SHORT COMMUNICATIONS

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Baddeleyite: new occurrences from two mafic–ultramafic layered intrusions, Russia

THE majority of baddeleyite (ZrO_2) occurrences are in alkaline silica-undersaturated rocks and carbonatites, and there are only a few known occurrences of baddeleyite from mafic and ultramafic complexes. Baddeleyite was found in a gabbro from Axel Heiberg Island, Canadian Arctic Archipelago (Keil and Fricker, 1974) and in an anorthosite from southern Norway (Gierth and Krause, 1974). Williams (1978) described accessory baddeleyite from the Rhum layered intrusion, Scotland. The presence of baddeleyite was recorded in the UG-2 chromitite layer, Bushveld igneous complex (McLaren and De Villiers, 1982) and in the Koitelainen layered intrusion, northern Finland (Tarkian and Mutanen, 1987), but compositions were not given. Another baddeleyite occurrence from basic cumulates was reported from the Laouni layered intrusion, Algeria (Lorand and Cottin, 1987). Hf-bearing baddeleyite has also been identified in the Penikat layered intrusion, northern Finland, although full analytical data were not given (Halkoaho *et al.*, 1989). In addition, Gierth and Krause (1974) and Williams (1978) did not provide microprobe data on baddeleyite for Hf. Thus, there is little complete information on either occurrence or chemical compositions of baddeleyite from mafic and ultramafic complexes.

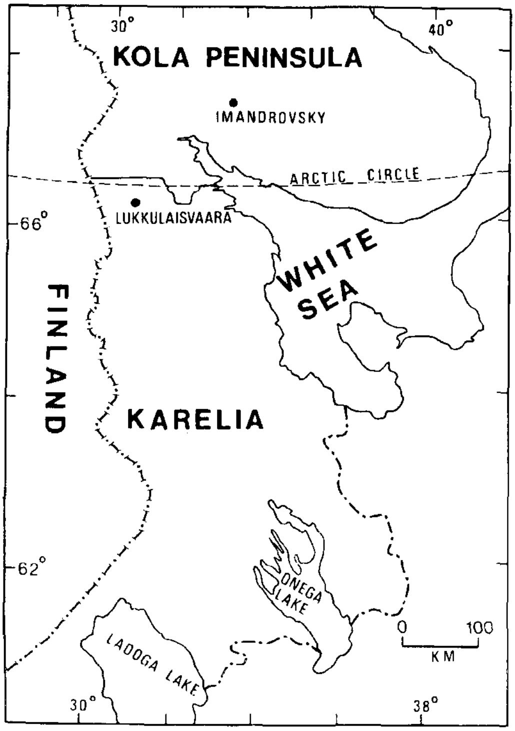

FIG. 1. Sketch map of the Karelia-Kola region, Russia, showing the position of the Lukkulaisvaara and Imandrovsky layered intrusions.

Early Proterozoic (~ 2440 Ma in age) mafic–ultramafic layered intrusions are relatively widespread in Karelia and the Kola Peninsula, Russia. While carrying out a mineralogical study of samples collected from two of these, the Lukkulaisvaara (northern Karelia) and Imandrovsky (Kola Peninsula) layered intrusions, we observed the presence of baddeleyite, details of which are presented here.

The Lukkulaisvaara intrusion, Oulanka layered complex, is located in the Lake Pyaozero area, close to the border between Russia and Finland (Fig. 1). The intrusion is elliptical in shape, approximately 7 km long and 3.5 km wide. It comprises a layered sequence (thickness about 0.5 km) of ultramafic and melanocratic mafic rocks (plagioclase-bearing lherzolite and harzburgite, olivine pyroxenite, plagioclase-bearing pyroxenite, troctolite and melanocratic olivine gabbronorite) overlain by gabbroic rocks (gabbronorite, norite, olivine gabbronorite, rare plagioclase-bearing pyroxenite) and rare anorthosite (about 3 km in total thickness). The gabbroic succession consists of numerous microgabbronorite bodies up to 0.1 km thick. These concordant or subconcordant bodies are considered to be sills (Barkov and Lednev, 1991). The Lukkulaisvaara baddeleyite was identified in the lowermost ultramafic cumulates and in a meta-anorthosite horizon located at the base of one of the microgabbronorite sills.

The ultramafic rocks that contain baddeleyite from Lukkulaisvaara have heteradcumulate textures. The sample most enriched in baddeleyite (seven baddeleyite grains ranging from 30 to 150 μm in length per polished section were observed) has a modal composition (vol. %) of olivine — 78%, plagioclase ~ 10%, orthopyroxene — 6%, clinopyroxene — 3%, phlogopite — 2%, ilmenite ~ 1%.

Compositional data obtained for this specimen are: cumulus olivine (Fo_{81}), postcumulus enstatite ($Wo_3En_{80.2}Fs_{16.7}$), augite ($Wo_{44}En_{46.6}Fs_{9.4}$) and intercumulus plagioclase (An_{67}). Baddeleyite is present as subhedral to anhedral elongate grains (typically up to 0.1 mm in length, up to 40 μm wide) occurring as an intercumulus phase. Anhedral baddeleyite inclusions at the boundaries of intercumulus ilmenite grains are common in these ultramafic rocks. An example is shown in Fig. 2, where host ilmenite is closely associated with intercumulus phlogopite. Other accessory minerals include intercumulus chlorapatite containing more than 6.0 wt.% chlorine and zircon that is observed neither in direct contact nor immediately adjacent to baddeleyite. It is noteworthy that in addition to baddeleyite which is interstitial to postcumulus pyroxenes, in the same polished section, one euhedral baddeleyite crystal hosted by enstatite has been identified (Fig. 3). A euhedral morphology does not necessarily imply that this baddeleyite was formed earlier than its host enstatite.

The second baddeleyite occurrence in the meta-anorthosite layer was in rocks containing hydrous silicates (epidote–clinozoisite, chlorite, Ca-amphibole and scapolite), disseminated base-metal sulphides (BMS) (predominantly, chalcopyrite, pyrrhotite and pentlandite in highly varying proportions) and ilmenite, rutile, tourmaline, apatite, baddeleyite, platinum-group minerals (PGM), Au–Ag alloys, galena–clausthalite and cobaltite–gersdorffite solid-solution series minerals as accessories. Though baddeleyite is relatively rare in the meta-anorthosite, five grains hosted by hydrous silicates were found. One of these appears as an intergrowth with apatite; another grain was located immediately adjacent to BMS. In one polished section, a baddeleyite grain partly mantled by zircon was observed. Unlike baddeleyite from the

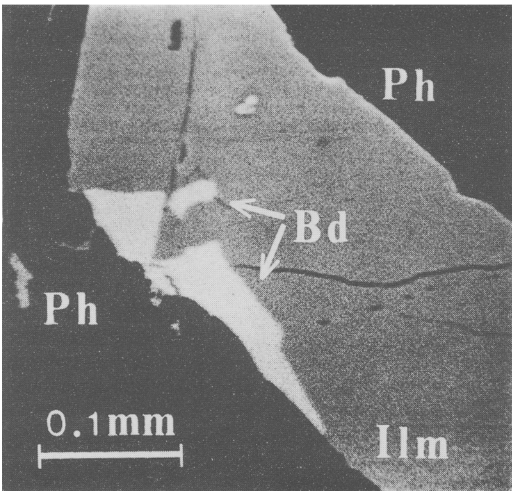

FIG. 2. Anhedral baddeleyite (Bd) occurring at the margin of the intercumulus ilmenite grain (Ilm). Ph = phlogopite. Back-scattered electron image.

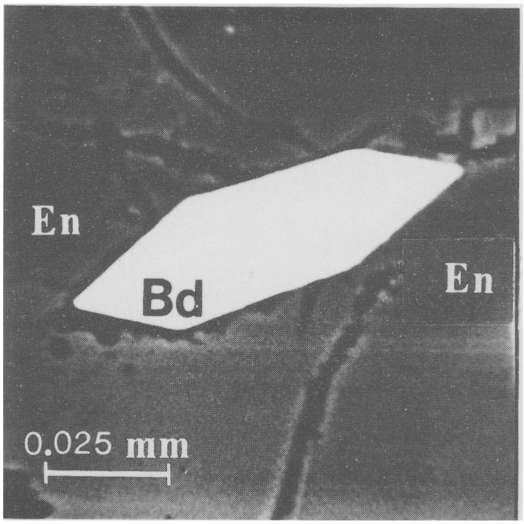

FIG. 3. Euhedral baddeleyite (Bd) enclosed within postcumulus enstatite (En). Back-scattered electron image.

ultramafic rocks, all grains found in the meta-anorthosite are anhedral. Grain size is variable, with the two largest grains reaching approximately 90 μm in their longest dimension.

The second mafic intrusion where baddeleyite is observed is the Imandrovsky intrusion, which is situated in the middle part of the Kola Peninsula (Fig. 1). A geological description of this intrusion has previously been presented by Dokuchaeva *et al.* (1982). Baddeleyite here occurs in the chromitite horizon located in the Lower Zone of the intrusion. The Lower Zone comprises melano–mesocratic gabbronorite and plagioclase-bearing pyroxenite layers. The chromitite seam consists of intensively altered rocks, in which the major silicate minerals are Ca-amphibole and chlorite. The BMS and sulpharsenides (pyrite, chalcopyrite, bornite, millerite, rare pyrrhotite, pentlandite, cobaltite–gersdorffite, galena and molybdenite), as well as PGM, are generally present as minute grains enclosed by hydrosilicates. This BMS–PGM assemblage is described in a separate paper (Barkov *et al.*, in press). Four grains of baddeleyite surrounded by zircon rims were found in one polished section. These grains, ranging in size from 50 μm in length to 170 × 40 μm are hosted by hydrosilicates. The replacement of baddeleyite by zircon may have resulted from an increase in SiO_2 activity within the residual intercumulus liquid.

Electron microprobe analyses of baddeleyite were performed using a MS-46 Cameca electron microprobe. Zirconium was analysed at 30 kV with a beam current of 40 nA; Hf at 20 kV and 20 nA; Ti, Fe, Ca and Cr at 20 kV and 40 nA. The following X-ray lines (and standards) were used: Zr-*K*α (synthetic ZrO_2), Hf-$L\beta_1$ (pure Hf), Ti-*K*α (lorenzenite), Fe-*K*α (hematite), Ca-*K*α (diopside), Cr-*K*α (pure Cr).

The ZrO_2 compound is known to crystallize as monoclinic, tetragonal, orthorhombic and cubic polymorphs (e.g. Roth *et al.* 1971). An X-ray powder diffraction pattern of the Lukkulaisvaara baddeleyite from the peridotite, obtained with a 57.3 mm Debye-Scherrer camera using Fe-*K*α radiation, corresponds to a monoclinic structural form; a = 5.154 (5), b = 5.198 (7), c = 5.316 (6) Å, β = 99°.

Representative electron microprobe analyses of separate grains of baddeleyite are presented in Table 1. The composition is close to ZrO_2, but contains significant amounts of Hf, Ti (and Fe) as minor elements. Additional trace elements were sought (Al, Mg, Mn, Na, K, V, Zn, Ce, La, Nd, Pr, Y, U, Th, Nb, Ta) but were not detected. The composition differs from samples reported from two other localities (Keil and Fricker, 1974; Lorand and Cottin, 1987) by having higher Hf contents. It is particularly noteworthy that in the Lukkulaisvaara baddeleyite there are significant differences in the Ti contents from earlier (ultramafic) cumulates compared with those from the more evolved meta-anorthositic cumulates. As shown in Table 1, baddeleyite from the meta-anorthosite has significantly higher Ti contents and lower Zr/Σ minor elements ratios than baddeleyite from the peridotite. Baddeleyite from Imandrovsky also contains relatively low Ti concentrations. It seems likely that in some cases the Ti content of baddeleyite may be a useful indicator of the degree of the magma differentiation.

TABLE 1. Electron microprobe analyses (wt.%) of baddeleyite

Intrusion	Lukkulaisvaara							Imandrovsky	
Rock type	peridotite				meta-anorthosite			chromitite	
Analysis No	1	2	3	4	5	6	7	8	9
ZrO_2	96.45	96.42	96.73	96.42	97.05	96.54	96.96	98.14	93.90
TiO_2	0.19	0.94	0.34	0.23	1.64	1.21	1.97	0.59	0.63
HfO_2	1.97	1.59	2.02	2.04	1.93	1.57	1.21	1.71	1.98
FeO*	0.34	0.23	0.21	0.32	0.29	0.30	0.45	0.10	0.26
CaO	nd	nd	nd	nd	0.11	0.12	0.06	nd	nd
Cr_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	0.15
Total	98.95	99.18	99.30	99.01	101.02	99.74	100.65	100.54	96.92
Zr/Hf†	83	104	82	81	86	105	138	98	81
Zr/ΣM‡	47	35	46	48	22	27	21	47	33

* All Fe as FeO
† Zr/Hf atomic ratio
‡ Zr/ΣM = Zr/(Ti + Hf + Fe + Ca + Cr) atomic ratio
nd = not detected

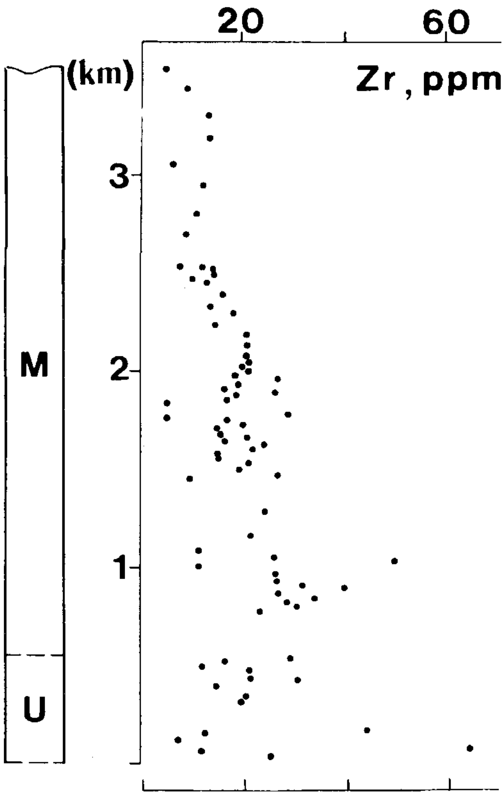

FIG. 4. Variation of the zirconium content (X-ray fluorescence analysis; ppm) in rocks of the Lukkulaisvaara intrusion with stratigraphic height. Abbreviations: U = dominantly ultramafic rocks, M = mafic rocks.

In the Lukkulaisvaara intrusion, the behaviour of Zr during the crystallization of parental magma (Fig. 4) is unusual. Since Zr behaves as a nearly perfect incompatible element (e.g. Eales and Robey, 1976; Cawthorn, 1983), its abundance should typically increase in the later crystallizing parts of the intrusions. However, the observed distribution of Zr (Fig. 4) is in good agreement with the minor cryptic layering of the Lukkulaisvaara intrusion (Barkov and Lednev, 1991), and reflects only a slight progress of fractionation during magmatic differentiation. It is interesting to note that a similar trend for Zr was recently reported from the Montcalm gabbroic complex, Canada (Barrie *et al.*, 1990).

The textural evidence from the ultramafic Lukkulaisvaara cumulates indicates crystallization of baddeleyite from pockets of intercumulus liquid, similar to baddeleyite from some other reported localities (e.g. Lorand and Cottin, 1987), and does not support a possibility that it crystallized early as a cumulus phase. We suggest that a genetic link exists between the presence of a volatile-rich fluid phase circulating through the lower Lukkulaisvaara cumulates and sporadic baddeleyite occurrences in them. The presence of Cl-rich hydromagmatic fluids is evident in the appearance of intercumulus chlorapatite grains (up to 0.7 mm in length), as well as in a significant increase in the modal amount of mica (phlogopite) and apatite in the lowermost cumulates. This distribution is similar to the findings of Boudreau and McCallum (1989) at the Stillwater complex, where apatites containing > 6 wt.% Cl are common only in the lower third of the complex.

The origin of the Cl-rich volatile fluids is not well understood. Two different possibilities can be considered to explain an appearance of such fluids in Lukkulaisvaara. One is that they might be derived from adjoining country rocks, and thus Zr and other incompatible elements were added to the parental magma as contaminants by introduced fluids. This interpretation is consistent with the evidence for contamination reported from some other layered intrusions of the Fennoscandian shield (Tarkian and Mutanen, 1987; Alapieti *et al.*, 1989; Mutanen, 1989; Barkov *et al.*, 1994). The alternative is that strong relative enrichment in volatiles could be a distinctive feature of the parental magma (cf. boninites).

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Precipitation of vaterite ($CaCO_3$) during oilfield drilling

In our paper (Friedman and Schultz, 1994) we mentioned a vaterite occurrence in the Appalachians of Quebec, where it has been reported from cone-in-cone calcite of carbonate concretions in Ordovician shales (Fong 1981). Reinhard Hesse of McGill University responded "the occurrence reported by Fong (1981) most likely does not exist. Fong was a former graduate student of mine and was led to submitting the abstract by the late G. Donnay, who thought she had found vaterite peaks on one of his XRDs. However, all attempts to duplicate this result with his material under my and Bob Martin's supervision failed to reproduce a vaterite XRD trace".

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