U-Pb (and U-Th) dating of micro-baddeleyite

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Baddeleyite (BAD-ü-LĒ-ite)* basics

- **chemical formula**: ZrO₂
- **monoclinic** (commonly twinned)
- **minor** HfO₂, TiO₂, FeO, SiO₂
- **U** between ~200 – 1000 ppm
- **low common Pb, Th/U <<0.2**
- **wide range of occurrences**
  - (terrestrial and extraterrestrial)
    - mafic and ultramafic rocks
      - (basalt, gabbro, diabase)
    - alkali rocks (carbonatite, syenite)
    - mantle xenoliths (from kimberlites)
    - metacarbonates
    - impact-related rocks (tektites)

*Wingate and Compston, 2000*

*National Library Service for the Blind and Physically Handicapped (NLS), Library of Congress*
Baddeleyite dating: applications and examples

**Bulk analysis (TIMS)**
- Mafic dikes and layered intrusions (e.g., Heaman et al., 1992)
- Detrital baddeleyite (e.g., Bodet and Schärer, 2000)

**In-situ methods (SIMS, LA ICP MS, EPMA)**
- Mafic dikes and gabbros (e.g., Wingate et al., 1998; French et al., 2000)
- SNC meteorites (Herd et al., 2007: 70±35 Ma and 171±35 Ma)
Micro-baddeleyite analysis: in-situ advantages

• **Bulk analysis difficulties:**
  - time-intensive, highly inefficient mineral separation
  - 100’s of grains (<20 μm) required
  - contamination risk (though inheritance unknown)
  - abrasion impossible (Pb-loss)

• **In-situ advantages:**
  - grains can be located and analyzed in thin-section
  - no separation required
  - petrographic context preserved
  - limited sample size (e.g., drill samples, extraterrestrial)
  - screening for concordant grains

Söderlund and Johansson, 2002
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Zirconium X-ray map of mafic dike rock
Previous SIMS U-Pb dating of baddeleyite

- SHRIMP II (Wingate and Compston, 2000)
  - Phalaborwa baddeleyite standard
  - $^{207}\text{Pb}/^{206}\text{Pb}$ ages accurate
  - $^{206}\text{Pb}/^{238}\text{U}$ ages deviate by up to -13% and +17%
  - crystal orientation affects U-Pb sensitivity
  - severe limitation on accuracy of U-Pb baddeleyite ages

Wingate and Compston, 2000
Baddeleyite U-Pb analysis with the ims 1270

- cross-calibration of three baddeleyite standards
- randomly oriented grains, NIST SRM 610 glass on same mount
- 144 spot analyses total
- two sessions (overnight, fully automated beam centering and charge-compensation): rotate mount 90°
- ~8-11 nA $^{16}$O$^-$ primary beam, 25-30 μm spot size, MRP = 4500
- $O_2^-$ flooding (700% increase in Pb$^+$)
U-Pb calibration results

**NIST SRM 610 glass**

\[
\frac{^{206}\text{Pb}}{^{238}\text{U}} = 0.2249
\]

\[\frac{^{206}\text{Pb}^*}{^{238}\text{U}} \text{ standard dev.}
  \begin{align*}
  &2.7\% \; (\text{session 1}) \\
  &3.9\% \; (\text{session 2})
  \end{align*}
\]

**Phalaborwa baddeleyite**

\[
\frac{^{207}\text{Pb}}{^{206}\text{Pb}^*} \text{ age} = 2059.8 \pm 0.8 \text{ Ma}
\]

\[
\frac{^{206}\text{Pb}}{^{238}\text{U}} = 0.3765
\]

\[\frac{^{206}\text{Pb}^*}{^{238}\text{U}} \text{ age standard dev.}
  \begin{align*}
  &3.6\% \; (\text{session 1}) \\
  &2.9\% \; (\text{session 2})
  \end{align*}
\]

**UO_2^+/U^+**

**UO^+/U^+**
Standard intercomparison

- new TIMS results for Kovdor and FC4 (Duluth)
- differences in calibration after rotation unrelated to crystal-orientation
- reproducibility on baddeleyite slightly poorer compared to glass
- highly accurate $^{207}\text{Pb}/^{206}\text{Pb}$ ages for Precambrian baddeleyite
- $^{206}\text{Pb}/^{238}\text{U}$ ages agree within measurement uncertainties ($\sim 1-2\% 2\sigma$)

Phalaborwa: Heaman and LeCheminant, 1993
NIST SRM 610: Walder et al., 1993; Hirata and Nesbitt, 1995
Baddeleyite U-Th dating

- Multicollection analysis of Phalaborwa baddeleyite (30 nA $^{16}$O$^-$ beam)
- U-Th relative sensitivity calibration comparable to zircon
- Yields equilibrium $(^{230}$Th)/$(^{238}$U)
- Potential for young mafic volcanics (e.g., Hawaii, Eifel)
Micro-baddeleyite: analytical parameters

- Pb useful yield ~0.4 % (similar to zircon)

- for 100 Ma baddeleyite, 500 ppm U, $^{206}\text{Pb}/^{238}\text{U}$ counting error of 1% requires ~25 μm$^3$ baddeleyite

- In-situ thin-section analysis

- use field aperture to exclude common Pb from crater margins and matrix minerals
- baddeleyite from Sette Daban (N Siberia)
- mafic sills within carbonate platform sequence
- analyzed grains between 30 and 10 μm (short dimension),
  depth resolution ~1-2 μm
SIMS micro-baddeleyite geochronology: future developments

• more testing of crystal-orientation effects on Pb-U sensitivity (EBSD analysis underway)

• multi-collection of Pb isotopes to increase duty cycle

• implement sample maps (e.g., by SEM) into sample stage control

• explore potential of ion-beam generated secondary electron imaging (UCLA ims1270 features Ga liquid metal source, and new channeltron particle detector)

scanning electron images of Ta-Si grid, 2 pA Cs⁺ (1.5 μm lateral resolution)
Conclusions

- SIMS U-Pb dating of baddeleyite possible at ~3-4% (rel. uncertainty) level

- Crystal-orientation effects under investigation, but appear to be minor/absent (O₂-flooding? secondary ion extraction geometry?)

- U-Pb ages accurate within internal reproducibility for randomly oriented crystals (e.g., in-situ baddeleyite in thin-section)

- U-Th calibration comparable to zircon

- Potential for U-series dating of young mafic volcanics