

## HAFNIAN ZIRCON FROM THE APICAL PART OF THE SUZHOU GRANITE, CHINA

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### ABSTRACT

Hafnian zircon generally is found in granitic pegmatite, but much more rarely in granite. Here, we describe an occurrence in the apical part of the Suzhou granite (unit II), in China. We distinguish three evolved facies: from the apical region downward, these are the albite-enriched, the topaz-bearing, and the biotite-bearing facies, which are characterized by significant enrichment in Nb, Ta, Zr, Hf, Th and the rare earths. In the biotite-bearing facies, the zircon contains less than 10 wt.% HfO<sub>2</sub>. Levels of HfO<sub>2</sub> greater than 25%, and even attaining 35%, characterize the hafnian zircon in the albite-enriched facies. This degree of enrichment is the greatest known so far in hafnian zircon. The level of Hf in zircon of the topaz-bearing facies is intermediate. The striking decrease in Zr/Hf with increasing degree of evolution of the granite reflects an important decoupling in these two elements. The Suzhou granite thus displays a pegmatitic character. Where the zircon is associated with niobo-tantalates, we document a close correlation between Hf/(Hf + Zr) in the zircon and Ta/(Nb + Ta) in the niobo-tantalates; this affinity between Hf and Ta seems more dependent on geochemical than crystal-chemical factors.

*Keywords:* zircon, hafnium, columbite–tantalite, tapiolite, granite, Suzhou, China.

### SOMMAIRE

Le zircon hafnifère se présente généralement dans des pegmatites granitiques, mais très rarement dans des granites. Toutefois, on le trouve dans la partie supérieure du granite II de Suzhou, en Chine. On distingue trois faciès bien évolués, qui sont du haut en bas: faciès à albite, faciès à topaze et faciès à biotite. Ces roches contiennent un important enrichissement en Nb, Ta, Zr, Hf, Th et terres rares. Dans le faciès à biotite, la teneur en HfO<sub>2</sub> du zircon est inférieure à 10% (poids). Le zircon hafnifère a été observé dans le faciès à albite, avec des teneurs en HfO<sub>2</sub> supérieure à 25%, pouvant atteindre 35%, c'est-à-dire le plus fort enrichissement en Hf connu à ce jour. Le zircon du faciès à topaze est intermédiaire. La forte diminution du rapport Zr/Hf du zircon avec le degré d'évolution des roches reflète un important fractionnement des deux éléments. Le granite de Suzhou présente donc un caractère typiquement pegmatitique. Dans le cas où le zircon est associé aux niobo-tantalates, il montre une corrélation étroite entre les rapports Hf/(Zr + Hf) du zircon et Ta/(Nb + Ta) des niobo-tantalates. Cette affinité entre Hf et Ta paraît plutôt géochimique que cristalochimique.

*Mots-clés:* zircon, hafnium, columbite–tantalite, tapiolite, granite, Suzhou, Chine

### INTRODUCTION

Since its discovery in a granitic pegmatite from Zambezia, Mozambique (Correia Neves *et al.* 1974), hafnon, HfSiO<sub>4</sub>, a mineral isotypic with zircon, has not

been found. However, examples of hafnian zircon having very variable levels of Hf have been described in several occurrences of granitic pegmatite (Levinson & Borup 1960, von Knorring & Hornung 1961, Nagashima *et al.* 1978, Černý & Siivola 1980, Fontan *et al.* 1980, Cassedanne *et al.* 1985, Lumpkin & Chakoumakos 1988). Zircon in granitic rocks commonly contains Hf, but concentrations are almost always less than 10% HfO<sub>2</sub>, with the exception of hafnian zircon (18.8% HfO<sub>2</sub>) in the Beauvoir granite

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in France, which confers to it a pegmatitic affinity (Wang *et al.* 1992a). Our mineralogical study of the Suzhou granitic complex, in China, indicates the presence of hafnian zircon containing up to 35% HfO<sub>2</sub>, which is much higher than the highest level recorded in granitic pegmatites (31%: von Knorring & Hornung 1961). There, the zircon is associated with the tantalum-bearing accessory phases tantalite and tapiolite. In this study, we have documented the compositional evolution of the zircon in order to characterize the distribution of Zr and Hf in the various facies of the Suzhou granite, as well as of Nb and Ta in the associated niobo-tantalates.

#### DESCRIPTION OF THE SUZHOU GRANITIC COMPLEX

The Suzhou granitic complex is located approximately 10 km west of the town of Suzhou, Jiangsu

Province, China (Fig. 1). It is intrusive into Devonian sandstone and is exposed over an area of 11 km<sup>2</sup>. It is the first example of a Nb-Ta-rich granite to be found in China. Because of the protected status of Suzhou (the city of Suzhou is called "Paradise City"), no detailed study has ever been undertaken (Liu 1987). The Suzhou granitic complex is composed of three map units (Fig. 1), which are, in chronological order of emplacement; granite I, amphibole- and biotite-bearing and coarse-grained, granite II, biotite-bearing, with albite predominant over K-feldspar, and granite III, K-feldspar-dominant, and coarse- to medium-grained. The rare-element mineralization in granites I and III are negligible despite the presence of zircon, the latter relatively poor in Hf.

Granite II is the intrusive unit that is the best exposed and also the most enriched in Nb, Ta, Zr, Hf, Th, and the rare earths. In its apical part, we distinguish three highly evolved facies, from bottom to top: a

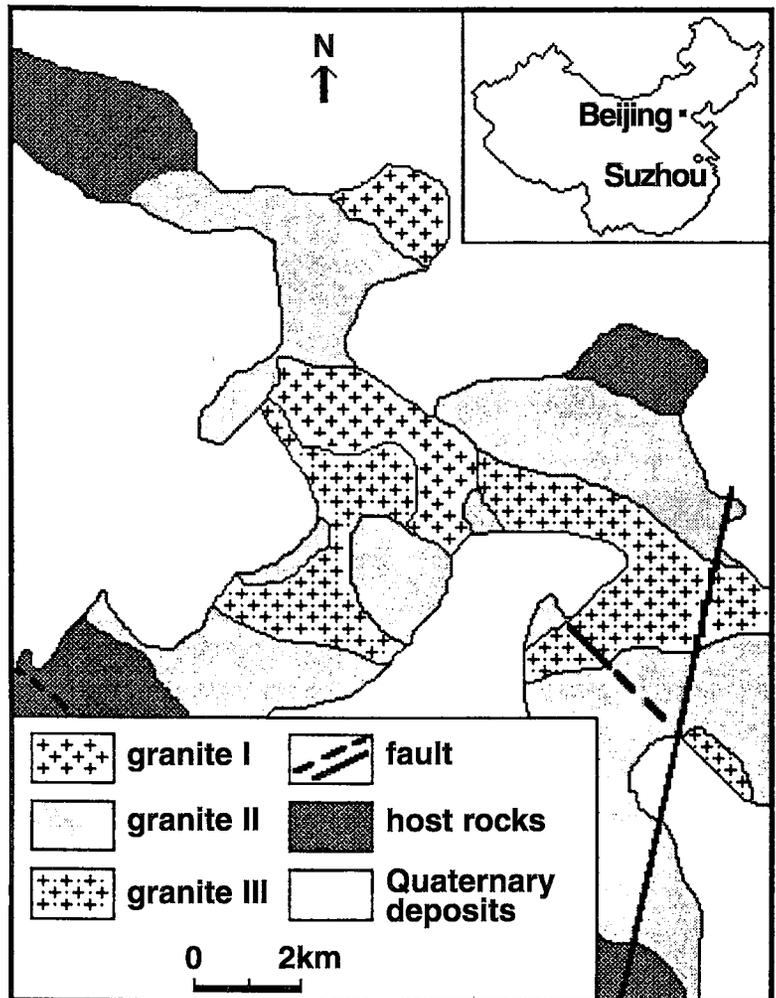


FIG. 1. Geological context of the Suzhou granitic complex (after Liu 1987).

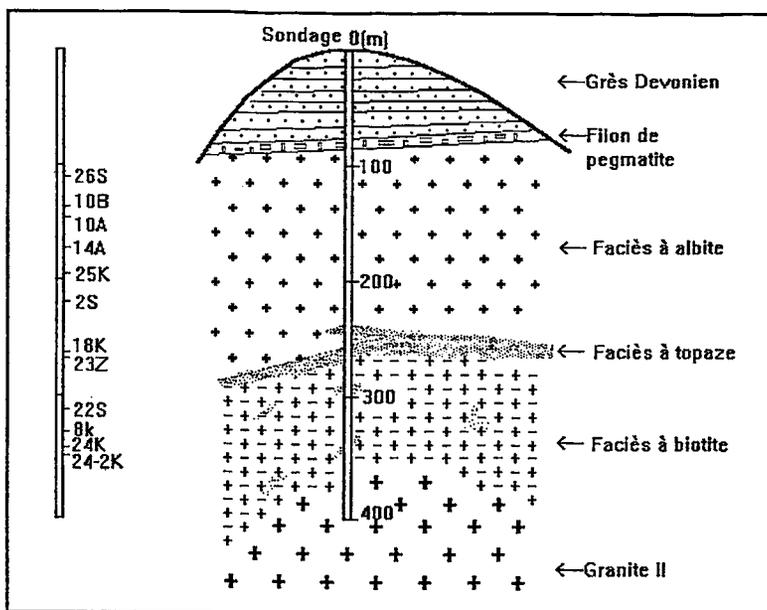


FIG. 2. Cross-section of the apical portion of granite II in the Suzhou pluton, drawn on the basis of field relationships and drill-hole data. To the left is shown the position of the samples used in this investigation.

biotite-bearing facies, a topaz-bearing facies and an albite-rich facies (Fig. 2, Table 1). The biotite-bearing facies consists of quartz, anhedral K-feldspar, albite and abundant biotite in very fine grains, with the following accessories: topaz, columbite, zircon and monazite. The topaz-bearing facies is less important in volume, and the major minerals are the same as in the previous facies; on the other hand, the feldspars are less abundant, and topaz is found in anhedral crystals that make up 20% of the rock. The topaz contains numerous melt inclusions,  $500 < T_h < 800^\circ\text{C}$ , which suggest that it has a magmatic origin (Zhou 1994), just as in the case of the Beauvoir granite (Raimbault *et al.* 1995). The albite-enriched facies is located at the top of granite II. It contains mostly albite and quartz; melt inclusions in the quartz homogenize between  $560$  and  $600^\circ\text{C}$ . Muscovite and K-feldspar are present in smaller quantities, and the accessories are: tapiolite, tantalite, zircon, thorite, and xenotime. Topaz is absent, as the concentration of F is very low (0.05% F: Wang *et al.* 1992b), despite the presence of veinlets of fluorite, which indicate a local concentration in F (Liu 1987). In 1985, a drill hole 400 m in length was put down across these three facies, and revealed a mineralized zone enriched in Ta and Hf (Wang *et al.* 1992b, Fig. 2); however, no mineral exploration was undertaken.

The petrological studies (Wang *et al.* 1992b, Charoy & Raimbault 1994) show that the Suzhou granite has

an igneous origin, the three facies being interrelated by differentiation. The small nodules of "biotitite", found in the apical part, are considered to be a product of metasomatism by Charoy & Raimbault (1994).

TABLE 1. AVERAGE BULK COMPOSITION, GRANITE II FACIES, SUZHOU PLUTON

		Albite-enriched facies (5)*	Topaz-bearing facies (2)	Biotite-bearing facies (4)
SiO <sub>2</sub>	wt. %	70.28	70.49	75.04
TiO <sub>2</sub>		0.00	0.02	0.00
Al <sub>2</sub> O <sub>3</sub>		17.32	16.20	13.69
Fe <sub>2</sub> O <sub>3</sub>		0.08	1.48	0.47
FeO		0.10	2.80	0.62
MnO		0.02	0.31	0.08
MgO		0.01	0.02	0.01
CaO		0.60	0.78	0.74
Na <sub>2</sub> O		7.59	1.11	4.30
K <sub>2</sub> O		3.71	2.74	4.63
P <sub>2</sub> O <sub>5</sub>		<0.01	<0.01	<0.01
LOI		0.29	1.78	0.48
F		0.05	3.78	0.33
Total		99.36	101.51	99.81
F=O		0.02	1.59	0.14
Total		99.34	99.93	99.67
Nb	ppm	81	135	213
Ta		97	32	14
Zr		332	126	436
Hf		138	38	54

\* The number in parentheses indicates the number of samples analyzed.

## ANALYTICAL METHODS

The chemical analyses were done with a Cameca SX50 electron microprobe (Université Paul Sabatier, Toulouse). The operating conditions were as follows: acceleration voltage 15 kV, sample current 20 nA, and diameter of electron beam 5  $\mu\text{m}$ ; the following standards were used: wollastonite (Si),  $\text{Hf}_{98}\text{Zr}_2$  (Hf),  $\text{UO}_2$  (U),  $\text{ThO}_2$  (Th), zircon (Zr), graftedite (P),  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (Y), and  $\text{Cr}_2\text{O}_3$  (Cr). We used the PAP program for data reduction (Pouchou & Pichoir 1991). The structural formulas were calculated on the basis of four atoms of oxygen.

## ZIRCON IN THE BIOTITE- AND TOPAZ-BEARING FACIES

In the biotite- and topaz-bearing facies, zircon is found as subhedral octahedra of small size ( $\approx 20 \mu\text{m}$ ), mainly included in the biotite, which implies an early stage of crystallization. It is commonly closely associated with columbite. Their intergrowth (Fig. 3) causes, in some cases, fissures in the columbite, probably due to metamictization; these fissures are completely analogous to those described in cassiterite from Beauvoir (Wang *et al.* 1992a). We also find, less commonly, micro-inclusions of zircon in uranium- and thorium-bearing minerals.

We have analyzed 15 crystals of zircon; representative results of ten analyses are shown in Table 2. The levels of  $\text{HfO}_2$  range from 1.76 to 7.08 wt.% for the biotite-bearing facies, and from 4.94 to 16.08% for the topaz-bearing facies, values comparable to

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITION OF ZIRCON IN THE BIOTITE- AND TOPAZ-BEARING FACIES OF GRANITE II, SUZHOU PLUTON

	1	2	3	4	5	6	7	8	9	10
	22S5-1	8K8-2	8K2-1	24K1-3	24K3-2	24K5-1	24-2K2	23Z1-3	18K1-2	18K1-1
$\text{SiO}_2$	30.82	31.92	29.21	32.20	32.08	31.24	32.05	23.97	31.56	30.49
$\text{HfO}_2$	8.50	2.70	2.32	1.76	3.63	7.08	4.94	8.28	8.75	16.08
$\text{UO}_2$	0.79	0.69	2.03	0.15	0.00	1.21	1.20	1.50	1.79	0.17
$\text{ThO}_2$	0.34	0.36	5.09	0.26	0.19	0.28	0.38	7.55	0.60	0.01
$\text{ZrO}_2$	58.07	62.19	55.73	63.01	62.70	59.23	60.60	40.16	55.73	49.49
$\text{P}_2\text{O}_5$	0.20	0.03	0.36	0.00	0.02	0.00	0.02	0.69	0.05	0.60
$\text{Y}_2\text{O}_3$	0.29	0.28	0.43	0.67	0.11	0.00	0.30	1.42	0.25	0.32
$\text{Cr}_2\text{O}_3$	0.00	0.00	0.03	0.07	0.00	0.00	0.00	0.05	0.01	0.00
Total	99.01	98.17	95.20	98.12	98.73	99.04	97.49	83.62	98.74	97.16
$\text{Si}^{4+}$	0.992	1.007	0.986	1.009	1.006	1.000	0.972	1.019	1.016	0.977
$\text{Hf}^{4+}$	0.078	0.024	0.022	0.016	0.032	0.065	0.046	0.096	0.081	0.153
$\text{U}^{4+}$	0.006	0.005	0.015	0.001	0.000	0.009	0.009	0.014	0.013	0.001
$\text{Th}^{4+}$	0.003	0.003	0.039	0.002	0.001	0.002	0.003	0.070	0.001	0.000
$\text{Zr}^{4+}$	0.911	0.957	0.918	0.963	0.958	0.925	0.961	0.795	0.878	0.804
$\text{P}^{5+}$	0.005	0.001	0.010	0.000	0.001	0.000	0.001	0.024	0.001	0.017
$\text{Y}^{3+}$	0.005	0.005	0.008	0.011	0.002	0.000	0.005	0.031	0.004	0.006
$\text{Cr}^{3+}$	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.002	0.000	0.000
Total	2.000	2.001	2.000	2.003	2.000	2.000	2.001	2.002	2.001	1.997
$\text{Hf}/(\text{Zr}+\text{Hf})$	0.08	0.03	0.02	0.02	0.03	0.07	0.05	0.11	0.08	0.16

Columns: 1-6: biotite-bearing facies, 7-10: topaz-bearing facies. Concentration of elements reported as oxides, in weight %.

those found in the Beauvoir granite (Wang *et al.* 1992a). The value  $\text{Hf}/(\text{Zr} + \text{Hf})$  of the zircon in the biotite-bearing facies is invariably less than 0.10, and that of the zircon in the topaz-bearing facies is between 0.05 and 0.16, indicative of a low concentration of hafnium.

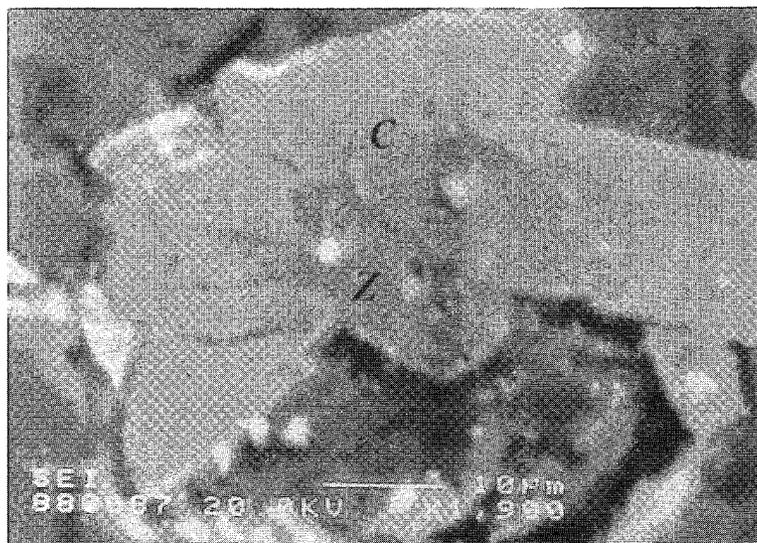


FIG. 3. Fissures in columbite (C), linked to the presence of metamict zircon (Z) nearby.

In these two facies, zircon is the main host of Th and U, with concentrations that are very variable. Crystals rich in thorium (Table 2, anal. 3, 8) are metamict, the analytical total varying between 95.2 and 83.6%. This shortfall is attributed to the presence of water, not detected, which is presumably in the form of molecular H<sub>2</sub>O rather than (OH) (Mumpton & Roy 1961, Speer 1980). The level of UO<sub>2</sub> does not exceed 2.03%, which is distinctly lower than in the zircon from the Beauvoir granite (up to 10.7% UO<sub>2</sub>; Cuney & Brouand 1987). Pictures of the distribution of Th and U indicate one of two patterns: (1) homogeneous distribution, the case of two crystals of zircon having high levels of Th and U (Table 2, anal. 3, 8). These images do not reveal the presence of micro-inclusions of uranium-bearing and thorium-bearing minerals. Here, Th and U must be involved in substitutions for Zr. The levels of Th are close to its maximum solubility in zircon, which is on the order of  $5.5 \pm 2.5\%$  ThO<sub>2</sub> by weight (Mumpton & Roy 1961), although this limit is surpassed in the case of zircon from the Sierra Blanca Peaks rhyolite in Texas (up to 9.4% ThO<sub>2</sub>; Rubin *et al.* 1989). (2) Heterogeneous distribution of micro-inclusions (2–5 μm) of thorite + coffinite (or uraninite) in zircon (Table 2, anal. 9). According to Černý & Siivola (1980), the presence of micro-inclusions of U- and Th-bearing minerals suggests an environment saturated in U and Th, favorable to a maximum concentration of these two elements in the structure at the conditions of growth. This maximum concentration seems to have been here much lower than in the first type. We must therefore attribute the distribution of Th and U, either in substitution for Zr in the structure or in the form of micro-inclusions of distinct minerals, to local variations in the conditions of crystallization.

#### HAFNIAN ZIRCON IN THE ALBITE-ENRICHED FACIES

In the albite-enriched facies, the crystals of zircon are subhedral to anhedral, of milky white color, and intergranular. In reflected light, their reflectivity is much stronger than in the case of zircon from the other facies, perhaps because of their non-metamict state. Their length varies between 0.2 and 0.8 mm. The grains are closely associated with, and even intergrown with, tapiolite or tantalite, thorite and xenotime. In the interior of the crystals, we commonly find small cavities (remains of fluid inclusions?), which may be distributed in a radial fashion depending on the growth pattern of the zircon.

We have carried out 38 analyses on 15 crystals of zircon; ten compositions are reported in Table 3. The totals, between 98 and 101%, show well that these crystals are not metamict. Hafnium is strongly concentrated in this facies, with variable concentrations (16.93 to 34.84% HfO<sub>2</sub>), not only in the same sample on a scale of centimeters (e.g., 25.69 to

TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITION OF HAFNIAN ZIRCON IN THE ALBITE-ENRICHED FACIES OF GRANITE II, SUZHOU PLUTON

	1 26S5-1	2 26SO-2	3 26S4-1	4 10B5-4	5 10B4-2	6 10B6-2	7 10B1-2	8 10A2-1	9 25K1-4	10 2S2(4)
SiO <sub>2</sub>	27.89	28.51	28.02	28.46	29.15	28.94	29.30	30.30	30.93	30.91
HfO <sub>2</sub>	34.84	33.40	32.28	33.25	32.16	30.38	27.04	25.92	16.93	21.59
UO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00
ThO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.17
ZrO <sub>2</sub>	35.02	35.98	35.83	36.82	36.50	38.72	41.72	43.71	50.60	47.77
P <sub>2</sub> O <sub>5</sub>	0.96	0.78	0.74	0.82	0.69	0.61	0.62	0.60	0.94	0.68
Y <sub>2</sub> O <sub>3</sub>	0.53	0.26	0.19	0.31	0.34	0.13	0.23	0.20	0.25	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.48	0.38	0.98	0.04	0.08	0.00	0.04	0.00	0.00	0.00
Total	99.72	99.31	98.04	99.70	98.92	98.78	98.95	100.74	99.74	100.95
Si <sup>4+</sup>	0.989	1.005	0.998	1.000	1.022	1.012	1.008	1.015	1.005	1.012
Hf <sup>4+</sup>	0.253	0.336	0.328	0.334	0.322	0.303	0.266	0.248	0.157	0.202
U <sup>4+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Th <sup>4+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Zr <sup>4+</sup>	0.605	0.618	0.622	0.631	0.624	0.660	0.700	0.713	0.802	0.763
P <sup>5+</sup>	0.029	0.023	0.022	0.024	0.020	0.018	0.018	0.017	0.026	0.019
Y <sup>3+</sup>	0.010	0.005	0.004	0.006	0.006	0.002	0.004	0.004	0.004	0.000
Cr <sup>3+</sup>	0.013	0.011	0.028	0.001	0.002	0.000	0.001	0.000	0.000	0.000
Total	1.999	1.998	2.002	1.996	1.997	1.996	1.997	1.997	1.995	1.995
Hf/(Zr+Hf)	0.37	0.35	0.35	0.35	0.34	0.32	0.28	0.26	0.16	0.20

Concentration of elements reported as oxides, in weight %.

33.25%: sample 10B), but also within a single crystal of zircon (e.g., 28.51 to 33.40%: crystal 26SO). We find that the levels of HfO<sub>2</sub> are the highest (1) in crystals from the apical part of the albite-enriched facies, (2) in those closely associated with tapiolite or tantalite, and (3) at the rim of crystals. These characteristics agree with earlier observations (Fontan *et al.* 1980, Wang *et al.* 1992a). The value Hf/(Zr + Hf) is between 0.16 and 0.37; according to the nomenclature proposed by Correia Neves *et al.* (1974), the crystals can be considered hafnian zircon. The zircon of granitic rocks normally contains less than 4% HfO<sub>2</sub> (Gulson 1970). In peraluminous granites and rhyolites enriched in rare elements, zircon is generally richer in Hf (Rubin *et al.* 1989, Congdon & Nash 1991, Huang *et al.* 1991, Wang *et al.* 1992a), although the concentration of HfO<sub>2</sub> usually is less than 10%. The Suzhou granite shows, as far as we know, the highest enrichment of Hf in zircon known. The examples of hafnian zircon described by several authors are invariably of pegmatitic origin (see above); yet five samples of zircon from the Suzhou granite have levels of Hf that surpass those in zircon from granitic pegmatites. Certain crystals may contain U and Th, but invariably at very low levels (<0.2%); crystals having ThO<sub>2</sub> > 0.25% are rare, and such values are found in isolated spots only. This finding confirms that zircon contains only low levels of Th and U in the presence of thorite (Lumpkin & Chakoumakos 1988), which, in the albite-enriched facies, is widespread and associated with zircon and niobo-tantalates.

## EVOLUTION OF Zr/Hf IN ZIRCON

The concentration of Hf in zircon is variable; it depends on the degree of evolution of the original magma. The average of Hf concentrations is 4.33% in the biotite-bearing facies, and attains 23.78 wt.% HfO<sub>2</sub> in the albite-enriched facies. A few crystals of zircon from the topaz-bearing facies have an average content of 9.51%, and are intermediate. The diagram Zr/Hf versus Hf (Fig. 4) reveals, from the biotite-bearing facies to the albite-enriched facies, a greater range of Zr/Hf values than in the Beauvoir granite (Wang *et al.* 1992a). The value of Zr/Hf decreases from 31.25 to 5.04 in the early facies containing biotite, to between 0.88 and 2.70 in the late facies enriched in albite, and is consistent with an important variation in the degree of fractionation among facies.

The whole-rock compositions of representative samples of the biotite-bearing, topaz-bearing, and albite-enriched facies indicate, respectively, Zr/Hf values of 8.08, 3.36, and 2.40, variations that imply a decoupled fractionation for Zr and Hf (Ellison & Hess 1986). Experimental studies (Keppler 1993, Linnen & Keppler 1996) reveal the importance of fluorine on the solubility of zircon and columbite-tantalite in the magma. In the Suzhou granite, we have documented an

enrichment in Hf in the albite-enriched facies that may be linked to hydrothermal activity during a late magmatic stage (Raimbault 1990, Raimbault *et al.* 1995), the Zr being complexed by fluorine, which would result in an enrichment of hafnium in the residual magma.

In the diagram of Černý *et al.* (1995), (Fig. 4), we note that the zircon in the albite-enriched and topaz-bearing facies invariably plots in the domain of pegmatites, whereas zircon in the biotite-bearing facies plots in domains of granitic and pegmatitic rocks. Thus the pegmatitic character, already pointed out in the case of the Beauvoir granite, also is found in the Suzhou granite, in which it is progressively expressed from the biotite-bearing facies to the albite-enriched facies.

## RELATIONSHIP BETWEEN ZIRCON AND NIOBO-TANTALATES

Several authors have emphasized the close association between hafnian zircon and minerals rich in Ta (von Knorring & Hornung 1961, Černý & Siivola 1980). Fontan *et al.* (1980) have emphasized the correlation between the values Hf/(Zr + Hf) in the zircon and Ta/(Nb + Ta) in the associated niobotantalates. Wang *et al.* (1992a) have described the

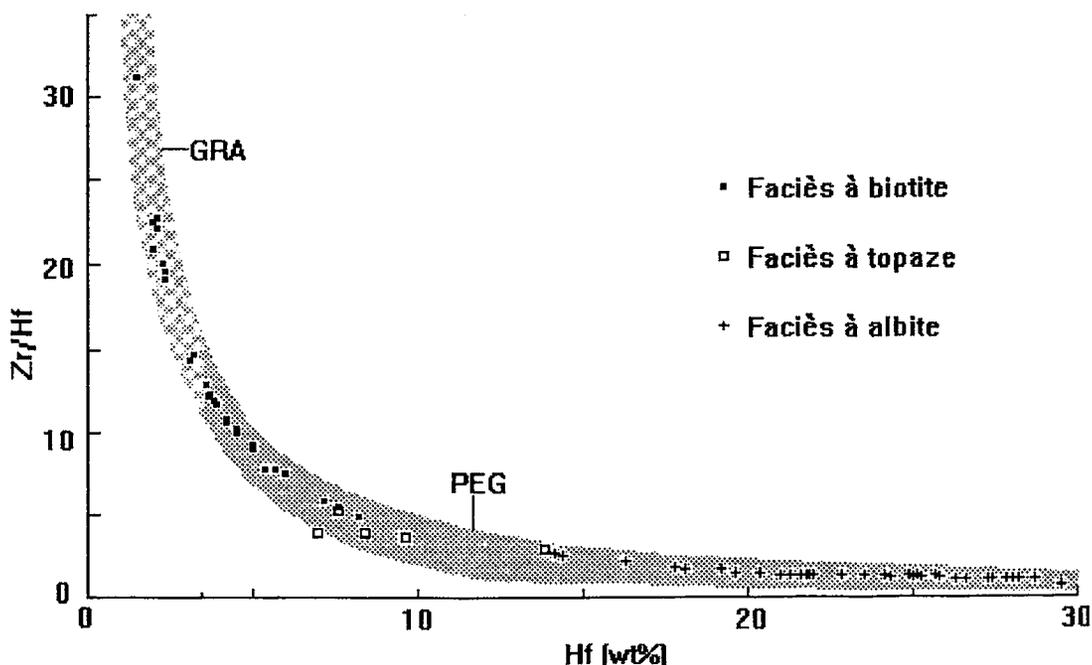


FIG. 4. Plot of the composition of zircon in the Suzhou granite, in terms of Zr/Hf versus concentration of Hf. The shaded areas indicate the compositional domains of zircon in felsic plutonic rocks of granitic (GRA) and pegmatitic (PEG) texture, respectively [after Černý *et al.* (1985), with modifications].

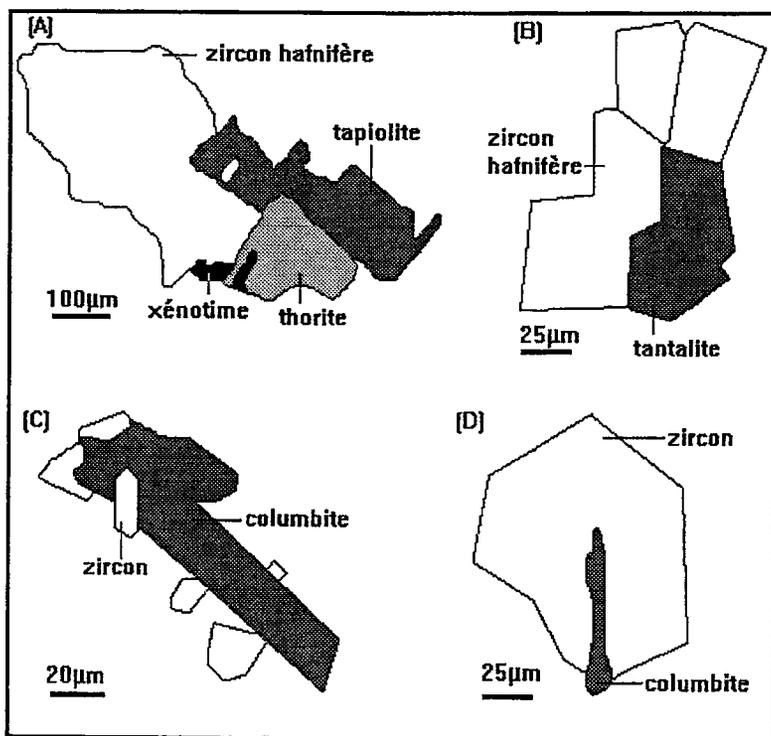


FIG. 5. Aspects of representative associations of zircon + niobo-tantalates. Samples: (A) 26S5, (B) 2S2, (C) 24-2K, (D) 8K5.

complex relations between zircon and Nb-Ta-bearing cassiterite, and indicated a close affinity between Hf and Ta. The abundance of zircon and of niobo-tantalates, and the frequency of their association in the facies of the Suzhou granite, led us to carry out a systematic study concerning the relationship between  $Hf/(Zr + Hf)$  in zircon and  $Ta/(Nb + Ta)$  in the niobo-tantalates.

Figure 5 shows four principal types of associations observed in all granitic facies at Suzhou. Thirteen cases of the association zircon + niobo-tantalates have been analyzed with an electron microprobe (Table 4). The levels of Hf correspond to those in zircon (*s.s.*) and in hafnian zircon, whereas the niobo-tantalates are made up of three examples of tapiolite, three of tantalite, and seven of columbite. In Figure 6, the data points plot almost along a straight line. The close correlation between the  $Hf/(Zr + Hf)$  in zircon and  $Ta/(Nb + Ta)$  in niobo-tantalates is clearly demonstrated. We have added to this figure two examples of such associations from pegmatites in the Pyrénées (Fontan *et al.* 1980); note that the two data points are in good agreement with those for the Suzhou suite. The affinity between Hf and Ta seems a general phenomenon that can be

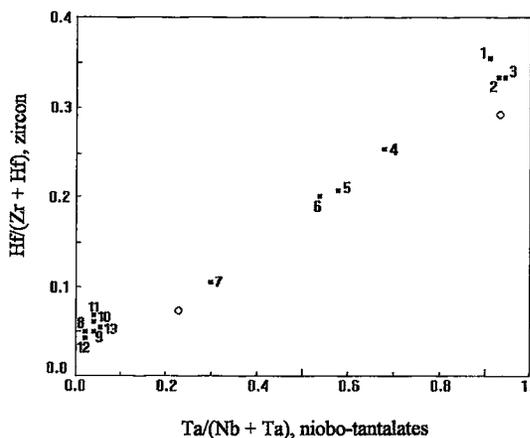


FIG. 6. Correlation between  $Zr/(Zr + Hf)$  values in zircon and  $Ta/(Nb + Ta)$  values in the associated niobo-tantalates. The numbers next to the data points refer to entries in Table 4. The symbol  $\circ$  indicates two additional examples of the same association (Fontan *et al.* 1980).

TABLE 4. REPRESENTATIVE CHEMICAL COMPOSITION OF ASSOCIATED ZIRCON AND NIOBO-TANTALATES

	1 26S5	2 10B5	3 10B4	4 10A2	5 SK25	6 2S2	7 23Z	8 24K4	9 24-2K	10 24K5	11 22S5	12 8K2	13 8K5
	Zrn (4)	Zrn (7)	Zrn (4)	Zrn (2)	Zrn (4)	Zrn (4)	Zrn (3)	Zrn (2)	Zrn (4)	Zrn (1)	Zrn (1)	Zrn (4)	Zrn (1)
SiO <sub>2</sub>	28.19	28.86	28.75	29.94	30.65	30.61	26.52	32.05	31.05	31.24	30.82	30.92	31.29
HfO <sub>2</sub>	33.64	30.57	30.66	25.33	21.08	20.45	9.82	5.55	5.28	7.08	8.50	3.74	6.35
UO <sub>2</sub>	0.00	0.00	0.00	0.00	0.04	0.04	1.10	0.23	0.62	1.21	0.79	1.28	1.72
TiO <sub>2</sub>	0.10	0.07	0.00	0.09	0.07	0.20	4.22	0.07	0.21	0.28	0.34	1.50	0.83
ZrO <sub>2</sub>	35.50	38.65	38.08	42.84	47.26	47.43	45.23	61.71	60.73	59.23	58.07	58.83	57.29
P <sub>2</sub> O <sub>5</sub>	0.76	0.59	0.60	0.58	0.70	0.58	0.68	0.10	0.10	0.00	0.20	0.11	0.01
Y <sub>2</sub> O <sub>3</sub>	0.34	0.20	0.27	0.29	0.16	0.11	0.91	0.14	0.27	0.00	0.29	0.24	0.06
Cr <sub>2</sub> O <sub>3</sub>	0.79	0.00	0.03	0.01	0.01	0.02	0.01	0.01	0.00	0.00	0.00	0.04	0.00
Total	99.32	98.94	98.39	99.08	99.97	99.44	88.49	99.89	98.26	99.04	99.01	96.66	97.55
Si <sup>4+</sup>	0.997	1.010	1.012	1.018	1.012	1.015	0.988	1.003	0.992	1.000	0.992	1.005	1.015
Hf <sup>4+</sup>	0.340	0.305	0.308	0.246	0.199	0.194	0.104	0.050	0.048	0.065	0.078	0.035	0.059
U <sup>4+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.002	0.004	0.009	0.006	0.009	0.012
Ti <sup>4+</sup>	0.001	0.001	0.000	0.001	0.001	0.002	0.036	0.000	0.002	0.002	0.002	0.011	0.006
Zr <sup>4+</sup>	0.612	0.660	0.653	0.710	0.761	0.767	0.822	0.941	0.947	0.925	0.911	0.932	0.906
P <sup>3+</sup>	0.023	0.017	0.018	0.017	0.020	0.016	0.021	0.003	0.003	0.000	0.005	0.003	0.000
Y <sup>3+</sup>	0.006	0.004	0.005	0.005	0.003	0.002	0.018	0.002	0.005	0.000	0.005	0.004	0.001
Cr <sup>3+</sup>	0.022	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Total	2.001	1.997	1.997	1.996	1.996	1.997	1.999	2.000	2.000	2.000	2.000	2.001	2.000
H*	0.36	0.32	0.32	0.26	0.21	0.20	0.11	0.05	0.05	0.07	0.08	0.04	0.06
	Tap (3)	Tap (4)	Tap (2)	Tan (2)	Tan (4)	Tan (2)	Col (10)	Col (2)	Col (2)	Col (1)	Col (1)	Col (1)	Col (1)
Nb <sub>2</sub> O <sub>5</sub>	4.41	3.38	2.92	17.71	24.54	26.39	44.50	76.16	73.33	71.14	70.40	75.49	71.49
Ta <sub>2</sub> O <sub>5</sub>	78.52	78.79	78.41	62.76	56.12	52.20	31.34	2.51	4.62	4.66	4.87	2.10	5.87
FeO	12.86	13.09	13.27	9.16	10.68	10.39	8.97	15.42	14.78	15.16	17.42	15.79	13.79
MnO	1.08	0.88	0.84	5.89	5.40	5.49	8.81	5.84	5.64	5.29	3.47	5.47	6.28
SiO <sub>2</sub>	0.51	1.10	1.14	0.20	0.07	0.10	0.26	0.04	0.09	0.00	0.14	0.06	0.02
TiO <sub>2</sub>	1.21	2.42	2.97	2.46	1.22	1.52	2.81	0.41	0.39	0.57	1.55	0.53	0.61
WO <sub>3</sub>	0.24	0.41	0.26	1.15	1.55	2.59	2.47	0.58	0.63	1.45	1.61	0.80	1.18
Total	98.83	100.07	99.81	99.33	99.58	98.68	99.16	100.96	99.48	98.27	99.46	100.24	99.24
Nb <sup>5+</sup>	0.165	0.124	0.107	0.600	0.807	0.862	1.299	1.935	1.907	1.878	1.835	1.931	1.874
Ta <sup>5+</sup>	1.768	1.739	1.729	1.279	1.110	1.026	0.550	0.038	0.072	0.074	0.076	0.032	0.093
Fe <sup>2+</sup>	0.891	0.889	0.900	0.574	0.650	0.628	0.484	0.725	0.711	0.741	0.840	0.747	0.669
Mn <sup>2+</sup>	0.076	0.061	0.058	0.374	0.333	0.336	0.482	0.278	0.275	0.262	0.170	0.262	0.309
Si <sup>4+</sup>	0.017	0.034	0.037	0.006	0.002	0.003	0.007	0.001	0.002	0.000	0.003	0.001	0.000
Ti <sup>4+</sup>	0.075	0.148	0.181	0.139	0.067	0.083	0.137	0.017	0.017	0.025	0.067	0.023	0.027
W <sup>6+</sup>	0.005	0.009	0.005	0.022	0.029	0.048	0.042	0.008	0.009	0.022	0.024	0.012	0.018
Total	2.997	3.005	3.017	2.993	2.998	2.986	3.001	3.004	2.994	3.002	3.015	3.008	2.990
T**	0.91	0.93	0.94	0.68	0.58	0.54	0.30	0.02	0.04	0.04	0.04	0.02	0.05

The number in parentheses indicates the number of analytical data-sets that have been averaged to give the composition quoted. Symbols: Zrn zircon, Tap tapiolite, Tan tantalite, Col columbite. \* H represents the value of the ratio Hf/(Zr + Hf) in zircon; \*\* T represents the value of the ratio Ta/(Nb + Ta) in the niobo-tantalates. The concentration of elements is reported as oxides, in weight %.

explained either by a crystal-chemical coherence between Hf and Ta, or by a geochemical parallelism in the behavior of Hf and Ta in the magma or in a late-stage fluid phase.

We note that where the zircon and niobo-tantalates are not in contact, the correlation is not as good. For example, in the same sample 26S, in cases of intergrowth with hafnian zircon, the Ta mineral is tapiolite in which Ta/(Nb + Ta) is equal to 0.91. In the case of an isolated grain of zircon, tantalite is the coexisting phase [Ta/(Nb + Ta) = 0.65]. It thus seems that the correlation between the ratios Hf/(Zr + Hf) and Ta/(Nb + Ta) is obeyed only where local equilibrium is attained between zircon and an (Nb-Ta)-bearing mineral. From the geochemical point of view, zirconium and hafnium are close to niobium and tantalum. In highly evolved rocks, notably in granitic pegmatite, tantalum may become completely separated from niobium and form independent minerals (von

Knorring & Hornung 1961), whereas hafnium is invariably incorporated in zircon (*s.l.*), the only exception being the case of hafnon in Mozambique (Correia Neves *et al.* 1974). In light of the preceding remarks, we contend that there exists a similarity in the thermal stability of the complexes of Ta and Hf, which ultimately leads to the simultaneous precipitation of Ta and Hf as tantalite or tapiolite and hafnian zircon, respectively, in the same local conditions, with a parallel evolution of Nb/Ta and Zr/Hf. The affinity between Hf and Ta would thus be more geochemical than crystal-chemical.

CONCLUSIONS

1. Zircon is an accessory mineral invariably present in the evolved facies of the Suzhou granite; however, its composition is quite variable. Zircon relatively poor in hafnium (HfO<sub>2</sub> < 10%) is present in the early facies

containing biotite and topaz.

2. The hafnian zircon of the late-stage albite-enriched facies may contain more than 25% HfO<sub>2</sub>, and may even attain 35%. This level is the highest known in zircon formed in a granitic or pegmatitic environment.

3. The great variation in the ratio Zr/Hf in zircon from different facies reveals a decoupling of Zr and Hf in the direction of enrichment in Hf, indication of a high degree of differentiation in the granitic magma. In view of the exceptional levels of enrichment of Hf in zircon, the Suzhou granite shows a typically pegmatitic character, already pointed out in the Beauvoir granite.

4. The zircon defines a close association, and locally an intergrowth, with niobo-tantalates. A study of thirteen cases of the association zircon + niobo-tantalates from the different facies has revealed a correlation between the ratios Hf/(Zr + Hf) in the zircon and Ta/(Nb + Ta) in the niobo-tantalates. This affinity between Hf and Ta is best explained by a geochemical parallelism in the extent of decoupling of Zr from Hf and of Nb from Ta in the conditions of local chemical equilibrium.

#### ACKNOWLEDGEMENTS

The first author expresses his gratitude to the Ministry of National Education and to the Foundation of Natural Sciences of China for financial help in connection with this research, and for his stay at Toulouse. He also thanks Prof. J.P. Fortuné, who graciously hosted him once again in the Laboratoire de Toulouse. The authors thank Dr. P. de Parseval, as well as Profs. Zhu Jin Chu, Liu C.S., and Shen W.Z. for their help during the field and laboratory studies. We thank T. Birkett, R.F. Martin and R. Linnen for their constructive criticism, which led to important improvements. Sincere thanks to Mrs. V. Martin for the English translation.

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Received January 3, 1996, revised manuscript accepted June 17, 1996.