

Crystal-chemistry of zirconolite and calzirtite from Jacupiranga, São Paulo (Brazil)

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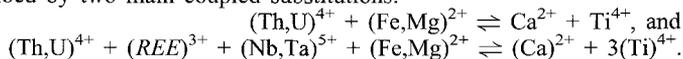
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ABSTRACT

A specimen of zirconolite, collected from the type locality of the mineral originally described as zirkelite at Jacupiranga, São Paulo, Brazil has been re-examined and its mineral chemistry more completely characterized. All crystals studied are metamict and display very fine lamellar oscillatory zoning (1–3 µm in width) superimposed on a sector zonation. Such zoning, observed in backscattered electron images, is primarily related to differences in the concentration of Th.

In comparison with other reported zirconolite samples from a variety of geological occurrences, Jacupiranga zirconolite has higher Ca, Th, (Nb + Ta) and lower Ti and REE, which is consistent with its occurrence in carbonatitic rocks. The compositional variation with respect to an ideal zirconolite is described by two main coupled substitutions:



Calzirtite, $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$, although intergrown with zirconolite and with identical major components, shows much less compositional variability with only minor amounts of Nb and Ta substituting for Ti. Unlike zirconolite, the REE and actinide elements are not easily accommodated in the calzirtite structure.

KEYWORDS: Jacupiranga, Brazil, zirconolite, calzirtite, mineral chemistry, compositional zoning.

Introduction

SEVERAL minerals have been reported in the literature which have stoichiometries close to $\text{CaZrTi}_2\text{O}_7$, but with different crystal structures. It is now known that the compound $\text{CaZrTi}_2\text{O}_7$ can exist as three superstructures with monoclinic, orthorhombic and trigonal symmetries, each recognized as polytypoids (Bayliss *et al.*, 1989). However, problems in identification and characterization have arisen in the past, in part because the frequent occurrence of actinide elements in the structure usually render the mineral partially or totally metamict, and in part because the often small grain size does not allow for routine crystallographic techniques to be employed. These problems have led to confusion in the nomenclature of these minerals, which has been addressed by Bayliss *et al.* (1989). They summar-

ized the crystallographic and chemical characteristics, detailed the historical documentation, and rationalized the nomenclature of those minerals which have stoichiometries close to $\text{CaZrTi}_2\text{O}_7$.

Under the Bayliss *et al.* (1989) IMA-approved nomenclature scheme, **zirconolite** is the non-crystalline (metamict) mineral, or the mineral with undetermined polytypoid of $\text{CaZrTi}_2\text{O}_7$; **zirconolite-3O** is the three-layered orthorhombic polytypoid of $\text{CaZrTi}_2\text{O}_7$; **zirconolite-3T** is the three layered trigonal polytypoid of $\text{CaZrTi}_2\text{O}_7$; **zirconolite-2M** is the two-layered monoclinic polytypoid of $\text{CaZrTi}_2\text{O}_7$, and **zirkelite** is the cubic mineral with formula $(\text{Ti,Ca,Zr})\text{O}_{2-x}$. Polymignite was discredited as being identical to zirconolite (metamict). Smith and Lumpkin (1993) have subsequently described two additional polytypes, zirconolite-4M and -6T, which appear to be supercells of the zirconolite-2M and 3T structures respectively.

The name zirkelite was originally introduced for a new Ca, Zr, Ti oxide mineral found associated with baddeleyite and perovskite in a sand deposit originating from disaggregation of a pyroxenitic rock at Jacupiranga, São Paulo (Hussak and Prior, 1895). This mineral occurs as flattened and twinned octahedra, opaque and black coloured in hand specimen; smaller fragments are transparent with a dark-brown or a reddish-brown colour. From the bulk chemical analysis of Prior (1896), Palache *et al.* (1944) derived a formula corresponding to $\text{Ca}_2(\text{Zr,Ti})_2\text{O}_5$. The same material was later re-analysed by Pudovkina *et al.* (1974) and Sinclair and Ringwood (1981), and more recently by Williams and Gieré (1996), these analyses being compatible with the $\text{CaZrTi}_2\text{O}_7$ stoichiometry of zirconolite (Table 1).

The determination of the structure of this mineral from Jacupiranga has been attempted by several workers, but produced mixed, and contradictory results. The material originally described by Hussak and Prior (1895) is metamict, and following the Bayliss *et al.* (1989) nomenclature scheme, is **zirconolite *sensu stricto***. In the study by Sinclair and Ringwood (1981), they reported that the natural (i.e. unheated) samples gave a weak cubic defect fluorite-type diffraction pattern (unlike the samples studied by Pudovkina *et al.* (1974) which were metamict), and would thus correspond to **zirkelite**. The cubic zirkelite structure was obtained by both Pudovkina *et al.* (1974) and Sinclair and Ringwood (1981) on heating to 800°C (Pudovkina *et al.*, 1974) and to 1100°C (Sinclair and Ringwood, 1981). However, on heating their samples to 1200°C, both these studies obtained complex X-ray spectra consistent with a monoclinic symmetry (Table 2), i.e. **zirconolite-2M**.

Here we report a detailed SEM and micro-chemical study of this mineral from Jacupiranga, Brazil, characterize its crystal-chemistry, and show that its composition is consistent with zirconolite from carbonatites. Additionally, we present new microprobe data on calzirtite intergrown with this mineral, and compare these with data for calzirtite from other occurrences.

Materials and methods

The specimen studied consists of a polycrystalline aggregate, ~1 cm wide, comprising several reddish-black coloured crystals, the largest being 500 µm in size, and with a flattened, pseudo-

octahedral habit. The specimen was obtained from Mr L.A.D. Menezes Jr. (a Brazilian mineral collector) and collected at the occurrence described by Menezes and Martin (1984), which corresponds to the type locality of Hussak and Prior (1895). It is thus not the identical specimen originally described by Hussak and Prior, but is from the same locality.

A single grain was hand-picked and analysed by X-ray diffraction (Cu- $K\alpha$, Ni-filtered radiation) using a Gandolfi camera. After exposure for 48 h, no X-ray diffraction pattern was observed, indicating it to be completely metamict. Therefore, following the Bayliss *et al.* (1989) nomenclature, and taking into consideration the chemical composition, this mineral is **zirconolite**. Three different crystals were embedded in an epoxy resin grain mount and examined by backscattered electron (BSE) imaging and electron microprobe (EMPA). The BSE images and energy-dispersive spot analyses were undertaken using a high-resolution Philips XL30 SEM-EDAX operated at 25 kV and 30 nA beam current.

Quantitative microprobe analyses were obtained using a Cameca SX50 wavelength-dispersive electron microprobe operated at 20 kV accelerating voltage and 20 nA beam current. For the major components Ca, Ti, Zr, Nb, Fe and Th, the standards used were synthetic CaTiO_3 , ZrO_2 , NaNbO_3 , pure Fe metal and ThO_2 . For the minor elements, the standards used were a combination of well-characterized natural minerals, synthetic compounds and pure metals. Background positions, particularly for the rare earth elements, were carefully selected to avoid contributions from potentially interfering lines, and corrections were made for interfering elements following the procedure given in Williams (1996).

Zirconolite: $\text{CaZrTi}_2\text{O}_7$

Zonation

The BSE images show that the three crystals studied exhibit a pronounced and complex compositional zonation. Such zoning is known to survive metamictization resulting from long exposure to natural radioactivity from actinide elements in the structure (e.g. Fauquier, 1959; Hogarth *et al.*, in press; Gieré and Williams, 1992). Distinct zoning patterns are present and, in one of the crystals, a finely-developed oscillatory, lamellar zoning is observed (Fig. 1a), each

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TABLE 1. Chemical analyses (from the literature) of zirconolite from Jacupiranga

	H&P	Prior	Pudovk.	S&R	P1	P2
MgO	0.49	0.22		0.4	0.71	0.37
CaO	11.61	10.79	14.4	11.5	9.80	11.10
TiO ₂	30.89	14.95	25.3	24.3	21.00	22.30
MnO	—	—	—	0.2	0.28	0.26
FeO	6.64	7.72	—	7.2	7.16	7.37
Fe ₂ O ₃	—	—	7.9	—	—	—
Y ₂ O ₃	—	0.21	—	—	—	—
ZrO ₂	48.90	52.89	32.8	35.2	31.40	33.20
Nb ₂ O ₅	—	—	10.5	11.3	9.98	11.20
Ce ₂ O ₃	—	2.52	1.5	2.6 [†]	3.09 [†]	3.86 [†]
Nd ₂ O ₃	—	—	0.5	—	—	—
Ta ₂ O ₅	—	—	—	0.2	2.75	1.76
ThO ₂	—	7.31	8.0	6.6	14.00	8.65
UO ₂	—	1.40	—	0.4	0.86	0.36
Total	99.55*	99.03*	100.9	99.9	101.03	99.03
Formula based on 7 Oxygens						
Ca	—	—	0.98	0.80	0.72	0.79
Ce	—	—	0.04	0.06	0.08	0.09
Nd	—	—	0.01	—	—	—
Th	—	—	0.12	0.10	0.22	0.13
U	—	—	—	0.01	0.01	0.01
ΣA	—	—	1.15	0.97	1.03	1.02
Zr	—	—	1.01	1.12	1.05	1.07
ΣB	—	—	1.01	1.12	1.05	1.05
Ti	—	—	1.20	1.19	1.08	1.11
Mn	—	—	—	0.01	0.02	0.02
Fe ³⁺	—	—	0.38	—	—	—
Fe ²⁺	—	—	—	0.39	0.41	0.41
Mg	—	—	—	0.04	0.07	0.04
Nb	—	—	0.30	0.33	0.31	0.34
Ta	—	—	—	0.01	0.01	0.00
ΣC	—	—	1.88	1.97	1.90	1.92
Cations	—	—	4.04	4.06	3.98	3.98

H&P: Hussak & Prior (1895); Prior: Prior (1896); Pudovk.: Pudovkina *et al.* (1974)

S&R: Sinclair & Ringwood (1981)

P1, P2 from Williams and Gieré (1996)

* Includes loss on ignition: H&P = 1.02%; Prior = 1.02%

[†] Σ(Y+REE₂O₃)

[‡] REE determined as Σ(Y, Ce, La, Dy) but considered as Ce in the formula calculation

lamella having an average width of 2–3 μm (Fig. 1b). Such patterns are believed to be structurally controlled with the lamellae parallel to the crystallographic planes of low Miller indices (Shore and Fowler, 1996). This crystal is also intergrown with another mineral (calzirtite, see below), which appears darker with respect to the medium-grey contrast of the zirconolite host. The second zirconolite crystal studied also shows

a very fine-scale oscillatory zoning, in this case superimposed on sector zoning, and the third crystal displays a patchy and irregular zonation pattern.

Compositional variation is a common feature of zirconolites, and manifests itself in a variety of complex zonation types. Zoning appears to be ubiquitous in zirconolites from carbonatites (Williams *et al.*, in prep.) where it can appear as

TABLE 2. Lattice parameters of zirconolite-2M from Jacupiranga (specimens heated at 1200°C)

	1	2	3
a (Å)	12.55(2)	12.58(2)	12.592(1)
b (Å)	7.23(1)	7.24(1)	7.270(1)
c (Å)	11.39(2)	11.40(2)	11.451(1)
β (°)	100.5	100.4	100.56
V (Å ³)	1016	1021	1030.5(3)

1, 2: Pudovkina *et al.* (1974) – two different samples
 3: Sinclair and Ringwood (1981).

one or more zoning types observed here. Zoning results from the structure of zirconolite being able to accommodate a wide range of cation sizes and charges (Williams and Gieré, 1996), and so reflects fluid compositional changes which may have occurred during crystallization and any subsequent crystal growth.

Chemical composition

More than 80 point analyses were obtained on different parts of the three grains and in particular, as a detailed traverse across the fine lamellar zoning in the crystal depicted in Fig. 1a. In Table 3, the average compositions for the high- and low-Z parts of the crystals are presented, and for the traverse across the lamella zone. From the data of Table 3 it is apparent that, despite a clear variation in concentration of some elements (notably Th, and to a lesser extent Ca), the three grains are relatively homogeneous within each of the high- and low-Z regions.

The ThO₂ content is relatively high for zirconolite, varying from 5.1% to 11.3%, (compared with a value of 4.5% for zirconolites from the database of Williams and Gieré, 1996). This variation however, does not reflect a continuously variable composition, but instead corresponds to the two distinct areas (low- and high-Z, Table 3) observed in the BSE images. Analyses across the area of fine-scale oscillatory-zoned lamellae (Fig. 1) have intermediate ThO₂ contents, but as the width of the lamellae approached that of the spot size of the electron microprobe (i.e. 2–3 µm), it is likely that the analyses for the lamellae (Table 3) represent values which correspond, to varying degrees, to a mixture of low- and high-Z compositional zones.

The zirconolite described here from Jacupiranga is that reported from Menezes and Martin (1984), and was sampled from the heavy mineral fraction from pyroxene-bearing sands of “...the decomposed magnetite-pyroxenite of Jacupiranga”. (Hussak, 1895; Hussak and Prior, 1895; see also Pudovkina *et al.*, 1974). Because it has not been found unambiguously within the pyroxenite, its paragenesis has been described as one of two “Placer Deposit” localities in the review of zirconolite localities (Williams and Gieré, 1996). When the composition of Jacupiranga zirconolite obtained here is compared with those from a range of different parageneses, there are many similarities, in particular for the actinide elements (Th + U), REE and (Nb + Ta), to indicate a strong affinity to zirconolites from a variety of carbonatite host rocks. This is best seen in the ternary diagram with (Th+U), (REE) and (Nb+Ta) as apices (Fig. 2). Although the mean

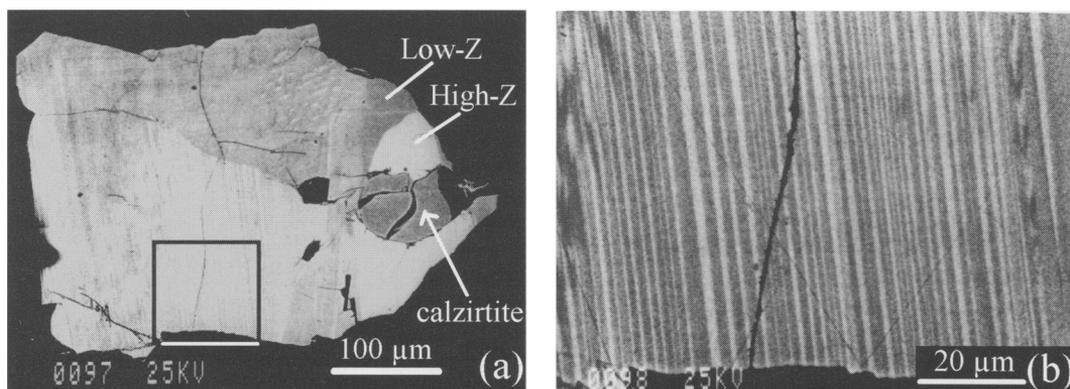


FIG. 1. BSE images of (a) crystal (1); (b) detail of the fine lamellar zone of crystal from boxed area in (a).

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TABLE 3. Electron microprobe analyses (this study) of zirconolite and associated calzirtite from Jacupiranga

	Low-Z (6 anal.)		Zirconolite				Calzirtite	
	mean	s. d.	High-Z (8 anal.)		Lamellar (37 anal.)		3 analyses	
			mean	s. d.	mean	s. d.	mean	s. d.
MgO	0.40	0.03	0.64	0.02	0.49	0.04	0.05	0.02
Al ₂ O ₃	0.14	0.01	0.12	0.01	0.12	0.01	0.07	0.02
SiO ₂	<0.03	—	<0.03	—	0.03	0.03	<0.03	—
CaO	11.56	0.20	10.36	0.16	10.83	0.23	11.87	0.09
TiO ₂	23.96	0.48	21.83	0.24	22.11	0.48	15.82	0.07
MnO	0.16	0.03	0.22	0.02	0.17	0.03	0.05	0.02
FeO	7.08	0.08	7.09	0.10	6.90	0.09	0.73	0.06
Y ₂ O ₃	0.33	0.05	0.32	0.03	0.31	0.04	0.04	0.03
ZrO ₂	32.75	0.59	31.22	0.33	31.27	0.42	67.33	0.57
Nb ₂ O ₅	10.71	0.26	11.47	0.22	11.22	0.31	1.90	0.06
La ₂ O ₃	0.15	0.01	0.14	0.01	0.14	0.01	<0.05	—
Ce ₂ O ₃	1.02	0.03	1.06	0.03	1.05	0.04	0.10	0.01
Pr ₂ O ₃	0.15	0.06	0.18	0.06	0.17	0.07	<0.10	—
Nd ₂ O ₃	0.64	0.24	0.87	0.12	0.80	0.17	<0.08	—
Sm ₂ O ₃	0.24	0.03	0.23	0.04	0.22	0.03	<0.08	—
Gd ₂ O ₃	0.23	0.04	0.16	0.06	0.15	0.05	<0.10	—
Dy ₂ O ₃	0.13	0.01	0.12	0.03	0.12	0.03	<0.07	—
Er ₂ O ₃	0.04	0.02	0.03	0.02	0.03	0.03	<0.06	—
HfO ₂	0.38	0.04	0.35	0.03	0.35	0.05	0.75	0.06
Ta ₂ O ₅	1.31	0.1	1.45	0.11	1.24	0.08	0.63	0.17
PbO	0.06	0.04	0.05	0.03	<0.05	—	<0.05	—
ThO ₂	6.86	0.86	9.82	0.56	7.59	0.51	<0.05	—
UO ₂	0.73	0.06	0.99	0.07	0.82	0.08	<0.05	—
Total	99.03	0.36	98.72	0.53	96.13	0.78	99.34	0.63
ΣY+REE ₂ O ₃	2.93	0.19	3.11	0.24	2.99	0.27	<0.25	—
Formula based on 7 Oxygens				Formula based on 16 O				
Ca ²⁺	0.821	0.011	0.758	0.009	0.800	0.013	1.916	0.019
Y ³⁺	0.012	0.002	0.012	0.001	0.011	0.001	0.003	0.002
La ³⁺	0.004	0.001	0.003	0.001	0.004	0.000	0.000	—
Ce ³⁺	0.025	0.001	0.026	0.001	0.027	0.001	0.003	0.002
Pr ³⁺	0.004	0.002	0.004	0.001	0.004	0.002	0.000	—
Nd ³⁺	0.015	0.006	0.021	0.003	0.020	0.004	0.000	—
Sm ³⁺	0.006	0.001	0.005	0.001	0.005	0.001	0.000	—
Gd ³⁺	0.005	0.001	0.004	0.001	0.003	0.001	0.000	—
Dy ³⁺	0.003	0.000	0.003	0.001	0.003	0.001	0.000	—
Er ³⁺	0.001	0.001	0.001	0.001	0.001	0.001	0.000	—
Pb ²⁺	0.001	0.001	0.001	0.001	0.000	—	0.000	—
Th ⁴⁺	0.104	0.014	0.153	0.009	0.119	0.009	0.000	—
U ⁴⁺	0.011	0.001	0.015	0.001	0.012	0.001	0.000	—
Σ Ca ²⁺	1.011	0.009	1.006	0.006	1.009	0.006	1.922	0.017
Zr ⁴⁺	1.059	0.014	1.040	0.007	1.051	0.008	4.944	0.014
Hf ⁴⁺	0.007	0.001	0.007	0.001	0.007	0.001	0.033	0.003
Σ Zr ⁴⁺	1.066	0.014	1.047	0.006	1.058	0.008	4.977	0.015
Ti ²⁺	1.195	0.019	1.122	0.006	1.147	0.019	1.792	0.005
Si ⁴⁺	0.000	—	0.000	—	0.002	0.002	0.000	—
Mg ²⁺	0.040	0.003	0.065	0.003	0.051	0.005	0.011	0.003
Mn ²⁺	0.009	0.001	0.013	0.001	0.010	0.001	0.007	0.002
Fe ²⁺	0.392	0.007	0.405	0.008	0.398	0.005	0.092	0.007
Al ³⁺	0.011	0.001	0.009	0.001	0.010	0.001	0.013	0.003
Nb ⁵⁺	0.321	0.009	0.354	0.006	0.350	0.011	0.129	0.004
Ta ⁵⁺	0.024	0.002	0.027	0.002	0.023	0.002	0.026	0.007
Σ Ti ²⁺	1.992	0.009	1.995	0.007	1.991	0.008	2.070	0.013
Cations	4.070	0.002	4.048	0.006	4.058	0.006	8.969	0.009

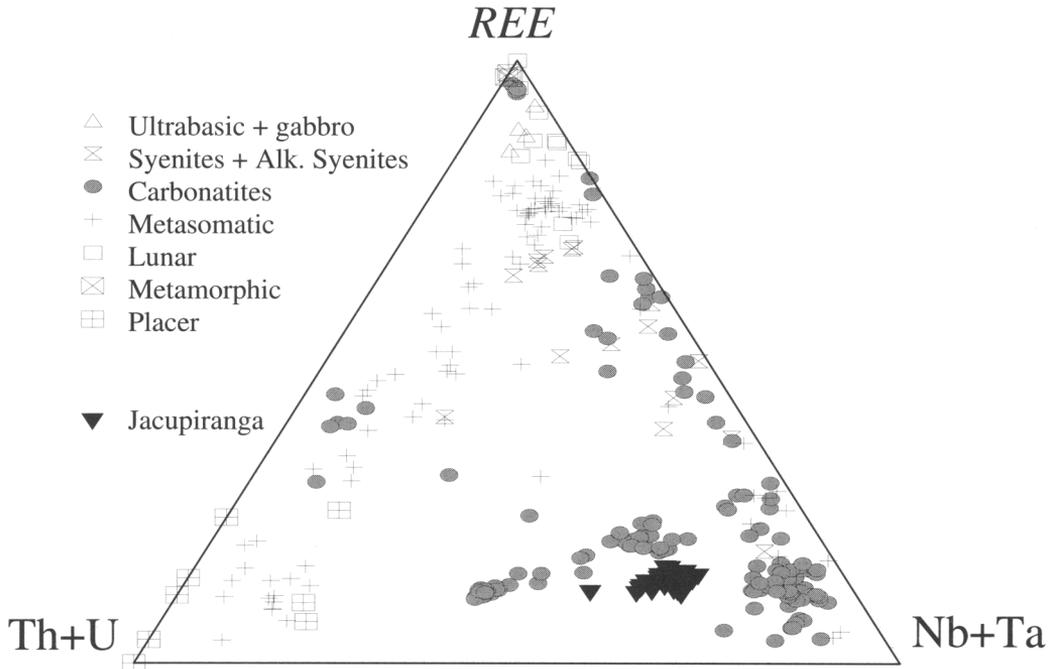


FIG. 2. Ternary plot of cations (Th+U), (Y+REE) and (Nb+Ta) of zirconolites from a range of parageneses. Data and source references are given in Williams and Gieré (1996).

ThO₂ and Y+REE₂O₃ contents for Jacupiranga zirconolite are typically slightly lower than average carbonatites (7.9% cf. 8.2% ThO₂, and 3.0% cf. 5.1% Y+REE₂O₃ -- data from Williams and Gieré, 1996), and the mean Nb₂O₅+Ta₂O₅ content is slightly higher (13.0% cf. 8.6%), overall, the Jacupiranga zirconolite data correspond more closely to a carbonatitic affinity than any of the other paragenetic types.

There is no significant variation in the REE contents between the low- and high-Z parts of the crystals, indicating that there was no fractionation of the REE during growth of the different compositional variants. The chondrite-normalized REE pattern (Fig. 3) rises steeply from La to Nd, remains relatively constant from Nd to Gd, then decreases towards the heavier REE. This pattern is typical of that for zirconolites from carbonatitic and alkalic parageneses (Gieré *et al.*, 1998).

Chemical substitutions

Zirconolite has five cation sites which can accommodate a variety of elements which range

in both ionic charge and size (c.g. Ringwood, 1985; Williams and Gieré, 1996). In natural (as well as synthetic) zirconolite, the chemical variation is extensive, with the predominant substitutions being Y+REE and actinide elements for Ca, Hf for Zr, and Nb, Ta, W, Fe and Mg for Ti.

In the unheated sample of zirconolite from Jacupiranga, the [8]-coordinated Ca-site (M8) is occupied by 20–25% of actinide elements (Th,U) + REE (Table 3), and in Fig. 4, it can be seen that there is an excellent correlation between the actinide elements (dominated by Th) and Ca, with the data points corresponding to three groups: high-Z, low-Z and lamellar. The high- and low-Z groups include all analyses from the lighter and darker zones, respectively, and the lamella group includes all analyses across the lamellar zone of Fig. 1b. As indicated above, the intermediate Th values of the lamella group are likely to be artifacts of the poor spatial resolution of the electron microprobe spot size with respect to the size of the lamellae. Thus, the individual lamellae probably correspond to the dark and the light

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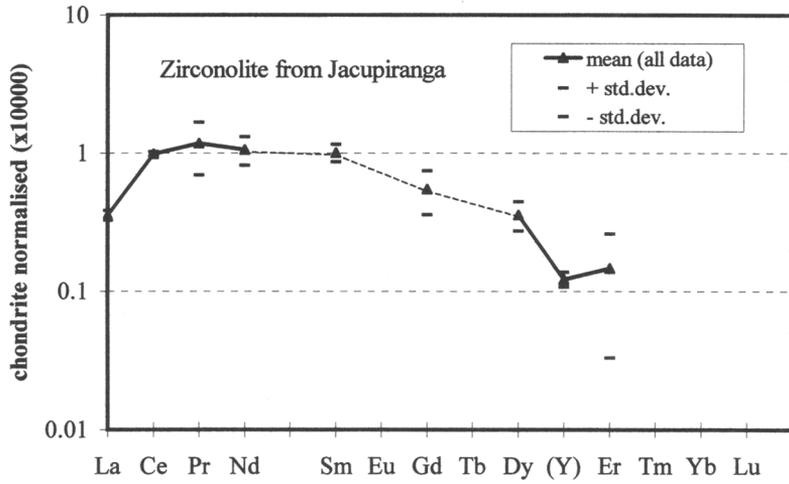


FIG. 3. Chondrite-normalized REE pattern for zirconolite from Jacupiranga (chondritic values from Wakita *et al.*, 1971).

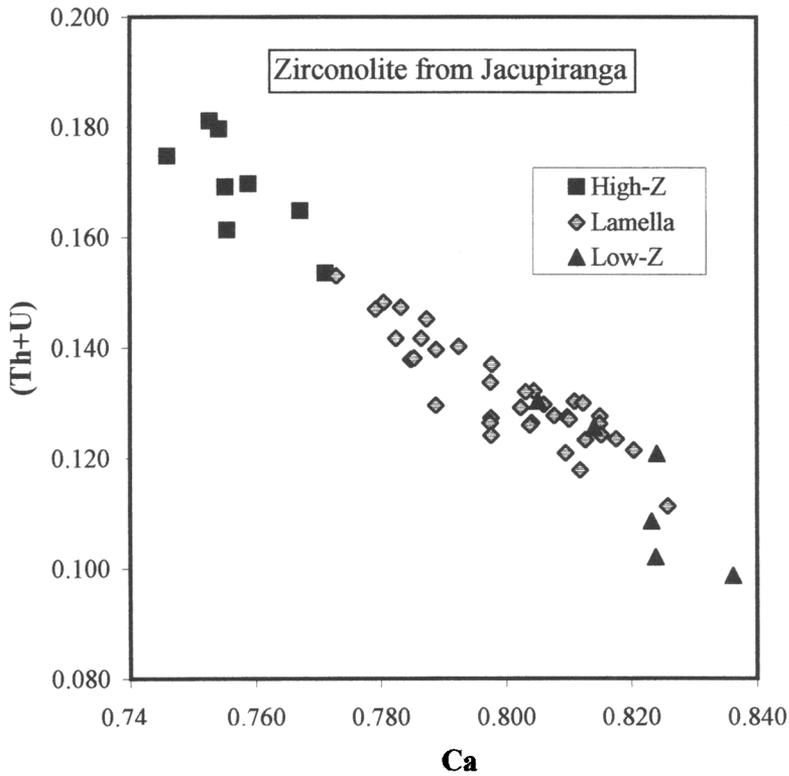


FIG. 4. Th+U plotted against Ca for the Jacupiranga zirconolite.

zones of the high- and low-Z groups and therefore represent oscillatory zones of high- and low-Th zirconolite compositions. The [7]-coordinated Zr-site (M7) (Table 3) is fully occupied by Zr together with minor amounts of Hf. As observed in some zirconolite analyses, this site can show a slight excess of cations (White, 1984; Williams and Gieré, 1996), with the possibility that excess Zr may enter either the Ca site (Gieré *et al.*, 1998), or one or more of the Ti sites (Cheary and Coelho, 1997).

Titanium occupies three sites (two octahedral, M4 and M6 and one [5]-coordinated polyhedron, M5) in which extensive substitutions of Fe and Nb for Ti, together with significant amounts of Ta and Mg (Table 3) can occur. In zirconolite, the incorporation of large, high-valence actinide cations is coupled with the simultaneous entry of smaller, lower-valence cations (e.g. Mg) into the Ti-site (Kesson *et al.*, 1983; Gieré and

Williams, 1992). In zirconolite from Jacupiranga, it can be seen from Fig. 5 that the $^{181}\text{Ca}+^{161}\text{Ti}$ content correlates well with the $^{181}\text{ACT}+^{161}(\text{Fe}+\text{Mg})$ content. Therefore, the accommodation of relatively large amounts of the actinide elements into the structure of the Jacupiranga zirconolites can be expressed by the coupled substitution $(\text{Th,U})^{4+} + (\text{Fe,Mg})^{2+} \rightleftharpoons \text{Ca}^{2+} + \text{Ti}^{4+}$. The well-defined linear trend of Fig. 5 also indicates that iron occurs mostly, if not entirely, in the divalent state, a feature characteristic of low-REE zirconolite samples (Williams and Gieré, 1988; Gieré and Williams, 1992; Gieré *et al.*, 1998). The major substitutions involving Ti-site cations are displayed in Fig. 6 which confirms that both divalent Fe (and Mg) and pentavalent Nb (and Ta) directly replace Ti, thus giving rise to a second coupled substitution of $(\text{Th,U})^{4+} + (\text{REE})^{3+} + (\text{Nb,Ta})^{5+} + (\text{Fe,Mg})^{2+} \rightleftharpoons (\text{Ca})^{2+} + 3(\text{Ti})^{4+}$.

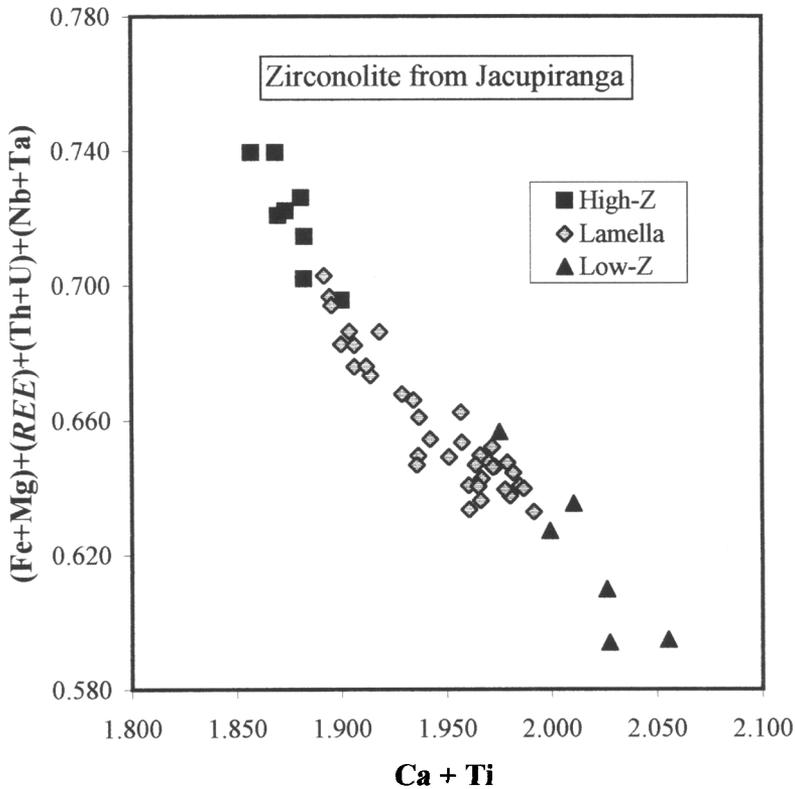


FIG. 5. $(\text{Th}+\text{U}+\text{Mg}+\text{Fe}^{2+})$ plotted against $(\text{Ca}+\text{Ti})$ for the Jacupiranga zirconolite.

ZIRCONOLITE AND CALZIRTITE

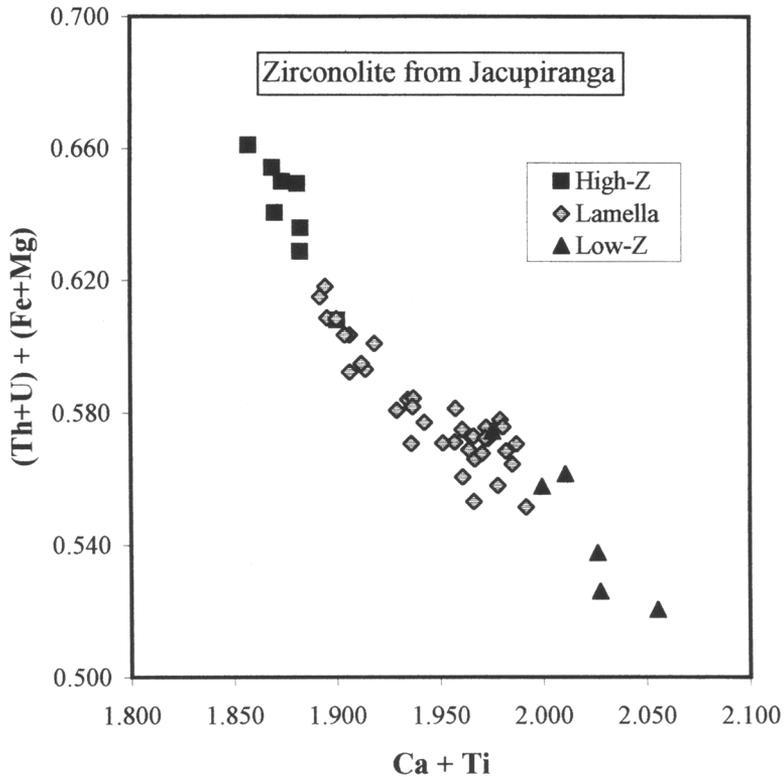


FIG. 6. All octahedral cation substitutions plotted against Ti for the Jacupiranga zirconolite.

Calzirtite: $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$

Table 3 also gives the average of three point analyses of a mineral intergrown with one of the zirconolite crystals (Fig. 1a). The chemical composition of this phase is clearly different from that of the host zirconolite and is consistent with the stoichiometry of the mineral calzirtite, $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$. Calzirtite is a rare accessory Ca-Zr-Ti oxide mineral described variously as tetragonal with space group *I4(1)/acd* (Rossell, 1982; Sinclair *et al.*, 1986), and as orthorhombic with space group *Pbca* (Callegari *et al.*, 1997), but which in the latter case, converted to the tetragonal symmetry after repeated heating at 700–1350°C. Calzirtite has been reported in metasomatic rocks from Siberia (Zdorik, 1961) and Japan (Henmi *et al.*, 1995); in several carbonatites in Russia (Bulakh *et al.*, 1967; Kogarko *et al.*, 1991; Williams and Kogarko, 1996), Germany (Sinclair *et al.*, 1986) and Canada (Williams and Platt, 1993), and in alluvial deposits associated with the

disaggregation of carbonatites (van der Veen, 1965). It has also been reported previously from Jacupiranga by Menezes and Martins (1984) and Sinclair *et al.* (1986).

Calzirtite shows significantly less compositional variation than zirconolite, with neither REE nor actinide elements being accommodated within the calzirtite structure, and only minor Nb and Ta substituting for Ti. This difference in compositional variability is in spite of these two minerals possessing identical major element components (i.e. Ca, Zr and Ti), and having been subjected to similar paragenetic conditions: calzirtite is intergrown with zirconolite both in Jacupiranga and also in Schryburt Lake, Canada (Williams and Platt, 1993). It is probable that the different crystal structures of these two Ca, Zr, Ti oxide minerals control the extent of element substitutions in the major cation sites for the major elements Ca, Ti and Zr.

Comparison of the composition of calzirtite, particularly for Nb (+Ta) and Ti, from

Jacupiranga with that of other localities (Fig. 7), shows some minor differences which may reflect the activities of these elements within the fluid (or melt) during crystallization of this mineral. Calzirtite from Jacupiranga has, in this study, significantly lower amounts of Nb+Ta than calzirtites from carbonatites at Guli (Russia), Schryburt Lake (Canada) and Kaiserstuhl, with 7.6% of (Nb+Ta) occupying the Ti-site compared with a mean of 16.0% for Guli, 13.4% for Schryburt Lake and 29.9% for Kaiserstuhl. The specimen of Jacupiranga calzirtite analysed by Sinclair *et al.* (1986) has significantly higher Nb than determined in this study, indicating that there is considerable sample-to-sample variation from this locality.

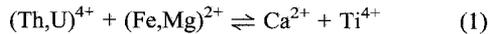
Conclusions

(1) Zirconolite from Jacupiranga is metamict. Its chemical composition is typical of zirconolites from carbonatitic rocks, with relatively high concentrations of Th, Fe and Nb.

(2) All of the grains studied display oscillatory, sector and irregular compositional zoning, predo-

minantly related to the distribution of Th (and antipathetically, Ca). All other elements analysed show little compositional variation. Complex zonation features such as described here appear to be typical of zirconolite, having been observed from several geological environments, and are the result of the extreme ease with which the zirconolite structure can respond to changes in the physico-chemical conditions of the system. Thus, differences in zirconolite composition may reflect even subtle chemical variations in fluid (or melt) composition (including those of the 'incompatible elements') as a function of time during its crystal growth. We suggest that zirconolite, if observed as an accessory mineral in samples, should be carefully checked for chemical zonation.

(3) The main substitutions controlling the composition of the Jacupiranga zirconolite can be expressed by the coupled substitutions:



and

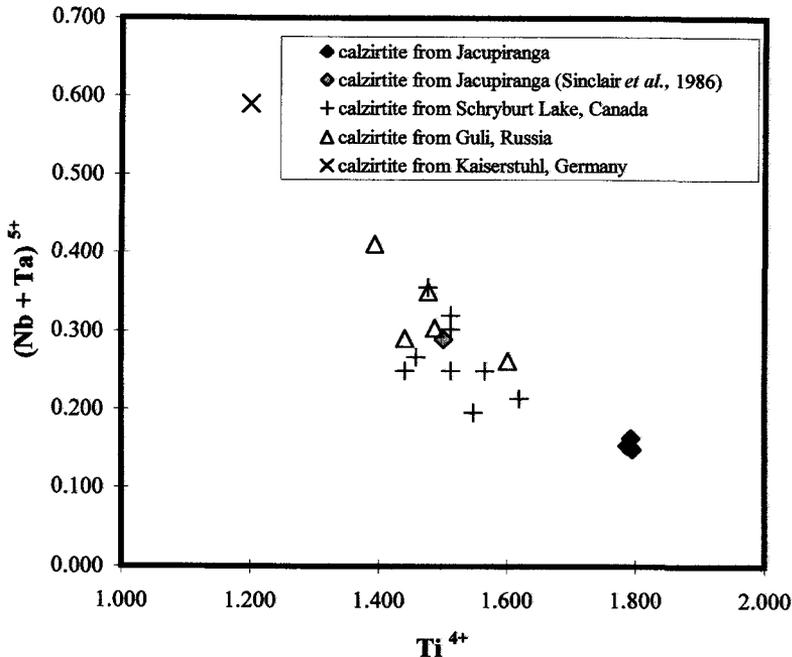
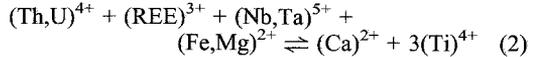


FIG. 7. (Nb+Ta) plotted against Ti for calzirtites from a range of localities. Data from Schryburt Lake are unpublished; Guli from (Williams and Kogarko, 1996) and Kaiserstuhl from Sinclair *et al.* (1986).

(4) Calzirtite, also a Ca,Zr,Ti oxide, is intergrown with zirconolite. Although it comprises the same major components as zirconolite, it is less able to accommodate substitutions of these elements by Fe, Nb, REE and actinides.

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