1 **Quadrupole LA-ICP-MS U/Pb geochronology of baddeleyite single crystals**

2
3 Cora C. Wohlgemuth-Ueberwasser^a, Ulf Söderlund^{b,c}, Victoria Pease^a, Mimmi K. M. Nilsson^b

4
5 ^a PetroTectonics Analytical Facility, Department of Geological Sciences, Stockholm
6 University, 106 91 Stockholm, Sweden, cora.wohlgemuth-ueberwasser@geo.su.se, phone
7 +46 8 674-7848

8
9 ^b Department of Geology, Lund University, 223 62 Lund, Sweden

10
11 ^c Laboratory of Isotope Geology (LIG), Swedish Museum of Natural History, Box 50 007, SE-
12 104 05 Stockholm, Sweden

13 14 15 16 **Abstract**

17 We present a straight forward method for accurate and precise U-Pb dating of baddeleyite
18 using quadrupole LA-ICP-MS. To establish the validity of our ICP-MS data we used FC-4b
19 baddeleyite from the Duluth complex as external standard whereas baddeleyite from the
20 Phalaborwa (South Africa) and the Sorkka (SW Finland) intrusions were treated as
21 unknowns. The analytical protocol includes the use of a matrix matched standard, which
22 allows for an accurate down-hole fractionation and laser-induced inter-element
23 fractionation correction. The quadrupole ICP-MS results for the Phalaborwa and Sorkka
24 samples analyzed are accurate, within error of the published ID-TIMS U/Pb ages and with a

precision of 0.3 % to 0.7 % (2σ) from concordia ages of ten to twenty analyses per sample.

No orientation effects were observed..

Introduction

Baddeleyite (ZrO_2) crystallizes instead of zircon or in addition to zircon in silica undersaturated systems¹. Like zircon, baddeleyite incorporates relatively high amounts of U in its crystal lattice but negligible initial common Pb at magmatic temperatures¹, making it a valuable mineral for U-Pb geochronology. Baddeleyite crystals typically form in mafic-ultramafic intrusions, such as thick dolerite dikes and syenites that tend to cool slowly; nevertheless baddeleyite crystals are typically less than 100 μm in longest dimension. *In-situ* LA-ICP-MS is a powerful tool for baddeleyite geochronology because of the relatively small analytical spot size, short analytical duration, and its capability to produce accurate ages from only a few grains.

In some rocks, baddeleyite may be too small (30 μm or less in longest dimension) for successful recovery using conventional separation techniques². Recovery may also be hampered when baddeleyite occurs as micro-inclusions in some minerals e.g. ilmenite or amphibole. In these situations *in-situ* micro-analytical techniques such as SIMS and LA-ICPMS are required. However, strong orientation effects have been reported for the SIMS analytical technique³, limiting SIMS to Precambrian rocks that provide precise $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, which are insensitive to crystal orientation⁴. More recent studies have partly overcome this problem by using an oxygen flooding technique to obtain accurate $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages of Phanerozoic rocks with a precision and accuracy of $<1 - 4\%$ ^{5,6,7}.

Earlier investigations of LA-ICP-MS U/Pb baddeleyite dating have had limited success. Xie *et al.*⁸ reported an age of 2065 ± 15 Ma for the Phalaborwa baddeleyite obtained from

reversely concordant ages and using a spot size of 60 μm . Sylvester *et al.*⁹ reported $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios that plot significantly above concordia. They attributed this to laser-induced Pb/U fractionation and have shown that this fractionation is up to six times higher in baddeleyite than in zircon. Furthermore they reported orientation effects with less scatter in Pb/U ratios drilling perpendicular to the {100} plane, and suggested 'line analysis' to minimize this effect. Renna *et al.*¹⁰ used a magnetic sector single collector ICP-MS and obtained discordant ages with an upper intercept age of 2049 ± 15 Ma for the Phalaborwa baddeleyite. Zhang *et al.*¹¹ reported discordant ages for a sample from the northern China Craton obtained using a quadrupole LA-ICP-MS system. In all these studies the zircon standard 91500 was used as external standard. Horn *et al.*¹² reported discordant age data for Phalaborwa using no external calibration standard, but a tracer solution. Hirata *et al.*¹³ used NIST610 as external standard and report a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2042 ± 20 Ma with uncertainties that were not calculated but estimated. Millonig *et al.*¹⁴ report concordant U/Pb ages for one baddeleyite sample using a sector field instrument and zircon standard GJ-1 as external standard applying larger spot sizes to the external standard compared to the samples. This might compensate for different downhole fractionation between zircon and baddeleyite for this sample.

Our approach differs from these previous studies in that we utilize a matrix matched standard, namely the FC-4b baddeleyite from the Duluth Gabbro. A recent study by Ibanez-Mejia *et al.*¹⁵ evaluated the capability of multicollector LA-ICP-MS for in-situ baddeleyite U/Pb geochronology and demonstrated the importance of matrix-matched standards. LA-MC-ICP-MS is more precise than LA-Q-ICP-MS, but LA-Q-ICP-MS instruments are more widespread and available to the scientific community. Thus it is important to evaluate the capability of the latter for baddeleyite U/Pb geochronology.

73

74 **Instrumentation**

75 LA-Q-ICP-MS analyses were carried out using an ESI NWR-193 nm excimer laser coupled to a
76 Thermo XSeries2 quadrupole mass spectrometer at the PetroTectonics Analytical Facility,
77 Stockholm University. Analytical conditions included a laser beam diameter of 25 μm , laser
78 frequency of 10 Hz, and a laser energy density of 4 J cm^{-2} . The signal was tuned for maximum
79 sensitivity for Pb and U while keeping the ThO/Th ratio below 0.5 %. Detailed analytical
80 conditions are given in Table 1. The tubing from the ablation chamber to the ICP source was
81 equipped with an in-house built signal smoothing device, consisting of several Tygon® tubes
82 that split the stream and re-joined it. No additional tracer solution was used to address
83 calculation of instrument drift. Instrument drift was corrected for during data processing
84 using the standard-sample bracketing method. The external standard was analyzed before,
85 between and after analysis of unknowns. Each analytical run included 20 seconds
86 background measurement, followed by 40 seconds signal acquisition in ablation mode and
87 10 seconds wash-out, the latter being long enough for a signal drop to 0.1 % using a two-
88 volume ablation cell with short wash-out times. The external standard FC-4b was analyzed
89 10 times and the two samples 20 times each. For comparison of the downhole-fractionation
90 of baddeleyite and zircon, zircon FC-5z from the Duluth gabbro was analyzed under the same
91 analytical conditions.

92 ***Position table 1***

93

94 **Analytical protocol**

95 Material from the Duluth Gabbro FC-4b (sample location: UTM-15, 0623128 E, 5291893 N)
96 was separated on a Wilfley table following the method of Söderlund and Johansson². The

97 densest fraction was cleaned of magnetic minerals using a pencil magnet and baddeleyite
98 grains were handpicked under a binocular microscope. Thirty grains were placed onto
99 double-sided adhesive tape in random crystallographic orientation and centered in a 2.5 cm
100 Teflon ring. Epoxy resin was poured onto the grains and left to harden for three days at
101 room temperature. The mount was subsequently removed from its tape and polished with 1
102 μm Struers DP® spray using a Struers rotopol® specimen polisher for 20 to 140 seconds,
103 depending on grain size of the embedded sample. The mount surface was then cleaned
104 ultrasonically and with ethanol. Additionally 20 baddeleyite grains each of the Phalaborwa
105 and Sorkka intrusions (Phalaborwa carbonatite, South Africa¹; Sorkka dolerite, Sweden and
106 Norway¹⁶) were mounted, polished, and analyzed by LA-Q-ICP-MS.

107 To ensure the analysis of inclusion-free parts of the mineral surfaces and to identify mineral
108 zoning, the baddeleyite grains were Au-coated and cathodoluminescence (CL) imaged using
109 a Hitachi S-4300 SEM at the Museum of Natural History, Stockholm. Applied parameters
110 included an acceleration voltage of 15 kV and a beam current of 10 μA .

111 Data reduction and calculation of ratios and ages were performed off-line through the
112 software Lolite^{17,18}, using the Lolite-integral VizualAge DRS (data reduction scheme) routine
113 of Petrus and Kamber¹⁹. The software applies corrections for instrument drift as well as a
114 correction routine for down-hole isotopic fractionation²⁰. The Isoplot software version 4²¹
115 was used to plot data according to corrected $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios. Errors in ages
116 are given at 2σ .

117 Background intensities as well as changes in instrumental bias were interpolated using a
118 smoothed cubic spline in Lolite. The software calculates uncertainties by treating the primary
119 standard - in our case FC-4b - one by one as an unknown, called “pseudosecondary
120 standard”. For each “pseudosecondary standard” the internal uncertainty is calculated. To

account for unquantified sources of error an “excess uncertainty” is calculated from the degree of scatter of the “pseudosecondary standards” by evaluating their MSWD. If the MSWD is >1 the excess uncertainty is increased to create a MSWD ≤1. A combination of the quadrature of the “excess uncertainty” with the internal error of the unknown generates the total analytical error as reported in table 2.

Results

Analyses with more than 10 % discordance have been rejected. All analyses were investigated for ^{204}Pb by controlling the intensities on masses ^{200}Hg , ^{201}Hg , ^{202}Hg and $^{204}\text{Hg}+\text{Pb}$. No common Pb was found in any of the grains analyzed. CL imaging (Figure 1) shows almost no zoning in FC-4b baddeleyite crystals, with rare zoning only occurring at the rims of the grains. Phalaborwa baddeleyite revealed three grains with strong zonation. Nevertheless these reflect magmatic zoning and do not influence concordia ages of the sample (e.g. Figure 1A corresponding to analysis 1 of Phalaborwa in Table 2). Sorkka baddeleyite was unzoned except for two grains; analyses number 11 and 17 (Table 2). These reveal strongly discordant ages and were excluded from the concordia age calculation.

Position figure 1

Position table 2

The external baddeleyite standard FC-4b (10 analyses) yielded a concordia age of 1099.2 ± 7.5 Ma, which is in good agreement with the published age of 1099.1 ± 0.5 Ma^{22,23,24} (Figure 2) and expected since during data processing the standard is forced to the assumed age.. Phalaborwa analyses gave a concordia age of 2059.9 ± 6.4 Ma, while the published age is 2059.8 ± 0.8 Ma¹ (Figure 2). One concordant analysis was rejected as an outlier since this

grain was about 1 Ga younger than the 19 other analyses (Table 2). The concordia age for Sorkka from our analyses is 1256.0 ± 6.3 Ma to be compared with the published TIMS age of 1256.2 ± 1.4 Ma¹⁶ (Figure 2). Two strongly discordant analyses were excluded from the age calculation (Table 2).

Position figure 2

Position figure 3

Discussion

A first analytical attempt using a laser energy density of 7 J cm^{-2} yielded short ablation times as the laser beam drilled through the baddeleyite grains into the epoxy resin. This was due to the small grain size of 40 to 100 μm for FC-4b, in contrast to Sorkka with 60 to 200 μm and Phalaborwa with up to 500 μm grain sizes. In order to keep the signal as stable as possible the frequency was kept at 10 Hz, but the laser energy density was reduced to 4 J cm^{-2} , leading to longer ablation times.

Our results show that LA-Q-ICP-MS can produce excellent U/Pb ages for baddeleyite. The precision of concordia ages obtained with our method is 0.7 % for FC-4b, 0.3 % for Phalaborwa and 0.5 % for Sorkka (2σ). All three baddeleyite ages are within error of the ID-TIMS ages. The major factor controlling the quality of the analytical results is the use of a matrix matched standard for external calibration (Figure 3). Since ablation rates and U/Pb fractionation of zircon and baddeleyite differ significantly, a proper U/Pb down-hole and inter-element fractionation correction is not possible using zircon as external standard. The use of a matrix-matched baddeleyite standard accounts for this and allows the accurate and precise estimation of concordant baddeleyite ages.

Analytical figures of merit are given in table 3 and include a precision range of 0.3 to 0.7 % on the concordia ages and an accuracy of 0.004 to 0.016 % compared to published values. This is comparable to typical results obtained for zircon geochronological studies using LA-Q-ICP-MS, e.g. Alagna *et al.*²⁵. Previous studies on baddeleyite using LA-Q-ICP-MS reported intercept ages with a precision of 1 – 2.2 %^{8,11,13}. Adding a tracer solution, reverse concordant ages with a precision of 0.4 % have been achieved¹², although the application of a wet plasma versus a dry plasma without any solution addition is known to produce higher oxide rates²⁶. Previous work using sector field instruments yielded concordant ages on multiple analyses of a single grain with a precision of 1.1 %¹⁴, and reverse concordant ages with a precision of 0.7 %¹⁰. A recent study utilizing multicollector LA-ICP-MS does not report a concordia age although concordant ages were produced. No orientation effects were observed within this study. Compared to earlier studies using quadrupole LA-ICP-MS we present the first concordant ages for baddeleyite samples with a better precision than previously reported.

Conclusions

Quadrupole LA-ICP-MS generates accurate and precise U/Pb ages for baddeleyite single crystals. FC-4b is an excellent standard reference material as it is free of zoning and has a homogeneous age distribution. The use of a matrix matched external standard is essential to obtain precise data as it allows for a valid down-hole fractionation correction. No orientation effects were observed within this study.

Acknowledgements

Kerstin Lindén is acknowledged for assistance in sample preparation and CL-imaging. The PetroTectonics Analytical Facility was established with funding from the Knut and Alice Wallenberg Foundation.

References

- 1 L. M. Heaman and A. N. LeCheminant A.N., *Chem. Geol.*, 1993, **110**, 95-126.
- 2 U. Söderlund and L. Johansson, *Geochem. Geophys. Geosyst.*, 2002, **3(2)**.
- 3 M. T. D. Wingate and W. Compston, *Chem. Geol.*, 2000, **168**, 75-97.
- 4 M. T. D. Wingate , I. H. Campbell, W. Compston and G. M. Gibson, *Precambr. Res.*, 1998, **87**, 135-159.
- 5 Q.-L. Li, X.-H. Li, Y. Liu, G.-Q. Tang, Y.-H. Yang and W.-G. Zhu, *J. Anal. Atom. Spectrom.*, 2010, **25**, 1107-1113.
- 6 A. K. Schmitt, K. R. Chamberlain, S. M. Swapp and T. M. Harrison, *Chem. Geol.*, 2010, **269**, 3-4.
- 7 S. H. Zhang, Y. Zhao and M. Santosh, *Prec. Res.*, 2012, **222-223**, 339-367.
- 8 L. W. Xie, Y. B. Zhang, H. H. Zhang, J. F. Sun and F. Y. Wu, *Chin. Sci. Bull.*, 2008, **53**, 1565-1573.
- 9 P. Sylvester, M. Tubrett and A. K. Souders, *Geochim. Cosmochim. Acta*, 2007, **71**, A991.
- 10 M. R. Renna, M. Tiepolo and R. Tribuzio, *Eur. J. Min.*, 2011, **23**, 223-240.
- 11 S. H. Zhang , Y. Zhao, Z.-Y. Yang, Z.-F. He and H. Wu, *Earth Planet. Sci. Lett.*, 2008, **288**, 588-600.
- 12 I. Horn, R. J. Rudnick and W. F. McDonough, *Chem. Geol.*, 2002, **164**, 281-301.
- 13 T. Hirata, *Chem. Geol.*, 2001, **176**, 323-342.

214 14 L. J. Millonig, A. Gerdes and L. A. Groat, 2013, *Chem. Geol.*, 2013, **353**, 199-209.

215 15 M. Ibanez-Mejia, G. E. Gehrels, J. Ruiz, J. D. Vervoort, M. E. Eddy and C. Li, *Chem. Geol.*,
216 2014, **384**, 149-167.

217 16 U. Söderlund, P. J. Patchett, J. D. Vervoort and C. E. Isachsen, *Earth Planet Sci. Letter*,
218 2004, **219**, 311-324.

219 17 J. Hellstrom, C. Paton, J. Woodhead and J. Hergt, *In Laser Ablation ICP–MS in the Earth*
220 *Sciences: Current Practices and Outstanding Issues*, Mineral. Assoc. of Canada, Quebec,
221 Canada, ed. P. Sylvester, 2008, 343-348.

222 18 C. Paton, J. C. Hellstrom, B. Paul, J. D. Woodhead and J. M. Hergt, *J. Anal. Atom.*
223 *Spectrom*, 2011, **26**, 2508-2518.

224 19 J. A. Petrus and B. S. Kamber, *Min. Mag.*, 2011, 1633.

225 20 C. Paton, J. D. Woodhead, J. C. Hellstrom, J. M. Hergt, A. Greig and R. Maas, *Geochem.*
226 *Geophys. Geosyst.*, 2010, **11**, 1-36.

227 21 K. R. Ludwig, *Berkeley Geochronology Center, Special Publication 5*, 2012, 75.

228 22 J. B. Paces and J. D. Miller, *J. Geophys. Res.*, 1993, **98**, 13997-14913.

229 23 M. D. Schmitz, S. A. Bowring and T. R. Ireland, *Geochim. Cosmochim. Acta*, 2003, **67**,
230 3665-3672.

231 24 S. A. Hoaglund, U-Pb geochronology of the Duluth Complex and related hypabyssal
232 intrusions: investigating the emplacement history of a large multiphase intrusive
233 complex related to the 1.1 Ga Midcontinent Rift. *MSc thesis, University of Minnesota*,
234 2010, 103 pages.

235 25 K. E. Alagna, M. Petrelli, D. Perugini and G. Poli, *Geostand. Geoanalyt. Res.*, 2008, **32**,
236 103-120.

237 26 A. J. R. Kent and C. A. Ungerer, *J. Anal. Atom. Spectrom*, 2005, **20**, 1256-1262.

238

239 **Figures and tables**

240

241 **Figure 1:** CL images of Phalaborwa (A, B), Sorkka (C), and FC-4b (D). Rare grains show
242 complex magmatic zoning as observed in A. Usually the grains from FC-4b are free of zoning
243 and inclusions with only minor zoning on the margin of the grains (D).

244

245 **Figure 2:** Concordia diagrams for FC-4b (as the external standard forced to the published
246 age), Phalaborwa, and Sorkka from LA-ICP-MS analyses (c + e= concordance and
247 equivalence).

248

249 **Figure 3:** Comparison of the down-hole fractionation correction for zircon FC-5z and
250 baddeleyite FC-4b.

251

252 **Table 1:** LA-ICP-MS analytical conditions.

253

254 **Table 2:** LA-ICP-MS analytical results.

255

256 **Table 3:** Analytical figures of merit.

257

A

500 μm

B

100 μm

C

100 μm

D

100 μm