Bull. Soc. belge de Géologie	T. 88	fasc. 1	pp. 25-31	Bruxelles 1979
Bull. Belg. Ver. voor Geologie	V. 88	deel 1	blz.25-31	Brussel 1979

THE OCCURENCE OF ZIRCON AND BADDELEYITE CRYSTALS IN THE KIMBERLITE FORMATIONS AT MBUJI-MAYI (BAKWANGA, ZAIRE).

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ABSTRACT. - Zircon and baddeleyite have been found in the kimberlite of Mbuji-Mayi, Zaïre. Coatings on both zirconium minerals are described. The uranium and hafnium content was determined. The problem of the genetic relationship between zircon and baddeleyite is discussed.

INTRODUCTION.

The history of the crystallization of kimberlite magmas is still hardly understood. Probably the breccia-shaped nature of the kimberlite is the reason why there is so much controversy about the origin of several minerals present in it.

Although zircon does not belong to the group of typical satellite minerals of diamond it is an accessory mineral of most kimberlites and is considered as typomorph of these rocks.

Kresten (1975) has summarized the important characteristics of zircon in a general study of kimberlitic zircons. On the base of the common association of zircon with phlogopite, ilmenite and diamond Kresten shows the close relationship between zircon and diamond. On the contrary baddeleyite has only rarely been mentioned in the kimberlite literature. It has been found in a few Yakutian (USSR) kimberlite pipes (Frantsesson 1970) closely associated with carbonatites.

Kresten (1973) describes four different types of coating of baddeleyite on zircon in kimberlites from Lesotho.

Raber and Haggerty (1977) mention the presence of baddeleyite as an "interface" mineral between zircon and rutile crystals, also between zircon and ilmenite from kimberlites.

Baddeleyite is an important mineral in the carbonatitic complex at Phalaborwa (South-Africa).

C. Fieremans (1966) noticed the relative abundance of baddeleyite grains in the mineral concentrates from the Mbuji-Mayi kimberlite breccia. The presence of baddeleyite as rather large grains (0,5 - 1 cm.) may be considered as an exceptional event.

Several hundred grains of zircon and baddeleyite from the Mbuji-Mayi kimberlite have been placed at the disposal of the authors by C. Fieremans.

The intention of this contribution is twofold :

1. to present new data about the mineralogy and the trace element content of zircons and baddeleyite from Mbuji-Mayi;

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2. to discuss the implications of these data on the genesis of baddeleyite and zircon, as well as on their paragenesis.

METHODS.

The identification of coatings on zircon and baddeleyite grains from Mbuji-Mayi was carried out by X-ray diffraction using a Debye-Scherrer and a Gandolfi-Camera ($CuK\alpha$ radiation, Ni-filter). Baddeleyite grains have been identified by microscopy, Behrman density balance and X-ray diffractometry ($CoK\alpha$ radiation, Fe-filter; Silicon was used as an internal standard).

Hafnium was determined by X-ray fluorescence techniques, using the $HfK\alpha$ line and $HfOCl_2 \cdot 8H_2O$ as internal standard. The precision is assumed to be 5%.

The uranium content was determined by means of the neutron activation method using the BR1 research reactor at the SCK-CEN Mol. 200 mg samples were irradiated together with uranylnitrate Standards $UO_2(NO_3)_2 \cdot 6H_2O$ from Merck . The total neutron flux was $2.1 \times 10^{11} n.cm^{-2}$. Consecutive measurements every 20 minutes were carried out by means of a NaI-spectrometer connected to a multichannel analyser. The uranium figures have been statistically extrapolated after correction for the accompanying elements. The precision of this method is 10 %.

ZIRCON.

According to a personal communication by C. Fieremans the zircon content of the Mbuji-Mayi kimberlite breccia is smaller than 0,5 gram/ton. The mean grain size of the zircons examined during this study is 0,5 cm. Twenty zircon crystals were about 1 cm large and three had a diameter of 2 cm. The crystals showed no definite faces but were rounded.

The colour varies from light yellow to orange-brown. Several zircon crystals are colourless.

Thin sections of several coloured specimen show certain lineations of black or brown, almost opaque inclusions. The nature of these inclusions has not yet been explained. A few zircon crystals contain a network of liquid inclusions. This phenomenon has been described by Kresten (1975).

Five zircon crystals showed a hard white, surface coating of baddeleyite. We compare the X-ray diffraction pattern of this coating to different types of coating on kimberlitic zircons from Lesotho as mentioned by Kresten (1973) (see Table 1).

The search for characteristic trace elements in well-defined rock types has stimulated several workers to determine the uranium, thorium and hafnium contents in kimberlitic zircons.

Since hafnium was the only substituting metal in the zircons examined Zr content was obtained by difference on the assumption that the formula was $(Zr, Hf)SiO_4$. The results are collected in table II.

In order to prove connection between the presence of zircon and the diamond content of kimberlitic intrusions, Kresten (1975) looked for characteristic features of kimberlitic zircon crystals. One of these is the frequency of liquid inclusions of zircon crystals from kimberlites. This can be confirmed for the zircons in Kimberlitic pipes at Mbuji-Mayi (see photo's), which are the richest in the world with regard to diamond grade. We are, however, sceptic about the usefulness of zircon in finding diamond deposits, because zircon is more sporadic than diamond in the rocks concerned.

TABLE 1

Comparison of X-ray diffraction patterns of coatings on kimberlite Zircons from Lesotho (Kresten 1973) and from Mbuji-Mayi. (Data 1 to 5 from Kresten, 1973).

1	2	3	4	5	6
Coating type 1 Kao satellite	Coating type 1 Monastery	Coating type 2 Dyke 170	Coating type 3 Noeniput	Coating type 4 Lemphane	Mbuji-Mayi
5,10 vvw	5,06 vvw	5,04 vw	5,07 vw		4,98 vvw
4,30 vvw			4,45 vw	4,42 vvw	4,41 vw
3,66 m b	3,67 w	3,68 mw	3,67 ms		3,67 w
	3,32 vw		3,32 vvw	3,31 vvw	3,30 vvw
3,159 vvs	3,147 vs	3,165 vs	3,149 vvs	3,161 vs	3,16 s
	3,029 vw				
2,946 s	2,948 vvs	2,947 vvs	2,942 w	2,956 vvs	2,94 vw
2,841 vs }	2,834 ms	2,836 vs	2,834 vs	2,837 vs	2,84 ms
2,618 mw } b	2,625 w	2,617 w	2,612 s	2,631 vw	2,614 w
2,572 w }				2,563 w	
	2,542 mw	2,556 mw	2,530 mw	2,516 vw	2,521 w
			2,485 vvw		
2,327 vvw		2,333 vw	2,323 vvw		2,332 vw
2,212 vw	2,205 w	2,213 w	2,203 mw b	2,214 vw	2,206 w
2,182 vvw		2,183 vw			2,191 vw
2,015 vvw	2,017 vvw	2,020 vw	2,017 w		2,018 vw
1,987 vvw	1,992 vvw	1,987 vw	1,985 w		1,989 vw
1,937 vvw					
1,842 w	1,846 vw	1,846 w	1,845 s		1,841 w
1,814 s	1,812 s } c		1,814 s		
1,805 s	1,805 s }	1,809 vs	1,800 ms	1,807 vs	1,807 mw
		1,779 vw	1,781 vvw		
1,690 w	1,696 vw	1,693 w	1,688 w		1,692 w
1,656 w	1,656 vw	1,655 mw	1,656 s		1,652 mw
1,640 vw					
1,606 vvw		1,611 w	1,606 vw		1,602 vw
			1,585 vvw		1,580 vw
	1,556 vw				
1,542 s	1,536 ms	1,543 vvs	1,537 ms	1,541 vs	1,541 mw
1,507 vvw			1,507 vw		1,507 vw
1,497 vvw			1,491 vw		1,492 vw
1,476 w	1,475 w	1,479 mw	1,473 w	1,479 w	1,475 w
			1,448 vvw		1,446 vvw
1,420 vw		1,421 vw	1,418 vw		1,419 w

TABLE II - Uranium and Zr/Hf ratios in Kimberlitic zircons from Mbuji-Mayi.

N°	colour	Hf wt %	Zr wt %	Zr/Hf	Uppm
1	white	1.30	48.79	37.53	45
2	light brown	1.30	48.79	37.53	14
3	light brown	1.61	48.55	30.15	16
4	white	1.58	48.57	30.74	28
5	light brown	1.34	48.75	36.38	21
6	white	1.05	48.97	46.63	15
7	white	1.41	48.71	34.54	n.d.
8	light yellow	1.39	48.72	35.05	n.d.
9	orange brown	1.18	48.88	41.42	n.d.
10	brown	n.d.	n.d.	n.d.	38
11	brown	n.d.	n.d.	n.d.	12
12	white	n.d.	n.d.	n.d.	16
13	white	n.d.	n.d.	n.d.	25

n.d. = not determined.

TABLE III - Comparison between zircons from Mbuji-Mayi and from other occurrences.

Occurrences	#	Range Zr/Hf	Aver.Zr/Hf	#	Range U	Aver.U
Lesotho (1)	30	16.4 - 79.3	35.2	16	7.3 - 23.7	12
Rep.S.Afr. (2)	35	28.8 - 49.5	39.6	11	6.7 - 66	23.7
Tanzania (2)	8	43.7 - 52.5	47.18	3	9.4 - 22.4	14.3
Yakutian pipes (3)	13	39 - 59	46.27		n.d.	n.d.
Mbuji-Mayi	9	30.15 - 46.63	36.66	9	12 - 45	23

(1) Data KRESTEN (1975)

(2) Data Zr/Hf KRESTEN (1975)
Data U KRESTEN (1975) + ARHENS <u>et al</u>. (1967)

(3) Data NEKRASOVA <u>et al</u>. (1969)

BADDELEYITE.

All except one grain of baddeleyite found at Mbuji-Mayi have rounded or subrounded forms. A large individual has an euhedral shape. It is a twinned crystal with zonal structure and striations on the surface plains.

All the crystals are brown-black or iron-black. The density measured with the Behrman balance varies between 5.64 and 5.80. The Vickers micro-hardness values fall between 980 and 1027. The reflectivity R is about 20 %. Whitish internal reflections are always present and influence the reflectivity. A few baddeleyite grains contain microscopic inclusions of hematite along uneven factures. The other grains are pure.

The mean size of the baddeleyite grains is 0,5 cm; a diameter of 1 cm is not exceptional. Several baddeleyite grains have been analyzed for trace elements by X-ray fluorescence techniques. Besides hafnium, uranium and niobium traces of iron and copper have been found.

Only Hf, U and Nb have been analyzed quantitatively. The mean values for four baddeleyite grains are Hf 9.200 ppm, U 1.200 ppm, Nb 120 ppm.

Uranium has been determined in four other grains by means of the neutron activation method. The values are 770, 640, 430 and 600 ppm. A chemical analysis published in 1968 by C. FIEREMANS did mention neither Hf nor Nb. But U_3O_8 amounted to 0.061 % by weight and TiO_2 to 9.78 %. The high titanium content could be due to rutile inclusions in the baddeleyite or to contamination of the material analyzed.

Four grains of baddeleyite exhibit a thin crystalline coating of a red brown mineral that covers a part of the surface. This coating consists of zircon. One baddeleyite grain shows an annexe of zircon (1 mm thick) in an small "bay" in the baddeleyite surface.

Thermodynamic data related to the binary system SiO_2-ZrO_2 (NICHOLLS et al, 1971) (RABER and HAGGERTY, 1977) (BUTTERMAN and FOSTER, 1967) show that baddeleyite might coexist with zircon at 1,327°C and 57 Kbar. These P-T conditions lay within the stability field of diamond.

TABLE IV : X-ray diffractogram of baddeleyite from Mbuji-Mayi (Si has been used as internal standard.

d (Å)	I	d (Å)	I
5.08	6	2.016	6
3.69	16	1.992	7
3.63	14	1.849	13
3.163	100	1.817	20
2.837	53	1.803	11
2.625	16	1.780	4
2.604	13	1.695	10
2.538	18	1.658	10
2.503 b	3	1.638	11
2.334	4	1.611	6
2.213	10	1.590	3
2.179	7		

DISCUSSION.

The coexistence of zircon and baddeleyite poses the problem of the genetic relationship between these minerals. Besides a coating of zircon on baddeleyite grains, a coating of baddeleyite on zircon grains has been found at Mbuyi-Mayi.

Before suggesting our personal genetic scheme for the zircon and baddeleyite crystallization we shall summarise several earlier hypotheses about zircon-baddeleyite parageneses.

1. KEIL and FRICKER (1974) describe baddeleyite from gabbrodikes, wherein it appears (interstitially) beside zircon and free silica, although not in contact with these phases. Hence the authors postulate a late stage of crystallization of baddeleyite and they suggest a relatively common presence of ZrO_2 in basalts. The baddeleyite fragments are always smaller than $50\,\mu m$.

2. KRESTEN (1973) describes several white ZrO_2- coatings on kimberlitic zircon crystals. He considers these coatings as the result of a desilicification of zircon due to a reaction with carbonatitic liquids or gases, which seem to be richer in uranium. A simular standpoint has been taken by Brookins (1977).

3. RABER and HAGGERTY (1977) found titanium-rich baddeleyite as an interface mineral between rutile and zircon, as well as between ilmenite and zircon. Baddeleyite was always of microscopic size. The authors explain these associations as the result of a subsolidus reaction triggered by carbonatitic liquid or gases. Calcium-bearing phases were present in the parent rock.

The case of Mbuji-Mayi is different from all the preceding ones because baddeleyite shows up as a macroscopic fraction. Several crystals are as large as 1 cm.

Being an oxide baddeleyite would be expected to crystallize very early from the cooling kimberlite magna. However the high U content of baddeleyite (10 to 20 times as high as that of zircon) is in contradiction with the very low U content of primary kimberlites. Moreover by our knowledge baddeleyite has never been mentioned in primary normal kimberlites.

The above mentioned association of zircon grown as a coating on top of baddeleyite grains from Mbuji-Mayi excludes the hypothesis of desilicifaction of zircon (by carbonates as proposed by KRESTEN).

FRANTSESSON (1970) mentions the mineral baddeleyite connected with the "Yanvarskaya" pipe, where it appears together with pyrochlore and kimberlitic minerals (o.a. diamond). He concludes that, from the point of view of terminology, the "kimberlite" of Yanvarskayia would be a carbonatite; but the presence of typomorphic kimberlitic minerals (for instance diamond) also justifies the classification of the rock as a kimberlite.

Although the kimberlite at Mbuji-Mayi has known an important stage of carbonatization and as such, could be considered as an ultimate phase of transformation influenced by a carbonatitic melt, it is difficult to draw a conclusion because the kimberlite underwent some changes during the introduction in the upper layers of the crust (near surface transformation).

Sofar no intrusions of typical carbonatitic or alkaline ultrabasic rocks have been detected in the neighbourhood of Mbuji-Mayi.

Until the different (some still missing) pieces of the puzzle of kimberlite formation are put together and until the usefulness of the trace element contents of the distinct phases has been confirmed by more data from other kimberlitic and carbonatitic deposits, the genetic interpretations will remain purely hypothetical.

However we like to suggest the following way of crystallization of zircon and baddeleyite in the kimberlite at Mbuji-Mayi. We postulate the presence of a carbonatitic melt in Mbuji-Mayi prior to the intrusion of a kimberlite magma, and from which early large baddeleyite crystals have grown. The carbonatitic rock has been consumed by the kimberlite magma, wherefrom zircon crystals, and zircons on baddeleyite grow.

Finally a carbonate-rich rest magma would create baddeleyite coatings on zircon grains.

AKNOWLEDGEMENTS

The authors like to thank Ir. C. FIEREMANS for delivering the samples for the study, as well as for valuable information about the geology of the deposit at Mbuji-Mayi.

The help of Professor P. SCHONKEN and Mr. M. VANWEZER during the neutron activation analysis of the minerals has been very appreciated. Professor G. KING accepted to read critically our English text.

Professor F. GEUKENS and W. VIAENE provided the facilities to fulfil this study.

Thanks to Mrs. L. DE HERTOGH for typewriting the manuscript.

BIBLIOGRAPHY.

AHRENS, L. H., CHERRY, R. D. and EHRLANK, A. J. - Observations on the Th.U relationship in zircons from granitic rocks and from kimberlites. - *Geochimica et Cosmochimica Acta, 1967, Vol.31, pp. 2379 to 2387.*

BUTTERMAN and FOSTER, *American Mineralogist 1967, Vol. 52, p. 880.*

FIEREMANS, C. - Contribution à l'étude pétrographique de la brèche kimberlitique de Bakwanga. *Mémoires de l'Institut géologique de l'Université de Louvain 1966, Tome 24, pp. 1-92.*

FRANTSESSON, E. V. - The petrology of the kimberlites translated by D. A. Brown, 1970. *Department of Geology - Australian National University, Canberra, A. CT.*

KEIL, K. and FRICKER, P. - Baddeleyite (ZrO_2) in gabbroic rocks from Axel Heiberg Island, Canadian Arctic Archipelago. *American Mineralogist, 1974, Vol. 59, pp. 249-253.*

KRESTEN, P. - The coating of kimberlitic zircons : a preliminary study in "Lesotho Kimberlites". *Editor Nixon, P. H. 1973.*

KRESTEN, P. - Uranium in kimberlites and associated rocks, with special reference to Lesotho occurrences. *Lithos 1974, Vol. 7, pp. 171-180.*

KRESTEN, P., FELS, P., BERGGREN, G. - Kimberlitic zircons : a possible aid in prospection. *Mineral Deposita 1975, Vol. 10, pp.47-56.*

NEKRASOVA, R. A. and ROZHDESTVENSKAYA, I. V. - The ZrO_2/HfO_2 ratio in zircons from kimberlites and alluvial sediments. *Geochemistry International 1970, Vol. 7, pp. 537-542.*

NICHOLLS et al. - Contributions to Mineralogy and Petrology. *1971, Vol. 33, p. 1.*

RABER, E. and HAGGERTY, S. E. - Zircon-oxide reactions in diamond-bearing kimberlites. *Second International Kimberlite conference. Ext.Abstracts,1977.*

VLASOW, K. A. - Mineralogy of rare elements. *Vol. 2 - 1966, Israel Program for Scientific translations.*