

New data on zircon from Matongo (Burundi)

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ABSTRACT

Zircon crystals from Matongo (Burundi) have a homogeneous core and a mantle of oscillatory zoning which is due to variations in the concentrations of ThO₂ (up to 0.7 wt.%), UO₂ (up to 400 ppm) and HfO₂ (0.2-0.6 wt.%) on a very small scale. Raman microspectrometry shows that the core of the crystals, which is richest in Th and U, is relatively metamict, whereas the outer mantle is relatively well crystallized. The ubiquitous presence of primary carbonate inclusions (calcite, magnesian calcite and nahcolite) corroborates the relationship of the Matongo zircon with the Upper-Rubuvu alkaline complex.

SAMENVATTING

Zirkoonkristallen van Matongo (Burundi) hebben een homogene kern en een mantel met een oscillerende zonering die veroorzaakt wordt door op zeer kleine schaal wisselende hoeveelheden ThO₂ (tot 0.7 gew.%), UO₂ (tot 400 ppm) en HfO₂ (0.2-0.6 gew.%). Raman microspectrometrie toont aan dat de homogene kern, die het rijkst is aan Th en U, relatief metamict is, terwijl de buitenmantel relatief goed kristallijn is. De algemene aanwezigheid van primaire carbonaatinsluitels (calciet, magnesiumhoudende calciet en nahcoliet) bevestigt de relatie tussen de zirkoon van Matongo en het Boven-Rubuvu alkalische complex.

KEYWORDS

Zircon, Raman microspectrometry, electron-microprobe analysis, inclusions, carbonatite, Burundi

Introduction

Thousands of isolated idiomorphic zircon crystals, up to 4 cm in size, occur in a laterite crust near Matongo, along the road from Bujumbura to Kayanza in Burundi. These zircon crystals have been described to some extent by Fransolet & Tack (1992). The crystals usually have a brownish colour and a dominant {101} morphology; X-ray diffraction showed that they are not metamict; in thin section, one or two concentric zones can be seen around a well-developed core. According to Fransolet & Tack (1992), this zonation does not correspond to variations in chemical composition, which was found to be stable, regardless of colour or zonation; trace-element contents are low: 0.8 to 1.1 wt.% HfO₂ and 0.12 to 0.17 wt.% ThO₂. The host rock of the zircon crystals

has never been observed, but the mineralogical properties of the crystals and a comparison with other alkaline complexes indicate that the crystals were formed from circulating alkaline fluids during a late-stage pegmatitic phase in the formation process of the Upper-Rubuvu alkaline plutonic complex (Fransolet & Tack, 1992). This origin is supported by the presence of primary carbonate inclusions in the zircon crystals (Tack *et al.*, 1996). The present study was carried out at the friendly request of L. Tack, to eventually corroborate the carbonatitic environment of the zircon crystals, but the opportunity was seized to do some detailed microprobe studies. All data in this paper have been obtained on thin and thick sections cut perpendicularly to the [001] of zircon.

Raman microspectrometry

The degree of metamictization in zircon crystals can be investigated in several ways, in principle with every method of structural analysis. Recently, several authors have shown the possibilities of Raman spectroscopy for this kind of studies (Nasdala *et al.*, 1995, 1996; Wopenka *et al.*, 1996). A Raman spectrum is a plot of the intensity of the inelastically scattered radiation as a function of the Stokes Raman shift, the portion of the scattered light that is increased in wavelength. The positions of Raman peaks in a spectrum are expressed in units of relative wavenumbers (Δcm^{-1}), the difference in frequency between the exciting laser radiation and the Raman-scattered radiation.

Raman spectra of the Matongo zircon were obtained with a Dilor Microdil-28 multichannel laser Raman microprobe, using a 514 nm Ar-ion laser as source of excitation. The instrument and the measurement conditions have been described by Burke & Lustenhouwer (1987) and by Burke (1994). The positions of the Raman peaks have been calibrated against the position of the single Raman-active peak of diamond (1332 Δcm^{-1}). The spectra have a spectral resolution of about 7 cm^{-1} and a wavenumber accuracy of about 0.7 cm^{-1} . The laser spot diameter at the surface of the sample was 2 μm using an Olympus 50x objective, so that small areas of zircon zones could be analysed separately.

The most intensive peaks in the Raman spectrum of zircon are interpreted as internal vibrations of the SiO₄ units. Fig. 1 only shows the frequencies with wavenumbers around 1000 Δcm^{-1} : the ν_3 vibration is the SiO₄ antisymmetric stretch and has a theoretical value of 1008 Δcm^{-1} , and the ν_1 vibration is the SiO₄ symmetric stretch with a theoretical value of 974

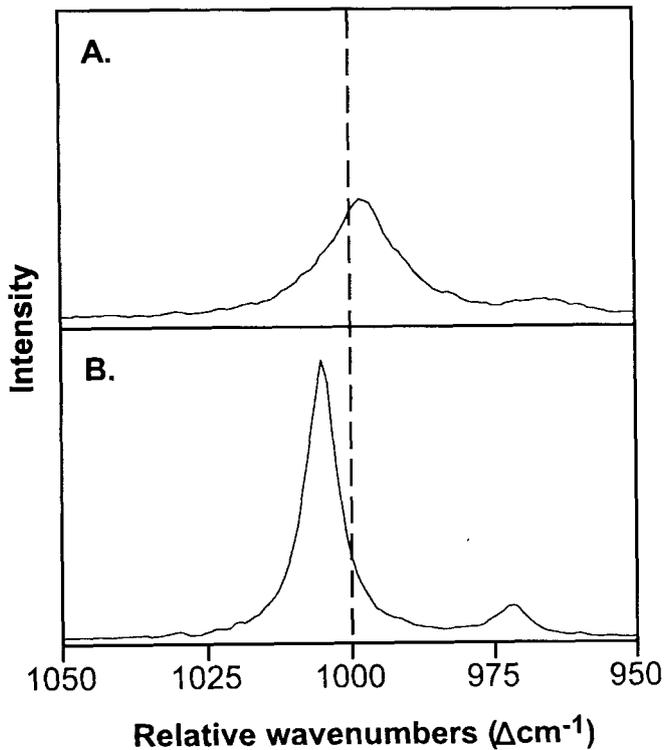


Fig. 1. Raman spectra of Matongo zircon; A: spectrum of the relatively metamict core; B: spectrum of a relatively well-crystallized zone in the outer mantle. The intensity scale is identical for both spectra.

Δcm^{-1} . The process of metamictization, however, greatly influences the Raman spectrum of zircon. With decreasing degree of lattice ordering, the peaks become less intense and broader, and their positions are clearly shifted to lower relative wavenumbers (Nasdala *et al.*, 1995, 1996; Wopenka *et al.*, 1996). This shift is especially large in the two bands around $1000 \Delta\text{cm}^{-1}$, and it is attributed to an increase in interatomic distances, i.e., the lattice of zircon is slightly expanded. The increase in peak widths and the accompanying decrease of intensity are attributed to the fact

that the distributions of bond lengths and bond angles between SiO_4 tetrahedra become increasingly irregular. Due to the very fine and intense oscillatory zoning of the Matongo zircon crystals (Fig. 2), which is not visible in thin or thick sections under light-optical microscopes, Raman spectra have only been obtained on the relatively homogeneous core, and on the broader zones of the outer parts of the crystals. Fig. 1 shows two extreme spectra: the lower one (B) is of the most crystalline zone in the outer mantle with peaks at 1005 and $972 \Delta\text{cm}^{-1}$, and the upper one (A) is from the core, the most metamict part of the crystal, with peaks at 998 and $965 \Delta\text{cm}^{-1}$, the latter one barely visible in Fig. 1. Both spectra were obtained at identical conditions of laser power, duration and number of accumulations. Different zones in the outer parts of the crystals yield only small differences for the two peaks: between 1002 and $1005 \Delta\text{cm}^{-1}$ for the ν_3 vibration, and 969 – $972 \Delta\text{cm}^{-1}$ for the ν_1 vibration.

Changes in all Raman parameters are evident from the two spectra in Fig. 1: decrease of intensity and relative wavenumber, and increase of peak width. The half-width of the intense Raman peak at about $1000 \Delta\text{cm}^{-1}$ is best suited for the investigation of changes connected with metamictization (Nasdala *et al.*, 1995, 1996). This peak in the lower spectrum of Fig. 1 has a half-width of about 7 cm^{-1} , whereas the same peak in the upper spectrum has a half-width of about 20 cm^{-1} . These values are similar to those given by Nasdala *et al.* (1995, 1996) for respectively intermediate and metamict zircon; their well-crystallized zircon specimens have half-widths of less than 5 cm^{-1} .

Electron-microprobe analysis

Chemical analyses on 43 spots across a crystal of the Matongo zircon were carried out with a Jeol JXA-8800M electron microprobe (wavelength-dispersive X-ray detection). The accelerating voltage was 20 kV , the probe current was 40 nA , the spot diameter was $5 \mu\text{m}$. The counting time was 20 s for the major elements Zr and Si, and 100 s for the minor and trace elements P, Hf, Th, U, Ti, Al, Fe and Ca.

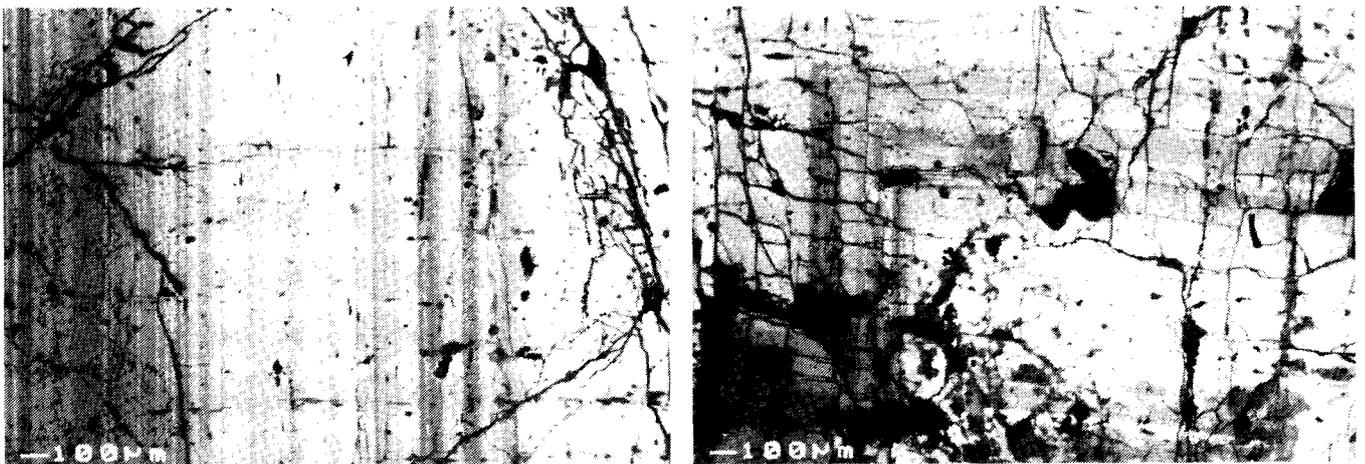


Fig. 2. Two examples of oscillatory zoning in Matongo zircon; back-scattered-electron photographs. Light zones have higher Hf, Th and/or U, darker zones have lower Hf, Th and/or U.

Table 1. Results (in wt. %) of selected electron-microprobe analyses of Matongo zircon.

	Outer zones				Core				Average of 43 analyses (Detection limit)	
SiO ₂	32.45	32.54	32.43	32.46	29.94	32.36	29.87	32.32	32.23	
P ₂ O ₅	0.03	0.04	0.01	0.01	0.26	0.03	0.22	0.05	0.03	(0.010)
ZrO ₂	65.63	65.59	65.30	67.02	64.17	68.17	64.75	67.79	66.79	
HfO ₂	0.58	0.44	0.52	0.25	0.20	0.24	0.22	0.20	0.35	(0.028)
ThO ₂	0.11	0.04	0.15	0.11	0.68	0.51	0.73	0.69	0.24	(0.020)
UO ₂	0.00	0.00	0.01	0.02	0.04	0.00	0.02	0.01	0.01	(0.019)
TiO ₂	-	0.01	0.01	-	0.15	-	0.15	-	0.01	(0.008)
Al ₂ O ₃	-	-	-	-	0.73	-	0.69	-	0.03	(0.005)
FeO	0.01	-	0.01	-	0.48	-	0.50	0.02	0.03	(0.010)
CaO	-	-	0.01	-	0.19	0.01	0.19	0.02	0.01	(0.006)
Total	98.81	98.66	98.45	99.87	96.84	101.32	97.34	101.10	99.73	

The Hf content has been checked for complete discrimination of the overlapping Zr K α second-order line: no Hf was measured on a pure zirconium metal standard. Only broader zones could be analysed as the oscillatory zoning is very fine and intense, as shown in back-scattered-electron photographs of the zircon crystals (Fig. 2). Rare-earth elements (REE) have not been analysed because the background of the Raman spectra is very low (Fig. 1), and because these spectra do not contain additional laser-induced fluorescence peaks attributed to REE ions; both phenomena indicate very low REE contents in zircon (Wopenka *et al.*, 1996), below the detection limits of electron-microprobe analysis.

Table 1 gives the results of selected analyses, obtained on a single Matongo zircon crystal. The trace-element contents differ somewhat from those given by Fransolet & Tack (1992), but this should not be a surprise in view of the macroscopic differences as reported between individual crystals. The present analyses yield lower HfO₂ contents (0.2 to 0.6 wt.%), but higher ThO₂ contents (up to 0.7 wt.%) and up to about 400 ppm UO₂. The core of the crystal has the highest ThO₂ and UO₂ contents: on average respectively about 0.65 wt.% and 250 ppm.

Some analyses of the core have low totals, of only about 97 wt.% (Table 1): this is probably due to the presence of molecular water and/or hydroxyl groups, which seem to be necessary to stabilize the metamict state of zircon (Woodhead *et al.*, 1991). These water and/or OH contents, however, are too low to be detected with Raman spectroscopy (Nasdala *et al.*, 1995).

Lighter zones in Fig. 2 correspond with higher contents of Hf, Th, and/or U, darker zones with lower contents of these elements. The correlation of the variation in chemical data with the different metamictization states as obtained from the Raman spectra is straightforward: zones with low Th and U contents are relatively well-crystallized; the core of the crystal, with its high Th and U contents, is relatively metamict (Fig. 1).

Inclusions

The Matongo zircon crystals contain abundant fluid and solid inclusions. Almost all fluid inclusions, however, show evidence of decrepitation, due to a sudden lowering of the pressure within the system. Because of this, most fluid inclusions are empty. Raman analyses on such inclusions show only traces of low-density CO₂, the main volume of fluid having been expelled from the inclusions by the decrepitation. Such inclusions cannot be used to construct isochores to provide data on the conditions of their formation.

The solid inclusions in zircon, especially the primary ones, contain mostly carbonates. Some solid inclusions show immiscibility phenomena: they contain carbonates, an opaque substance and glass. The frequency of the ν_1 vibration mode of carbonate minerals depends on their composition, and thus allows their identification, even as extremely small inclusions (less than 1 μm) because this mode is very intense. Raman microspectroscopy of these carbonate inclusions in the Matongo zircon shows the presence of different carbonate minerals: calcite (ν_1 at 1086 Δcm^{-1}), magnesian calcite (1088 Δcm^{-1}), and nahcolite (NaHCO₃, 1046 Δcm^{-1}). Similar carbonate inclusions have been described by Ting *et al.* (1994a and b) from the Sukulu carbonatite in Uganda.

Discussion

Oscillatory zoning is a common feature of zircon (Halden *et al.*, 1993; Shore & Fowler, 1996). In the Matongo zircon the pattern of variation among zones is symmetrical about the contact between the core and the outer mantle. The interpretation of such zoning is not without problems. In the Matongo zircon, the zoning is due to variations in the concentrations of Th, U and/or Hf on a very small scale, and variations of a similar scale are not observed in the level of the major elements. According to Halden *et al.* (1993) this type of oscillatory zoning is presumably connected with

nonequilibrium effects associated with differential diffusion of trace components through the fluid phase to the growing face of the crystal.

Fransolet & Tack (1992) stated that a radiometric age determination of the Matongo zircon would be useful to date the late-stage phase of the Upper-Rubuvu alkaline complex. In view of the described zoning in composition and metamictization (Fig. 1 and 2) this age determination should be carried out with some care.

The relationship of the Matongo zircon crystals with the Upper-Rubuvu complex has been consolidated by the nature of the primary carbonate inclusions in the zircon. Ting *et al.* (1994b) discussed the presence and the importance of inclusions of calcite, magnesian calcite and nahcolite for the interpretation of alkalis in carbonatite systems.

Acknowledgements

Crystals of the Matongo zircon have been provided by Luc Tack (Royal Museum for Central Africa, Tervuren). Electron-microprobe analyses have been carried out by Wim J. Lustenhouwer (Vrije Universiteit Amsterdam). Jacques L.R. Touret (Vrije Universiteit Amsterdam) has described the inclusions. Facilities for Raman microprobe and electron-microprobe analyses were provided by the Vrije Universiteit Amsterdam and by NWO, the Netherlands Organization for Scientific Research.

This paper is dedicated to Prof. Jules Moreau, who transmitted to me during his lectures in 1963-1965 the most important aspect of mineralogy: the love for it.

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