

Primary baddeleyite (ZrO_2) in kimberlite from Benfontein, South Africa

D. E. SCATENA-WACHEL

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA

AND

A. P. JONES

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, USA

ABSTRACT. Baddeleyite was found during an electron microprobe study of kimberlite from the Benfontein Sills, which are famous for their igneous carbonate and cumulus features. Based on its close textural association with both groundmass and cumulus oxides (spinel, ilmenite, perovskite), the baddeleyite appears to be primary and crystallized directly from the kimberlite magma. The baddeleyite is remarkably pure, with average ZrO_2 and HfO_2 of 96.4 ± 1.3 and 1.72 ± 0.08 wt. % respectively. Minor element ranges found were: TiO_2 0.32–0.80, CaO 0.31–0.80, FeO 0.43–1.31, MgO 0.06–0.24, SiO_2 0.04–0.19, Cr_2O_3 0–0.07, and Al_2O_3 0–0.10 wt. %. Several additional trace elements were sought (Ce, Cs, Mn, Nb, Nd, Sr, Y, Yb, and U) but were not detected.

BADDELEYITE is an uncommon mineral found in terrestrial, lunar, and meteoritic rocks. Small crystals of baddeleyite have been reported by Smith and Hervig (1979) in the Shergotty meteorite. Lunar baddeleyite has been observed in association with ilmenite in KREEP basalts (El Goresy *et al.*, 1971), intergrown with zirconolite and tranquillityite (Lovering and Wark, 1971), in norite (Steele, 1975), and as a late differentiate in the mesostasis of ophitic basalts (Brown *et al.*, 1971, 1972). Terrestrial occurrences of baddeleyite include diamond sands and gem gravels from India and Brazil (Palache *et al.*, 1944), tholeiitic gabbro sills and alkaline basaltic rocks (Keil and Fricker, 1974), and alkaline and carbonatitic rock associations such as at Jacupiranga, Brazil (Palache *et al.*, 1944).

Baddeleyite is also known to occur in certain kimberlitic materials. Secondary baddeleyite in kimberlite has been studied as encrusting rinds on zircon crystals from Lesotho (Nixon *et al.*, 1963), rounded grains in concentrates from kimberlitic washings in Zaire (Fiéremanns, 1966), and as crystals in thin sections (Marshintsev, 1970; Raber and Haggerty, 1979). Baddeleyites from the

Monastery Mine and the Mothae Pipe in South Africa represent subsolidus products in reaction selvages between zircon, ilmenite, and rutile (Raber and Haggerty, 1979). Single crystals of baddeleyite found in concentrates from the Aykhal pipe in Siberia are considered to be 'post-magmatic' (i.e. secondary) based on their textural association with carbonate, apatite, and baryte, which make up at least 40–60% of the rock (Marshintsev, 1970).

We report a new occurrence of nearly pure baddeleyite from the Benfontein Sills in South Africa, which apparently crystallized as a primary phase associated with groundmass oxides in a carbonate-rich kimberlite magma.

Petrography. Sample Bnf-Se-la was studied as a polished thin section taken from an oxide-rich layer in the lowermost sill of the Benfontein Sills complex, similar to those illustrated by Dawson and Hawthorne (1973). Prominent petrographic features include rounded carbonate segregations up to 1 cm in diameter, and carbonate dendrites up to 0.5 cm in length in a carbonate matrix. Cumulus phases include euhedral olivine in varying degrees of alteration, subhedral olivine, Ti- and Al-rich magnetite; these are set in a carbonate-olivine matrix.

In transmitted light the baddeleyite is transparent, colourless to pale green, shows high relief, and has moderate to high birefringence. Additionally, it has high reflectivity, and, like rutile, shows strong internal reflections, which are yellow to white in baddeleyite. Some crystals have poorly discernible zonal growth bands, which, together with their high relief, superficially resemble zircon. Numerous small grains ($< 5 \mu\text{m}$) were observed throughout the thin section and approximately twenty-five areas $5\text{--}80 \mu\text{m}$ in size were identified, of which nine were analysed in detail. The larger areas

are either of cracked subhedral grains or clusters of small, stubby, prismatic grains, some showing poorly developed pyramidal terminations. No twinning was positively identified, but a few clusters have irregularly symmetrical or nearly square outlines.

The individual baddeleyite grains and grain clusters are similar in size to the other opaque oxides and are similarly set in groundmass carbonate with minor serpentine. Several baddeleyite grains directly abut cumulus spinel grains (Al-Ti-magnetite) and clearly predate the formation of distinct rims of secondary magnetite (see fig. 1) and

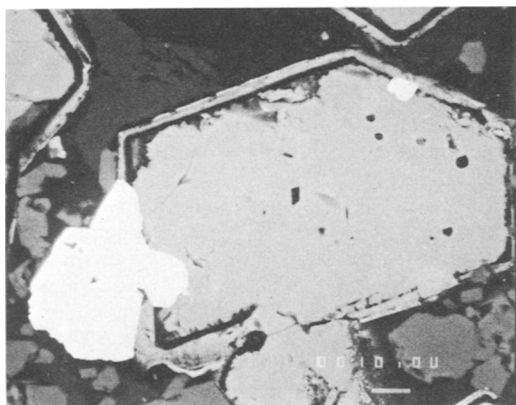


FIG. 1. Scanning electron microscope photograph (back-scattered electrons, JEOL JSM-35) of baddeleyite grain (bright area) directly associated with cumulus Al-Ti-magnetite grain (light grey larger grain with rim). Note the baddeleyite relation with Al-Ti-magnetite rim (?post-cumulus), separated by a thin band of alteration (serpentine, chlorite, and carbonate, black rims to grain). The small dark inclusions within the cumulus Al-Ti-magnetite grains are tiny olivines and calcite. Scale bar = 10 μ m.

perovskite (not shown). In detail, the SEM studies showed this relation to hold true throughout the section, although several baddeleyite grains are discrete and are simply set in groundmass carbonate. The textural evidence suggests that crystallization of much of the baddeleyite was contemporaneous with Al-Ti-magnetite and perovskite, which were major phases in the groundmass of the Benfontein Sills kimberlite (Dawson and Hawthorne, 1973). By analogy, we interpret at least some of the baddeleyite to be a primary groundmass phase crystallized directly from the CO_2 -rich kimberlite magma at Benfontein.

Analytical procedure. Baddeleyite was most easily recognized by its brilliant turquoise-blue luminescence in the electron microprobe (ARL EMX-SM) and in the

luminescence microscope. Using a 25 kV focussed beam with 200 nA sample current, elements found to be below the statistical detection limit (< 100 ppm) were Ce, Cs, Mn, Nb, Nd, Sr, Y, Yb, and U. The major and minor elements were analysed using a 15 kV, 50 nA sample current with focussed beam. Zr was determined by manually setting the ADP crystal spectrometer to the peak and analysing each grain; this minimized the loss of precision due to mechanical reproduction of the spectrometer on a sharp peak. The major elements Zr and Hf were always analysed with both minor and trace elements as a check and to provide a basis for matrix (ZAF) corrections. A total of eighty-six analyses on nine of the larger grain areas (25–80 μ m) were performed. Standards were: Zr, natural baddeleyite; Hf, Corning V-glass; Si, Mg, diopside glass; Ca, calcium phosphate; Ti, rutile; Cr, Cr_2O_3 ; Fe, Mn-hortonolite; Al, spinel.

The determined percentages of ZrO_2 and HfO_2 were 96.4 ± 1.3 and 1.72 ± 0.08 (1σ , $n = 86$), respectively. Similar precision was obtained for repeated analyses of the Zr and Hf standards. Table I reports compositional ranges for minor elements. Beam overlap and secondary fluorescence were checked as possible causes of the observed variation by measuring Zr and two elements in adjacent phases while stepping the beam across the baddeleyite grain into the bordering phase in 2 μ m increments. A sharp interface (< 2 μ m) was always observed between the baddeleyite and the adjacent mineral, with Zr below detection in Zr-free adjacent phases. There was no correlation between minor element concentration and the composition of the adjacent phase. For example, baddeleyite with the lowest Ca concentration was surrounded by calcite.

Further scrutiny of the sample with the SEM revealed two previously unrecorded Ba-rich phases in addition to baryte in the groundmass. Quantitative analyses with both the SEM and electron probe indicated these to be a Ba-Ca-carbonate with the ratio Ba:Ca close to 1:1 (c.f. benstonite $\text{Ba}_6\text{Ca}_7(\text{CO}_3)_{13}$), and an apparently new Ba titanate. The opaque titanate (5 μ m, square outline) is associated with perovskite and baddeleyite at the very rim of a cumulus spinel grain. The Ba titanate has the following composition: TiO_2 51–54, BaO 16.1–16.7, Fe_2O_3 15.6–16.1, MgO 2.1–3.4, SiO_2 1.9–3.6, Nb_2O_5 1.6, Al_2O_3 1–1.7, CaO 1.3, ZrO_2 0.4–0.5 wt. % and Cr, Mn, Sr, Na, and K near detection levels (< 0.05 wt. %). Some contribution to the Al, Si, and Mg from beam overlap on to adjacent chlorite and serpentine cannot be ruled out. Furthermore, a wavelength scan suggested Ce may be present up to 0.5 wt. %. Unanalysed REE, Y, U, and Th may explain the rather low analytical totals (94–96%).

Comparison with previous data. Table I summarizes the Benfontein analyses and compares the results with other baddeleyite grains analysed by electron microprobe. The Hf content of the Benfontein baddeleyite grains was quite constant, with an average value of 1.72 ± 0.08 (1σ) oxide wt. %, and only one analysis fell outside the 2σ statistical range. The average Zr/Hf weight ratio of Benfontein baddeleyite was 48.9 ± 2.4 . As shown in Table I, published Zr/Hf ratios range from 25 to 92, corre-

TABLE I. Comparison of electron microprobe analyses of Benfontein baddeleyite with other terrestrial and lunar samples

	Terrestrial				Lunar		
	Kimberlitic		Gabbroic				
	(1)		(2)		(3)	(4)	(5)
	Subsolidus						
	Primary Benfontein	Monastery	Mothae	Rock A 394	61156,5	12036,9	Luna 20 22002,3
ZrO ₂	96.4	93.22	90.63	97.8	87.25	91.9	94.7
HfO ₂	1.72	—	—	0.93	—	3.23	1.65
CaO	0.31–0.80	0.09	0.65	—	0.53	—	0.16
TiO ₂	0.32–0.80	3.68	6.10	0.56	7.93	1.97	1.82
FeO	0.43–1.31	0.68	0.63	1.3	0.80	3.25	0.45
MgO	0.06–0.24	0.19	0.09	—	0.10	< 0.02	0.14
SiO ₂	0.04–0.19	0.00	0.00	0.08	0.21	0.39	0.18
Cr ₂ O ₃	0.00–0.07	0.18	0.11	—	0.27	—	0.13
Al ₂ O ₃	0.00–0.10	0.51	0.11	—	0.15	—	0.54
MnO	n.d.	0.18	0.05	—	0.16	0.02	0.17
Y ₂ O ₃	n.d.	—	—	—	1.27	—	—
Nb ₂ O ₅	n.d.	—	—	—	1.03	—	0.49
Total	100.3*	98.73	98.37	100.67	99.70	100.74	100.49
Zr/Hf	49	—	—	92	—	25	50

n.d.: Not detected above 100 ppm level.

* Average total of 86 analyses.

(1) Raber and Haggerty (1979).

(2) Keil and Fricker (1974). From Canadian Arctic Archipelago.

(3) Haggerty (1973).

(4) Keil *et al.* (1971). Analysis includes Na₂O < 0.02. 'Hafnian' baddeleyite from an ophitic basalt.

(5) Brett *et al.* (1973). Analysis includes V₂O₃ = 0.06%. Baddeleyite from soil sample.

sponding to a range in HfO₂ of about 3.2–0.9 wt. %. Semi-quantitative spectrographic analysis of the Aykhal baddeleyite (Marshintsev, 1970) reports unusually low Hf (0.03–0.1 %). A wide range in Hf content is not surprising since Hf in terrestrial zircons is known to vary from 0.6 to 7.0 oxide wt. % (Spear, 1980).

Two lunar analyses show significant Nb and Y (0.49–1.03 and 1.27 oxide wt. % respectively), but these elements are below detection (< 100 ppm) in Benfontein. The low Nb in baddeleyite from Benfontein is not surprising, since both perovskite and rutile, as well as ilmenite, are known to concentrate Nb in kimberlites (e.g. Mitchell, 1972; Dawson, 1980) and these are present in the Benfontein Sills kimberlite. The low Y would agree with formation of the baddeleyite from a light-rare-earth-enriched kimberlite magma that was in equilibrium with garnet.

Discussion. The usual Zr-bearing accessory

mineral in kimberlites is zircon (e.g. Raber and Haggerty, 1979); thus the prominence of baddeleyite in the Benfontein sample was unexpected. Zircon is scarce in the sample and was encountered only once. The zircon exhibited no textural relation to the baddeleyite. The association of baddeleyite with the oxide-rich horizons is compatible with whole-rock data (Dawson and Hawthorne, 1973; Table 4) which shows much higher concentrations of Zr in oxide-rich samples (~ 2300 ppm) compared with the 'normal' kimberlite from Benfontein (~ 260 ppm). However, it is difficult to establish the modes of baddeleyite from the average Zr in the whole-rock since some zircon is present, and most of the Zr in the kimberlite is accounted for by small levels in comparatively abundant perovskite.

The petrographic textures indicate that baddeleyite is a primary phase in the Benfontein Sills kimberlite. This implies that the cumulus processes which demonstrably affected the dense oxides

(Dawson and Hawthorne, 1973) should also be considered for baddeleyite. This could place constraints on the formation of models for the evolution of kimberlitic magmas. The fact that baddeleyite is associated with kimberlites and carbonatites may favour the existence of a genetic link between these two magma types, as is already indicated from experimental studies (e.g. Wyllie, 1978). The Aykhal kimberlite (Marshintsev, 1970) is interesting because it contains baddeleyite which is coarse grained (up to 0.5 mm). In detail, the Aykhal kimberlite is quite different from the Benfontein kimberlite, since the former is a breccia and contains more carbonate (30–55%), with small amounts of baryte; olivine (including pseudomorphs) is rather scarce and forms only a few percent of the Aykhal rocks. These are features more commonly associated with carbonatites than with kimberlites.

Studies of the crystal structure of baddeleyite may yield future important information about the temperature and pressure of its formation in the Benfontein kimberlite. Synthetic monoclinic baddeleyite inverts to a tetragonal form upon heating, as noted by Palache *et al.* (1952). More recent experimental work in the systems Nb_2O_5 – ZrO_2 and Ta_2O_5 – ZrO_2 by Roth *et al.* (1971) summarized the phase diagrams of ZrO_2 for pressures up to more than 100 kbar and temperatures to more than 2400 °C. ZrO_2 is known to crystallize in the monoclinic, tetragonal, orthorhombic, and cubic systems, with a transition from monoclinic to tetragonal occurring at approximately 1150 °C at atmospheric pressure. The trigonal form mentioned by Palache *et al.* (1951) was not reported by Roth *et al.* (1971). Future work on natural baddeleyite may involve attempts at the determination of different structure-types. Thus, for example, tetragonal or even cubic structural forms of ZrO_2 may be expected in the mantle, and orthorhombic forms (high pressure) may be sought in shocked material. The Benfontein baddeleyite crystallized with other cumulus and groundmass oxides from a kimberlite magma. If this occurred at its present exposure level the baddeleyite should be monoclinic. However, if any tetragonal or cubic forms are subsequently established, this would imply some crystallization (or equilibration) at higher pressures, prior to kimberlite emplacement (i.e. in the mantle).

With the advent of isotopic techniques (such as the ion microprobe) which provide spatial resolution on a microscopic scale, the comparative study of Hf isotopes in conjunction with Zr/Hf ratios may provide further insights into baddeleyite and its relationship (if any) to zircon. It would be interesting to examine Zr/Hf ratios for coexisting zircon and baddeleyite since, at least in some lunar

examples, it appears that these may differ (e.g. Brown *et al.*, 1971).

Acknowledgements. We would like to express our thanks to Peter J. Wyllie for supplying the Benfontein kimberlite material, Ian M. Steele for sharing his electron microprobe and luminescence microscope expertise with us, Andrew Davis for assistance with back-scattered electron photography, Julius Jellinek for Russian translation, and J. B. Dawson for helpful correspondence. We would also like to thank I. M. Steele, R. N. Clayton, and R. W. Hinton for helpful comments on the manuscript. This work was supported by the National Aeronautics and Space Administration through grant NGL-14-001-169 (R. N. Clayton) and by the National Science Foundation through grant EAR-81085999 (P. J. Wyllie).

REFERENCES

- Brett, R., Gooley, R. C., Dowty, E., Prinz, M., and Keil, K. (1973) *Geochim. Cosmochim. Acta*, **37**, 761–73.
- Brown, G. M., Emeleus, C. H., Holland, J. G., Peckett, A., and Phillips, R. (1971) *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta*, Suppl. 2, **1**, 583–600.
- (1972) *Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta*, Suppl. 3, **1**, 141–57.
- Dawson, J. B. (1980) *Minerals and Rocks: Kimberlites and Their Xenoliths*. Springer-Verlag, New York, p. 85.
- and Hawthorne, J. B. (1973) *J. Geol. Soc. Lond.* **129**, 61–85.
- El Goresy, A., Ramdohr, P., and Taylor, A. (1971) *Earth Planet. Sci. Lett.* **13**, 121–9.
- Fiéremans, C. (1966) *Mem. Inst. Geol. Univ. Louvain*, **24**, 1–92.
- Haggerty, S. E. (1973) *Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta*, Suppl. 4, **1**, 777–97.
- Keil, K., and Fricker, P. E. (1974) *Am. Mineral.* **59**, 249–53.
- Prinz, M., and Bunch, T. E. (1971) *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta*, Suppl. 2, **1**, 319–41.
- Lovering, J. F., and Wark, D. A. (1971). *Ibid.* 151–8.
- Marshintsev, V. K. (1970) In *Geologiya, petrografiya i mineralogiya magmaticheskikh obrazovaniy servovostochnoy chasti Sibirskoy platformy* (Kovalskii, V. V., and Yurkevich, R. K., eds.). Moscow: Akademiya Nauk SSSR, Sibirskoye Otdeleniye, Yakutsky Filial.
- Mitchell, R. H. (1972) *Am. Mineral.* **57**, 1748–53.
- Nixon, P. H., Von Knorring, O., and Rooke, J. M. (1963) *Ibid.* **48**, 1090–132.
- Palache, C., Berman, H., and Frondel, C. (1944) *Dana's System of Mineralogy*, 7th edn., **1**. New York: John Wiley and Sons, 608–10.
- Raber, E., and Haggerty, S. E. (1979) In *Kimberlites, Diatremes, and Diamonds: Their Geology, Petrology, and Geochemistry* (Boyd, F. R., and Meyer, H. O. A., eds.). Proceedings of the 2nd International Kimberlite Conference, **1**. American Geophysical Union, Washington, D.C., 229–40.
- Roth, R. S., Waring, J. L., Brower, W. S., and Parker, H. S. (1971) In *Solid State Chemistry* (Roth, R. S., and Schneider, S. J., Jr., eds.). Proceedings of the 5th Materials Research. NBS Special Publication 364, 183–95.

- Smith, J. V., and Hervig, R. L. (1979) *Meteoritics*, **14**, 121-42.
- Spear, J. A. (1980) In *Reviews in Mineralogy, Volume 5: Orthosilicates* (Ribbe, P. H., ed.). Min. Soc. Am., Washington, D.C., p. 72.
- Steele, I. M. (1975) *Am. Mineral.* **60**, 1086-91.
- Wyllie, P. J. (1978) *Proceedings of the First International Symposium on Carbonatites*. Departamento Nacional de Producao Mineral, Brasilia, 59-78.

[Manuscript received 20 July 1983]