amorphous-like behavior. The largest ones display a well-developed internal fibro-radiated cryptocrystalline arrangement with oscillatory extinction (Figure 3d). BSE images of the smaller aggregates reveal variable zoning patterns given by a relatively darker, grayish, (with lower backscattered coefficients and thus lower mean atomic numbers) internal zone surrounded by a brighter whitish zone, while those of the larger ones depict oscillatory patterns alternating relatively darker, grayish, and whitish µm-sized zones.

The larger botryoidal aggregates comprise brownish globules assembled together, sometimes suggesting coalescence features (Figure 2d,e), with undetectable birefringence; they typically present thin overgrows of tiny radiated colorless zircon microcrystals with pyramidal terminations and normal birefringence. Some globules present subrounded

cores that are opaque under transmitted light and much darker in BSE images. In other globules, the external colorless microcrystalline zone is dominant over the internal zone, and they show oscillatory concentric zoning (Figures 2e and 3a). These aggregate types present variable CL colors, from typical bluish to slightly violet in the internal zones and slightly violet to reddish at the most external colorless zones (Figure 3b).

The spherulitic aggregates are almost colorless, transparent, and constituted by fibroradiated micro-crystals or crystal fibers with well-developed pyramidal terminations and oscillatory extinction (Figures 2f and 3c). BSE images reveal a concentric oscillatory zoning pattern with intercalated, μ m-sized slightly grayish and whitish zones.

BSE images depict minute dark spots with quadrangular, rectangular or elongated shapes trapped in-between globules and their overgrowths (Figure 2d,e) or along crystal fibers in the case of the aggregates with fibro-radiated arrangements, distributed according to the radiated and zoning zircon patterns (Figures 2f and 3c).

Qualitative EDS spot analysis carried out simultaneously with BSE imaging indicate that the clearest zones in all aggregates contained Zr, Si and (eventually) some Hf, while the grayish zones additionally contain minor and variable quantities of Al, Ca, Y, REE, and (particularly) Fe. The darkest nuclei observed within some globules (Figure 2d) present (besides Si and Zr) significant quantities of Fe and (eventually) some quantities of Al, Ca and K. The irregular darker zones in the core areas of the fibro-radiated cryptocrystalline aggregates (Figure 3d) are relatively Fe-rich and Zr-poor, as exemplified by the X-ray dot maps presented in Figure 3e,f. Most of the minute dark spots could not be probed; some of them in the botryoidal and spherulitic aggregates with apparent idiomorphic outlines mainly contain Fe and may arguably be hematite or magnetite.

The primary zircon crystals (Figure 4), examined for comparison purposes, are idiomorphic, colorless and pristine, with 40–80 μ m along the **c** crystallographic axis and present both prismatic and pyramidal crystal forms. They occur as isolated crystals and as inclusions in mesoperthite, quartz or amphiboles. BSE images show oscillatory (Figure 4a) or, more typically, slightly patchy (Figure 4c) zoning patterns.



Figure 4. BSE images of magmatic zircon crystals in peralkaline granite from the Corupá Pluton. (a): Euhedral crystals showing oscillatory zoning patterns included in K-feldspar (Kfs); (b) euhedral crystal with slightly zoning and an apatite (Ap) inclusion between K-feldspar and arfvedsonite (Arf); (c) Euhedral crystal with slightly patchy zoning pattern associated with pristine (main brighter area) and hydrothermally altered (darker areas) chevkinite-(Ce) (Cvk-Ce). White dots, red circles, and blue circles indicate the locations of WDS, LA-ICPMS, and LA-MC-ICPMS spot analysis, respectively. The white bars measure 50 μm.

3.2. Elemental and Isotope Geochemistry

The chemical and Lu-Hf isotopic compositions for primary (magmatic) zircon crystals and hydrothermal aggregates are presented in Tables 1 and S2 (WDS), 2 (LA-ICPMS), and 3 (LA-MC-ICPMS), and discussed below. Given the spatial resolution, except for some WDS analyses of some relatively thicker crystal fibers, the analytical results for the trace elements and Lu-Hf isotopes of the hydrothermal varieties are representative of the average crystal aggregates.

Table 1. Representative chemical compositions (wt.%, WDS) and cation proportions for primary (P) and hydrothermal (H) zircon crystals and aggregates, respectively. WDS spot locations for points 1,c and 3,c as given in Figure 4a,c, respectively. H1 = botryoidal aggregates and transparent overgrowth (r); H2 = lenticular fibro-radiated (1,c and 1,r from Figure 3e) and spherulitic fibro-radiated crypto- and micro-crystalline varieties. c = core; I = intermediate zone; r = rim; n.a. = not analyzed; b.d. = below detection limit. All Fe computed as Fe₂O₃.

Grain Type	Р	Р	H1	H1	H1	H2	H2	H2	H2
Point ID	1,c	3,c	2,i	2,i	3,r	1,c	1,r	2,i	5,r
SiO ₂	32.24	32.26	31.22	30.95	31.58	19.43	31.50	30.94	30.01
ZrO_2	65.34	65.45	58.39	57.97	58.61	36.25	61.38	59.10	54.25
HfO ₂	0.86	0.84	1.35	1.59	1.55	0.91	1.64	1.44	1.24
ThO_2	b.d.	0.07	0.50	0.21	0.15	0.09	0.13	0.13	1.89
UO_2	b.d.	0.05	0.06	0.07	0.04	0.06	0.11	0.13	0.11
TiO_2	0.09	0.04	0.14	0.06	0.06	0.05	0.08	0.18	0.12
Al_2O_3	0.02	b.d.	0.24	0.12	0.09	0.20	0.13	0.06	0.14
La_2O_3	0.05	0.07	0.09	n.a.	n.a.	b.d.	0.09	n.a.	n.a.
Ce_2O_3	b.d.	b.d.	0.26	0.23	0.26	0.19	0.16	0.22	0.24
Nd_2O_3	b.d.	b.d.	0.05	0.20	0.12	0.10	0.07	0.15	0.17
Sm_2O_3	b.d.	b.d.	0.06	0.16	0.14	0.04	0.07	0.12	0.25
Gd_2O_3	b.d.	0.09	0.07	0.34	0.40	b.d.	b.d.	0.20	0.50
Dy_2O_3	b.d.	0.06	0.11	0.52	0.53	0.04	0.11	0.24	0.63
Er_2O_3	0.07	0.09	0.07	0.30	0.23	0.11	0.10	0.19	0.40
Yb ₂ O ₃	0.09	0.16	0.50	0.16	0.19	0.11	0.09	0.16	0.37
Y_2O_3	0.45	0.63	1.00	2.32	2.27	0.67	0.87	1.62	3.62
Fe ₂ O ₃	0.26	0.02	1.83	0.44	1.00	39.85	0.68	0.87	1.42
MnO	0.02	b.d.	0.19	0.02	b.d.	0.52	0.09	0.10	0.12
MgO	b.d.	b.d.	0.02	b.d.	b.d.	0.02	b.d.	b.d.	b.d.
CaO	b.d.	b.d.	0.27	0.14	0.11	0.15	0.11	0.07	0.35
Na ₂ O	b.d.	0.03	0.12	0.04	0.04	0.02	0.09	0.07	0.09
K ₂ O	b.d.	0.02	0.05	b.d.	0.03	0.02	0.04	0.02	b.d.
Nb_2O_5	b.d.	b.d.	0.14	0.07	0.02	0.14	0.20	0.05	0.22
P_2O_5	0.09	0.07	0.20	n.a.	n.a.	b.d.	0.13	n.a.	n.a.
Sum	99.58	99.94	96.93	95.90	97.41	98.97	97.87	96.03	96.15
Cation p	proportions o	on the basis of	f 4 O						
Si	0.993	0.993	0.993	1.004	1.006	0.638	0.993	0.998	0.988
Zr	0.982	0.983	0.906	0.917	0.910	0.580	0.944	0.929	0.871
Hf	0.008	0.007	0.012	0.015	0.014	0.009	0.015	0.013	0.012
Th	0.000	0.000	0.004	0.002	0.001	0.001	0.001	0.001	0.014
U	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001
Ti	0.002	0.001	0.003	0.001	0.002	0.001	0.002	0.004	0.003
Al	0.001	0.000	0.009	0.005	0.003	0.008	0.005	0.002	0.005
La	0.001	0.001	0.001	0.000	0.000	0.000	0.001	0.000	0.000
Ce	0.000	0.000	0.003	0.003	0.003	0.002	0.002	0.003	0.003
Nd	0.000	0.000	0.001	0.002	0.001	0.001	0.001	0.002	0.002
Sm	0.000	0.000	0.001	0.002	0.002	0.000	0.001	0.001	0.003
Gd	0.000	0.001	0.001	0.004	0.004	0.000	0.000	0.002	0.005
Dy	0.000	0.001	0.001	0.005	0.005	0.000	0.001	0.002	0.007
Er	0.001	0.001	0.001	0.003	0.002	0.001	0.001	0.002	0.004
Yb	0.001	0.001	0.005	0.002	0.002	0.001	0.001	0.002	0.004
Y	0.007	0.010	0.017	0.040	0.038	0.012	0.015	0.028	0.063
Fe III	0.006	0.000	0.044	0.011	0.024	0.984	0.016	0.021	0.035
Mn	0.000	0.000	0.005	0.001	0.000	0.014	0.002	0.003	0.003
Mg	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000
Ca	0.000	0.000	0.009	0.005	0.004	0.005	0.004	0.002	0.012
Na	0.000	0.002	0.008	0.002	0.003	0.001	0.006	0.004	0.005
K NT	0.000	0.001	0.002	0.000	0.001	0.001	0.002	0.001	0.000
IND	0.000	0.000	0.002	0.001	0.000	0.002	0.003	0.001	0.003
Ľ Surra	0.002	0.002	0.005	0.000	0.000	0.000	0.003	0.000	0.000
Sum	2.004	2.005	2.034	2.023	2.026	2.264	2.018	2.022	2.044

The WDS compositions of primary zircon are relatively homogenous and to approach ideal ZrSiO₄, with maximum Hf, REE + Y, and Fe values of 0.008, 0.009 and 0.006 cations per formula unit (cpfu), respectively. On the other hand, the hydrothermal varieties contain significantly higher contents of Hf, Th, U, Ti, Al, REE + Y, Fe, Mn, Ca, and Nb amounts of up to 0.015, 0.014, 0.02, 0.007, 0.023, 0.091, 0.044, 0.015, 0.022 and 0.006 cpfu, respectively, a feature common to both natural and synthetic hydrothermal altered zircon [20,21,47]. As a whole, the hydrothermal varieties present lower analytical totals (down to ca. 95 wt.%), which could be explained by the presence of minute pores within or between crystal fibers and/or H₂O [48], which led to relatively poor structural formulae and variable cation excess (from 0.02 to 0.04 cpfu) in the Zr site; the total occupancy of this site by elements other than Zr varies between 0.14 and 0.06 cpfu. Some of these, particularly Al, Fe, Ca, Mn, are known as "non-formula" elements because they cannot be well-accommodated in the zircon Si or Zr sites, probably occurring in interstitial sites [46] or nanopores [21,48].

The dark, Fe-rich irregular cores, observed in the cryptocrystalline fibro-radiated aggregates (Figure 3d), contain Fe_2O_3 up to ca. 39.9 wt.% (0.984 Fe cpfu) and SiO_2 and ZrO_2 down to 22.4 and 40.8 wt.%, respectively. The structural formulae are incompatible with the zircon structure and give sums up to 2.264 cpfu on the basis of 4 O (see Tables 1 and S2).

The compositional WDS core-to-rim profile for the pristine spherulitic aggregate shown in Figure 3c is depicted in Figure 5 to illustrate its main zoning pattern. From the core to the most external rim, Fe, Al, Ca, and U show similar behavior, their contents initially decreasing towards the intermediate zone and then increasing towards the aggregate rims; Nb show a similar pattern but significantly decreased in the most external rim, while Th show an abrupt increase and the Th/U ratios increased towards the rim. On the other hand, Y and Dy increase more or less uniformly towards the rim and Hf and Ti remain almost unchanged.



Figure 5. WDS compositional core-to-rim profile illustrating the main chemical (minor and some trace elements) variations, expressed in cations per formula unit (cpfu), of the spherulitic zircon aggregate shown in Figure 3f.

3.2.1. Trace Element and REE Patterns

Trace-element patterns for hydrothermal and primary zircon are compared in Figure 6. In relation the host granite, both the primary and hydrothermal zircon presented welldeveloped positive U and Hf and negative Ti anomalies. Except for Ti and Mn, the hydrothermal species are significantly enriched in most of the measured trace elements. Their concentrations are 10–100-fold higher than those observed in the host rock on average, while in the case of the primary zircon, the concentrations of Nb, Ta, La, Ce, Pb, Sr, and Pr are 0.002–0.5-fold those in the host. The $Th_{Zircon}/Th_{Host rock}$ and $U_{Zircon}/U_{Host rock}$ ratios vary from ca. 10–60 and 100–300 to ca. 3 and 30, respectively. Thus, compared to the primary zircon, the hydrothermal aggregates are particularly rich in Nb, Ta, Pb, Sr, Ti, Mn, and the total REEs; for instance, some of these elements, such as La and Pr, have concentrations of up to 1000-fold higher (see also Table 2). The hydrothermal varieties also have higher Th/U and Ti/Nb (up to 3.9 vs. 1.2 and 1.2 vs. 0.34, respectively) and lower Zr/Hf (up to 45 vs. 74) ratios. The higher Th/U values of the hydrothermal zircon compared to the primary zircon are somewhat unusual because they are opposed to values commonly observed in zircon from several granitic occurrences [4,20].



Figure 6. Trace-element distribution patterns for primary and hydrothermal zircon, normalized to the CO-2A host granite sample. Symbols: blue cross—primary zircon; green star—botryoidal aggregates; magenta star—fibro-radiated crypto-crystalline aggregates; brown core—(1), colorless overgrowth (2); red star—spherulitic fibro-radiated micro-crystalline aggregate in allanite-(Ce).

The REE patterns (Figure 7) show that the primary crystals are characterized by high fractionation degrees of the HREE over the LREE and in both the LREE and HREE sides. They display well-developed positive Ce anomalies (2.5 < Ce/Ce* < 7.2 (Ce/Ce* = $(Ce_N/(La_N*Pr_N)^{0.5})$, where N stands for normalized to chondritic values)) and negative Eu anomalies $(0.02 < \text{Eu}/\text{Eu}^* < 0.03, (\text{Eu}/\text{Eu}^* = \text{Eu}_N/(\text{Sm}_N^*\text{Gd}_N)^{0.5})$. On the other hand, the hydrothermal zircon presents relatively flat patterns, with HREE over LREE fractionations approaching the unity or even lower values and negative Eu anomalies $(0.02 < Eu/Eu^*)$ < 0.06). The botryoidal and the spherulitic varieties present the highest HREE/LREE fractionation degrees and subtle positive Ce anomalies. The fibro-radiated cryptocrystalline aggregates are relatively LREE-rich and HREE-poor, with a pattern closer to the host rock and a slight fractionation degree in the LREE side and of the MREE over the HREE; the Ce anomaly was absent. In these varieties, the transparent overgrowths contain higher REE concentrations than the brownish internal zones. The Sm_N/La_N ratios vary in the ranges of 4.6–15.5 and 0.6–4.8 in the primary and hydrothermal zircon, respectively. These features are much like those described for primary and hydrothermal zircon in igneous rocks elsewhere [3,15,20,49].

Table 2. Trace-element compositions (ppm, LA-ICPMS) of primary (P) and hydrothermal (H) zircon crystals and aggregates, respectively, as well as the associated analytical errors (1 σ). P1 and P2 spot locations as provided in Figure 4a,c, respectively. H1 = botryoidal globules; H2a = fibro-radiated crypto-crystalline, brown core; H2b = fibro-radiated crypto-crystalline, colorless overgrowth; H3 = spherulitic, colorless, fibro-radiated aggregate associated with allanite-(Ce), as shown in Figure 2f.

Spot ID	P1	1σ	P2	1σ	H1	1σ	H1	1σ	H2a	1σ	H2b	1σ	H3	1σσ
Р	170	16	154	15	328	63	475	79	719	555	<500	-	326	64
Ti	3.9	0.6	5.3	0.7	491.0	23	729.0	35	393.0	143	858.0	159	569.0	33
Mn	0.7	0.4	2.7	0.4	273.0	11	131.0	5	1689.0	253	560.0	36	474.0	20
Sr	0.5	0.02	0.6	0.01	105	5	74	3	113	20	22	4	127	6
Y	2773	55	2908	60	13,461	721	19,520	956	3070	485	4803	257	15,218	842
Nb	11.30	0.02	15.30	0.02	1009	55	1132	49	731	112	735	35	1366	66
Mo	7.3	0.2	6.5	0.1	8.3	0.6	5.7	0.6	14.0	10	<11	-	7.4	0.9
Ba	< 0.1	-	< 0.1	-	168	8	88	4	329	60	731	50	104	5
La	5.3	0.1	1.3	0.01	876	40	257	10	2132	339	2646	103	543	23
Ce	31.4	0.2	27.0	0.2	5005	212	1017	39	3523	538	10,697	365	2619	111
Pr	1.7	0.01	0.6	0.02	523	23	126	5	330	52	1327	52	318	15
Nd	13.3	0.1	6.7	0.06	3414	263	986	74	1154	199	4648	216	1991	173
Sm	15.4	0.1	12.9	0.1	1200	91	781	51	299	58	930	64	917	68
Eu	0.22	0.02	0.31	0.02	28	2	8.6	0.7	3	2	9	3	11	1
Gd	70.10	0.01	65.41	0.06	1495	117	1790	122	285	61	957	71	1335	105
Tb	25.73	0.01	25.81	0.01	325	26	522	38	61	12	142	10	307	26
Dy	304.4	0.1	301.2	0.1	2489	255	3614	354	427	76	716	45	2421	274
Но	109.31	0.01	105.60	0.01	528	58	817	86	116	20	145	10	610	75
Er	431.60	0.02	433.00	0.02	1622	179	2420	257	392	66	440	29	2015	247
Tm	86.80	0.01	87.90	0.01	264	31	356	41	71	13	74	7	347	46
Yb	765.1	0.1	790.3	0.1	1876	179	2295	201	457	84	465	41	2294	232
Lu	110.50	0.01	108.20	0.01	188	20	215	22	54	10	72	7	222	26
Hf	6827	50	65,100	35	12,480	869	12,852	765	13,289	2050	14,867	709	9538	645
Ta	1.10	0.01	1.30	0.01	117	12	92	9	131	22	152	11	271	31
Pb	7.6	0.1	12.0	0.1	193	9	135	5	193	34	289	17	220	9
Th	138.0	0.1	132.9	0.1	1757	92	1665	69	615	100	1215	59	2296	105
U	117.0	0.1	118.0	0.1	489	22	542	23	338	54	312	16	1037	49



Figure 7. REE patterns for the primary and hydrothermal zircon and the CO-2A host granite, normalized to the chondritic values of Boynton [50]. Symbols: black diamond—host rock; others as in Figure 6.

3.2.2. Lu-Hf Isotope Geochemistry

Lu and Hf isotope data (Table 3) for primary and hydrothermal zircon are represented in Figure 8. Initial (176 Hf/ 177 Hf)_t ratios and related $\varepsilon_{Hf(T)}$ parameters were computed for t = 580 Ma in both cases, as the age of the hydrothermal event could not be constrained and it is likely that the it was not much younger than the main magmatism. The (176 Hf/ 177 Hf)₅₈₀ ratios range from ca. 0.28165 to 0.28200, corresponding to $-25.8 < \varepsilon_{Hf(580)} < -17.7$, thus indicating an isotopically evolved source for the original magma. It must be noted that the values of the hydrothermal varieties are close to those measured in primary zircon crystals, considering the involved analytical errors. These results are compatible with an essentially orthomagmatic source for such elements.

Table 3. In-zircon Lu and Hf measured (meas) and calculated isotope data for primary (P) and hydrothermal (H) zircon crystals and aggregates, respectively. Points Zr7-3.1, Zr6-2.2 and Zr8-1.1 spot locations are as given in Figure 4a–c, respectively. H1 = crypto- and micro-crystalline fibro-radiated aggregates; H2 = botryoidal globules. Initial (176 Hf/ 177 Hf)_(t) and related $\varepsilon_{Nd(t)}$ parameter computed for 580 Ma.

Spot ID	Туре	¹⁷⁶ Hf/ ¹⁷⁷ Hf _{meas}	2σ	¹⁷⁶ Lu/ ¹⁷⁷ Hf _{meas}	2σ	ε Hf ₍₀₎	¹⁷⁶ Hf/ ¹⁷⁷ Hf ₍₅₈₀₎	ε Hf ₍₅₈₀₎
Zr1-1.1	H1	0.28173	0.00008	0.00418	0.00001	-36.9	0.281683	-25.8
Zr2-1.1	H1	0.28179	0.00003	0.00229	0.00002	-32.4	0.281830	-20.6
Zr2-2.1	H1	0.28190	0.00003	0.00197	0.00005	-30.8	0.281879	-18.8
Zr3-3.1	H1	0.28189	0.00002	0.00145	0.00003	-31.2	0.281874	-19.0
Zr4-4.1	H2	0.28187	0.00004	0.00327	0.00017	-31.9	0.281834	-20.4
Zr4-1.1	H2	0.28183	0.00003	0.00189	0.00002	-33.2	0.281812	-21.2
Zr4-1.2	H2	0.28177	0.00003	0.00216	0.00002	-35.4	0.281747	-23.5
Zr5-1.2	Р	0.28174	0.00004	0.00343	0.00001	-36.5	0.281703	-25.1
Zr6-2.1	Р	0.28180	0.00006	0.00283	0.00001	-34.4	0.281769	-22.7
Zr6-2.2	Р	0.28187	0.00004	0.00338	0.00006	-31.9	0.281833	-20.4
Zr7-3.1	Р	0.28194	0.00005	0.00263	0.00003	-29.4	0.281911	-17.7
Zr7-3.2	Р	0.28178	0.00003	0.00272	0.00002	-35.2	0.281748	-23.5
Zr8-1.1	Р	0.28189	0.00004	0.00261	0.00003	-31.2	0.281862	-19.4
Zr9-1.1	Р	0.28172	0.00003	0.00235	0.00002	-37.1	0.281698	-25.2
Zr10-1.1	Р	0.28183	0.00002	0.00252	0.00001	-33.4	0.281800	-21.6



Figure 8. In-zircon initial $({}^{176}\text{Hf}/{}^{177}\text{Hf})_{580}$ vs. $({}^{176}\text{Lu}/{}^{177}\text{Hf})_{meas}$ diagram for primary and hydrothermal zircon crystals and aggregates, respectively. Note the similar variation range.

4. Discussion

The mineral paragenesis associated with the zircon aggregates in the studied peralkaline granite from the Corupá Pluton and their morphology provide undoubted evidence for a hydrothermal origin. Their chemical compositions were found to be characterized by relatively high contents of "non-formula" and HFSs (particularly the L- and MRE) elements, features most commonly associated with hydrothermal dissolution–reprecipitation processes acting on previous magmatic or metamorphic zircon crystals [21].

4.1. The Formation of Crypto- and Microcrystalline Zircon Aggregates

The observed textures and microstructures in the zircon aggregates are relatively rare and intriguing. Their crypto-to-microcrystalline nature contrasts with the epidotegroup minerals, whose aggregates are composed of relatively well-formed crystals and should be related to crystal-growth issues and the characteristics of the hydrothermal fluid. For instance, the spherulitic textures observed in chalcedony and other organic and inorganic materials have been interpreted as resulting from spiral crystal growth in a partially polymerized low-temperature fluid [51]. The formation of fibro-radiated hydrothermal or secondary mineral aggregates in low-temperature environments is often interpreted as the result of the precipitation of crypto-to-microcrystals radiating from some kind of seed; if this was the case, a Fe oxide or other Fe compounds are potential candidates in the studied example. The development and partial preservation of globular structures, with some evidence of coalescence, within the botryoidal aggregates are more puzzling and may suggest that during the hydrothermal stage, some process enabled the formation of Zr-rich silicate colloidal solutions or gel-like compounds from which alumino-silicate phases, fluorite, and zircon components unmixed. The preservation of these microstructures and of the amorphous-like Zr-silicate and cryptocrystalline zircon can be tentatively associated with poor element diffusion in a low-temperature environment, as supported by some crystallization experiments starting from synthetic gels [52,53]. Where fluid flux and/or element diffusion were facilitated, as in the outer zones of the globules and in the spherulites, crystal nucleation was reduced and relatively larger crystals developed.

The crystallization of similar zircon aggregates in some occurrences of typically agpaitic granites elsewhere has mainly been related to the substitution of previously crystallized, magmatic and/or post-magmatic Zr-silicates such as eudialyte-group minerals, elpidite and armstrongite–gittinsite [22,44,45]. For instance, pseudomorphs after eudialytegroup minerals constituted by hydrothermal zircon, quartz, and rare-metal-bearing and other hydrothermal phases were described in granites from the Ambohimirahavavy complex [22].

In the studied case, there was no clear evidence indicating a similar origin, as no previous Zr-silicates occurred in the peralkaline granites nor in the enclosing main syenites and the zircon aggregates probably directly precipitated from the hydrothermal fluid. In the granites and syenites, chevkinite (a typical and relatively abundant accessory mineral) and amphiboles contain only minor and trace abundances of Zr, respectively [33,54], so this element is mainly hosted in zircon; however, the analytical results showed that primary zircon from the granite had significantly lower HFSE contents than the hydrothermal varieties. Chevkinite is easily altered by hydrothermal fluids (see Figure 4c), and this process releases significant amounts of REEs (particularly the LREEs) besides Fe and Th [54], which should have contributed to the fluid composition [33]; however, this was not as clear for Zr and Hf, and their source remains unclear. Nevertheless, the Hf isotopic data suggest an orthomagmatic origin.

The transition from the late-magmatic to the post-magmatic stages in the granites from the Corupá Pluton was shown to be marked by a notable change in the chemical environment, and the peralkaline mineralogy characterized by the sodic amphiboles in the former gave way to the precipitation of a Ca- and Al-bearing, metaluminous, assemblage particularly characterized by the precipitation of epidote-group minerals [33]. The occurrence of allanite-(Ce), ferriallanite-(Ce), zircon and fluorite in the hydrothermal assemblage indicates that the fluid phase contained significant amounts of HFSEs (particularly the REEs) and F. It is well-known that the HFSEs form stable complexes and may be concentrated in and transported by aqueous, halogen (F and Cl)-bearing, saline and acid fluids [26,55–59]. Hence, it is suggested here that a similar F-bearing silicate fluid was exsolved from the crystallizing melts during the late evolution of the syenitic–granitic magmatic system and carried these elements.

Subsequent changes in fluid properties, particularly pH neutralization [57,60], allowed for the precipitation of the HFSEs and their incorporation into the structures of hydrothermal epidote-bearing minerals, particularly allanite-(Ce) and ferriallanite-(Ce), and zircon aggregates. These changes are complex and not well-known; they may be driven by the precipitation of hydrothermal mineral phases, interactions with the wall-rock and reactions with previous mineral phases, and/or mixing with fluids derived in the country rocks [26,55,57]. A previous interpretation of the formation of epidote-group minerals in the hydrothermal assemblage did not favor significant external contributions [33]; in this case, the source for Ca and Al must be related to the re-equilibration of the primary alkali-feldspar, which is abundant in the granite host, and the consequent release of its minor anorthite component to the fluid; however, in several occurrences worldwide, such as the Strange Lake peralkaline complex, the involvement of Ca-bearing external meteoritic fluids seems to have been well-demonstrated [55], and this hypothesis cannot be excluded with the available data.

4.2. Crystallization Conditions

The intensive parameters for the late magmatic and hydrothermal crystallization stages in the Corupá Pluton were not precisely constrained. The geological characteristics indicated a relatively low pressure (<ca. 200 MPa) for magma emplacement and crystallization, and the observed mineralogical assemblages suggested relatively reducing (near the quartz–fayalite–magnetite (QFM) buffer) and oxidizing (near the hematite-magnetite, HM buffer) environments at the onset of magmatic and post-magmatic stages, respectively [32,33,54].

The Ti-in-zircon crystallization temperatures of the magmatic analyzed crystals were estimated with the formalism developed by Ferry and Watson [9] while assuming a silica activity (a_{SiO2}) = 1, a reasonable value for evolved granites in which quartz was a close-to-*liquidus* phase. The estimation of the a_{TiO2} was somewhat more difficult, as rutile is absent and ilmenite is the unique primary Fe-Ti oxide present in the host rock. Taking a_{TiO2} values of 0.3, 0.5 and 0.7, as well as the Ti average concentrations and related errors given in Table 2, the obtained temperatures are 772, 738, and 708 °C, respectively, with an estimated error around 50–70 °C for a 95% confidence level. Given the observed mineral paragenesis, it is suggested that the titania activity was moderate to low. The obtained temperatures set an upper limit to the granite *solidus*, while chlorite thermometry for the main syenites (unpublished data) provided hydrothermal temperature values of around 250–300 °C. Available experimental data suggest that hydrothermal zircon may precipitate in a large range of temperatures, from *solidus* temperatures down to 150 °C [52,53], and zircon re-equilibration by diffusion–reaction processes may take place even under weathering conditions [21].

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/min12050628/s1. Table S1: Analytical results for trace elements in zircon reference materials 91500 and GJ-1 and respective recommended values; Table S2: Chemical compositions (WDS, wt.%) and structural formulae for primary and hydrothermal zircon, Pluton Corupá, Sample CO-2. Fb = fibro-radiated; c = core; I = intermediate zone; r = rim; over = overgrowth.

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