

1 **Rutile R632 - a new natural reference material for U-Pb and Zr**  
2 **analysis**

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16

17 **Abstract**

18

19 A new natural rutile reference material is presented, suitable as a reference for U-Pb dating  
20 and Zr-in-rutile thermometry by microbeam methods. U-Pb dating of rutile R632 using LA-  
21 ICP-MS magnetic sector field and quadrupole MS and ID-TIMS analyses yields a Concordia  
22 age of  $496 \pm 3$  Ma. The high U content ( $>300 \mu\text{g g}^{-1}$ ) enables high precision U-Pb ages despite  
23 its young age. The sample also has a Zr content of  $4294 \pm 196 \mu\text{g g}^{-1}$ , which makes it an  
24 excellent complementary reference material for Zr-in-rutile thermometry. Individual rutile  
25 grains have homogeneous composition of a number of other trace elements including V, Cr,  
26 Fe, Nb, Mo, Sn, Sb, Hf, Ta and W. This newly characterized material significantly expands

1 the range of available rutile reference materials relevant for age- and temperature  
2 determinations.

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#### 4 **Introduction**

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6 Rutile is the most common polymorph of  $\text{TiO}_2$  and occurs in a wide range of rocks. It mainly  
7 forms as a prograde metamorphic mineral in mid to high temperature settings and is  
8 widespread in metapelites, eclogites, but also in magmatic rocks and some hydrothermal  
9 systems (e.g. Meinhold 2010; Zack and Kooijman 2017). For more information on rutile  
10 occurrence and petrology the reader is referred to Meinhold (2010) and Zack and Kooijman  
11 (2017). Together with zircon and tourmaline, rutile is one of the most durable minerals,  
12 surviving weathering and transport and is thus a widespread accessory mineral in sediments  
13 and sedimentary rocks. There are several uses of rutile in geological sciences as the mineral  
14 structure can hold a wide range of trace elements that can provide geochemical and  
15 geothermochronological information related to its formation, origin and geological history.

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17 The incorporation of U and the exclusion of Pb during growth makes rutile a suitable mineral  
18 for U–Pb dating. The closure temperature ( $T_C$ ) for Pb in rutile is not well constrained and in  
19 an early study defined as ca. 420°C (Mezger *et al.* 1989) while later studies suggest a higher  
20 value of ca. 500–630°C (Cherniak *et al.* 2000; Vry and Baker 2006; Kooijman *et al.* 2010).  
21 Since rutile forms mainly during high-grade metamorphism and  $T_C$  is moderate, the U–Pb  
22 system in rutile records cooling, rather than formation ages (although formation ages can be  
23 preserved in the cores of large grains or if cooling conditions are fast enough, or in  
24 hydrothermal settings (e.g. Zack and Kooijman, 2017). The low  $T_C$ , compared to the zircon  
25 and monazite U–Pb geochronometers, makes rutile a highly suitable mineral for the  
26 reconstruction of retrograde sections of the temperature–time ( $T-t$ ) paths of metamorphic  
27 rocks, particularly when combined with other geochronometers.

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The incorporation of Zr into rutile during formation is temperature dependent. The buffering of the Zr concentration in rutile in quartz and zircon saturated rocks is the basis of the Zr-in-rutile (*ZiR*) thermometer that can preserve peak temperature conditions, even for rocks from ultrahigh temperature metamorphic terranes (e.g. Zack *et al.* 2004a; Tomkins *et al.* 2007; Ewing *et al.* 2013; Pape *et al.* 2016). The same individual rutile crystal can thus give information about the peak temperature and the cooling history of a sample. Rutile also incorporates significant amounts of Hf, but discriminates strongly against Lu. Thus, it has the potential to provide close to initial Hf isotope ratios that can constrain the evolution of crustal and mantle source reservoirs (e.g. Choukroun *et al.* 2005; Aulbach *et al.* 2008; Ewing *et al.* 2014). Due to its preference for high field strength elements, rutile has found applications in provenance studies where the Cr/Nb ratio is suggested to indicate a metabasic or metapelitic origin (e.g. Zack *et al.* 2004b; Meinhold *et al.* 2010). All these applications rely on the determination of absolute element concentrations and isotope ratios with good accuracy and precision and ideally for individual crystals or parts of crystals.

Despite the many uses of rutile in the geological sciences there are relatively few well-characterized reference materials available that can be used for calibration of analytical methods. For a rutile to be suitable as reference material for both age and chemical microbeam analysis it is important that it is homogeneous on the scale of the analytical method for a wide range of trace element concentrations and isotope ratios. In most natural samples the Zr content tends to be very heterogeneous among grains from the same rock sample (e.g. Ewing *et al.* 2013; Pape *et al.* 2016), which is caused by the specific genesis of individual rutile crystals in a rock. Currently only the rutile sample R10/R10b and R19 (Luvizotto *et al.* 2009; Schmitt and Zack 2012) are the commonly used primary reference materials for both geochronology and/or *ZiR* thermometry.

**Desired qualities in a reference material**

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2 A primary trace element reference material must have homogeneous, well-characterized  
3 element concentrations and an age reference material must have isotopic homogeneity,  
4 yielding the same age throughout the material over the desired analytical scale (usually a few  
5 tens of microns), and a low common Pb content. Natural reference materials are preferred  
6 when measuring natural samples since chemical and physical properties should be as close as  
7 possible to the sample material for a more reliable comparison, i.e. matrix matching. It has  
8 been shown that while internal standardization can correct for matrix differences between the  
9 sample and reference material matrix matching is preferred for the high field strength  
10 elements and required for element pairs that fractionate strongly during laser ablation as in the  
11 case for U and Pb (Sylvester, 2008). Of the few rutile reference materials currently available  
12 (R10/R10b, R19, Sugluk-4, PCA-S207), all but one record ages exceeding 1 Ga. While these  
13 reference materials are ideal for the determination of U-Pb ages on rutile unknowns that are  
14 older than 1 Ga, a younger reference material would be preferred for younger grains where  
15 the determination of  $^{238}\text{U}/^{206}\text{Pb}$ , which is for the purpose of the measurement an elemental  
16 ratio, is critical for the precision and accuracy of the resulting age. In this case, matrix-  
17 matched reference materials lead to more accurate matrix-dependent isotopic fractionation  
18 corrections, and provide more realistic estimates of uncertainty given the lower abundance of  
19 radiogenic Pb in both reference materials and unknowns. Analysis of a suite of rutile  
20 reference materials with a range of ages permits flexibility of data reduction, particularly for  
21 detrital populations where a wide range of dates might be obtained. To date, R19 is the only  
22 matrix-matched, young rutile age reference material and it contains approximately 15 $\mu\text{g/g}$  of  
23 U (Luvizotto et al., 2009). The addition of another young, more U-enriched rutile reference  
24 material to the geochronology toolbox allows more accurate determination of reference  
25 material ages on lower sensitivity instruments (e.g. quadrupole mass spectrometers) and may  
26 provide a better match to young, higher U unknowns. The application of the *ZiR* thermometer  
27 relies on the accurate determination of the Zr concentration in rutile. This is commonly done

1 by LA-ICP-MS or EPMA, of which the latter provides higher spatial resolution. To obtain  
2 accurate Zr concentration data by EPMA it is necessary to measure the  $L\alpha$  line for Zr  
3 correctly, which involves subtraction of the appropriate baseline. Standardization for Zr on  
4 the electron microprobe is commonly done using zirconium metal, Zr-bearing glass or zircon.  
5 These primary reference materials contain orders of magnitude more Zr than natural rutile  
6 and do not matrix-match with rutile. A rutile with known Zr content can be used as a  
7 reference material to verify the calibration for absolute Zr concentration measurements. The  
8 Zr content of currently characterized rutile reference materials ranges from 100 to 1000  $\mu\text{g/g}$ .  
9 Reference materials R10/R10b are most commonly applied and they have Zr concentrations  
10 of  $789\pm 13 \mu\text{g g}^{-1}$  (corresponding to  $ZiR$  temperatures of  $\sim 730^\circ\text{C}$ ; Watson et al., 2006).

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12 In this study, a new natural rutile reference material (R632) is characterized. Trace element  
13 data were obtained by electron probe microanalysis (EPMA) and Laser Ablation Inductively  
14 Coupled Plasma Mass Spectrometry (LA-ICP-MS) analysis at two different facilities. U-Pb  
15 element concentrations and isotope ratios were determined in two different laboratories by  
16 LA-ICP-MS and also by Thermal Ionisation Mass Spectrometry (TIMS).

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18 Existing rutile reference materials

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20 There are some rutile reference materials in use for age determination and trace element  
21 analyses of which the R10 and R10b are the most homogeneous and by far the most  
22 investigated. The age and trace element concentrations of commonly utilized rutile reference  
23 materials are summarized below.

24

25 *R10 & R10b* (Luvizotto et al., 2009; Schmitt and Zack, 2012) – Two individual single rutile  
26 crystals of  $\sim 1\text{cm}^3$  from Gjerstad, Norway. This is the most commonly used rutile reference  
27 material and each crystal has been cut into about 200 pieces. R10 and R10b have homogenous

1 trace element concentrations and a concordant U-Pb age of  $\sim 1090 \pm 5$  Ma. The U, common Pb  
2 and Zr concentrations are  $\sim 50 \mu\text{g g}^{-1}$ ,  $\sim 0.08 \mu\text{g g}^{-1}$  and c.  $790 \mu\text{g g}^{-1}$ , respectively. They are  
3 also used as reference material for  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios and Lu concentrations.

4

5 *R19 (Luvizotto et al. 2009)* – A single crystal from Blumberg, Australia, R19 is a low U ( $\sim 15$   
6  $\mu\text{g g}^{-1}$ ) crystal with an ID-TIMS age of  $489.5 \pm 0.9$  Ma. R19 is used as a secondary age and  
7 low U/Pb ratio reference rutile. It is also used as a reference material for  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios and  
8 Lu concentrations. Trace element concentrations are considerably less uniform than for R10  
9 and Zr concentrations are low, ranging from  $249\text{--}349 \mu\text{g g}^{-1}$ .

10

11 *R13 (Schmidt and Zack 2012)* – Rutile R13 is from Giftkuppe, Namibia, and has a U  
12 concentration of  $\sim 20 \mu\text{g g}^{-1}$  and yielded SIMS ages of  $504 \pm 4$  and  $505 \pm 6$  Ma. There is no other  
13 chemical data presented for this material.

14

15 *Diss (Luvizotto et al. 2009)* – The Diss rutile is used as a reference for  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic  
16 ratios and Lu concentrations. The Diss rutile has not been widely distributed as a reference.

17

18 *JIMP-1B (in Schmitt and Zack 2012)* – JIMP-1B is the primary rutile reference material for  
19 the SHRIMP lab in Perth, Australia. It was sampled in the Windmill Hills, Australia. SIMS  
20 ages for this material obtained by Schmitt and Zack (2012) are  $2642 \pm 3$  Ma, but no other  
21 chemical data is provided.

22

23 *Sugluk-4 (Bracciali et al. 2013)* – The rutile comes from the Cape Smith Belt of Québec,  
24 Canada, and is used as a U–Pb age reference material. The reported ID-TIMS age is  $1719 \pm 14$   
25 Ma and it has U concentrations of  $24\text{--}98 \mu\text{g g}^{-1}$ . Trace element concentrations are not  
26 homogeneous in Sugluk-4.

27

1 *PCA-S207 (Bracciali et al. 2013)* – This rutile comes from the East Lake Athabasca region,  
2 Canada, and is used as a secondary age reference material. The reported age is  $1865 \pm 8$  Ma  
3 and it has U concentrations of  $12\text{--}40 \mu\text{g g}^{-1}$ . Trace element concentrations are similar to the  
4 Sugluk-4 rutile; uncertainties for element concentrations are high, especially for Fe, Nb and  
5 Zr.

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### 7 **Material description of rutile R632**

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9 Sample R632 is a rare example of the unique association of corundum-, spinel- and  
10 sapphirine-bearing anorthitic to phlogopitic metasomatites exposed along the Sakena River to  
11 the NW of Ihosy, southern Madagascar (Lacroix 1939; Raith *et al.* 2008). The exceptionally  
12 rutile-rich rock consists of spinel, pargasite, anorthite, phlogopite, and accessory chlorapatite.  
13 Spinel ( $X_{\text{Mg}} 0.81$ ) typically occurs as elongate equigranular-polygonal aggregates within a  
14 coarse-grained matrix that is largely composed of granoblastic pargasite ( $X_{\text{Mg}} 0.87$ , Al<sup>[4]</sup>  
15  $\sim 2.15$ , Ti  $\sim 0.25$ ,  $X_{\text{K}}^{\text{A}} \sim 0.26$ ); spinel is locally replaced by phlogopite ( $X_{\text{Mg}} 0.89$ ; Ti  $\sim 0.20$   
16 p.f.u.) (*Fig. 1a*). In places the polygonal aggregates of spinel grade into symplectitic  
17 intergrowth domains of spinel and anorthite. A moat of polygonal anorthite ( $\text{An}_{99}$ ) separates  
18 the spinel aggregates from the pargasite matrix. The striking porphyroblastic nature of spinel  
19 aggregates and their anorthite moats, supported by the replacement textures observed in  
20 corundum- and spinel-bearing metasomatites of the exposure (Raith *et al.* 2008), suggests  
21 their formation through replacement of tabular corundum grains via the reaction *corundum* +  
22 *pargasite*  $\rightarrow$  *spinel* + *anorthite* + *fluid*. Rutile forms large (up to 1 mm) randomly  
23 distributed, amber, anhedral grains that predominantly occur at grain boundaries of  
24 granoblastic spinel, pargasite, and anorthite (*Fig. 1b,c*). The development of grain boundary  
25 triple junctions with the adjoining polygonal phases points to their mutual recrystallisation  
26 and chemical equilibration. Thermodynamic modelling of the pressure-sensitive reaction  
27 (Raith *et al.*, 2010) in combination with *P-T* pseudosection data for the associated cordierite-

1 sillimanite biotite gneisses (Raith *et al.* 2008) indicates equilibration of the  
2 *pargasite+spinel+anorthite+rutile* assemblage at *P-T* conditions of 750°C and <6-7 kbar in  
3 the presence of an aqueous fluid. The locally significant replacement of anorthite by fine-  
4 grained thomsonite, and thin carbonate+zeolite fillings of fractures traversing the sample  
5 occurred during a late stage of near-surface hydrous alteration of the rock.

6

## 7 **Experimental**

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### 9 **Sample preparation**

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11 The sample material was disintegrated using a SelFrag<sup>TM</sup> (high voltage puls power  
12 fragmentation) and separated with conventional magnetic and heavy liquid density separation  
13 methods. The rutile grains were handpicked under a binocular microscope and then mounted  
14 in acrylic resin for LA-ICP-MS and EPMA analyses.

15

### 16 **Electron Microprobe Analysis**

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18 Chemical analyses of major, minor and trace elements in rutile by EPMA were performed on  
19 a JEOL JXA-8200 Superprobe at the Institute of Geological Sciences, University of Bern  
20 (*Table 2*). The beam current was set at 100 nA with an acceleration voltage of 15 kV and a  
21 beam diameter set to ~1 µm.

22

23 The grain mounts were carbon coated prior to analyses. Element concentrations of Si, Zr, Nb,  
24 Cr, Ti, and Fe were determined using five wavelength-dispersive X-ray spectrometers  
25 (WDS). The X-ray peak and background intensities were measured for 150 and 75 s (Cr, Nb),  
26 30 and 15 s (Si), 20 and 10 s (Fe, Ti), and 300 and 150 s (Zr). X-ray intensities were  
27 determined on  $L\alpha$  lines (Nb, Zr) and  $K\alpha$  lines (Si, Cr, Fe, Ti) using the spectrometer crystals



1 PETH (Zr, Nb), TAP (Si), LIF (Cr), LIFH (Fe) and PETJ (Ti). An in-house synthetic zircon  
2 reference material was used as primary reference material for Zr calibration. The detection  
3 limit for Zr is about 45  $\mu\text{g/g}$  and between 40 and 120  $\mu\text{g/g}$  for the other elements measured.  
4 The CITZAF package (Armstrong 1995) was applied for automated matrix correction. During  
5 all analyses, Si was used as a monitoring element for identification of micro-inclusions like  
6 zircon that would yield measurements with anomalously high Zr contents.

7

8 Two to four point measurements were performed on each grain. Natural rutile reference  
9 sample R10b was used as quality control for primary calibration and as bracketing material  
10 every 13<sup>th</sup> measurement to monitor possible machine drift (Table 3). Based on these and  
11 additional measurements of R10b, an analytical uncertainty of 5% ( $\sigma$ ) is assigned to the EMP  
12 measurements.

13

#### 14 **Laser-Ablation ICP-MS**

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16 Rutile grains were analysed for trace elements (core and rim analyses in 27 grains and thus a  
17 total of 54 spot analyses, Table 3) at the Institute für Mineralogie, Westfälische Wilhelms-  
18 Universität, Münster, using the Photon Machines Analyte G2 Excimer Laser Ablation system  
19 coupled to a Thermo Fisher Scientific Element2<sup>TM</sup> magnetic sector field single collector ICP-  
20 MS (analytical information is listed in Table 1). Trace element data reduction was done using  
21 [Glitter 4.4.4 \(Griffin \*et al.\* 2008\)](#). TNT666 and TNT777 glasses (Klemme *et al.* 2008) were  
22 used as reference materials. As natural secondary reference materials R10 (Luvizotto *et al.*  
23 2009), Sugluk-4 (Braccialli *et al.* 2013), and PCA-S207 (Braccialli *et al.* 2013) were used. All  
24 results for all measured trace elements were in good agreement with published concentrations  
25 for the glasses and rutiles (Table 3).

26

1 U-Pb analyses were performed in the same laboratory with the same analytical settings as the  
2 trace element analyses (16 spot analyses in 16 grains were performed, *Table 4*). Age data  
3 reduction was done with in-house software following Kooijman et al. (2012). Rutile R10  
4 (Luvizotto et al., 2009) was used as a primary reference material. Secondary references used  
5 were PCA-S207 and Sugluk-4 (Bracciali et al., 2013), which yielded U-Pb Concordia ages of  
6  $1873\pm 2$  Ma ( $n=13$ ) and  $1731\pm 10$  Ma ( $n=6$ ), respectively (published ages are  $1865\pm 8$  and  
7  $1719\pm 14$  Ma, respectively). These data are referred to as LA-ICP-MS Mü.

8

9 A second batch of 20 spots in 10 grains was analysed for U-Pb isotopes and abundances  
10 (*Table 4*) in the Petrotectonic Facility at the Institute for Geological Sciences, Stockholm  
11 University, using the New Wave Research-193 Excimer Laser Ablation system coupled to a  
12 Thermo XSeries™ II quadrupole MS (analytical information is listed in *Table 1*). The age  
13 data reduction was done with the Iolite and Visual Age software (Petrus and Kamber, 2012).  
14 Rutile reference R10 (Luvizotto *et al.* 2009) was used for standardisation. Rutile R13 was  
15 used as a secondary reference material (Luvizotto *et al.* 2009) and yielded a Concordia age of  
16  $509\pm 8$  Ma (published SIMS ages of  $504\pm 4$  and  $505\pm 6$  Ma; Schmidt and Zack 2012). These  
17 data are referred to as LA-ICP-MS St.

18

19 Due to the low common Pb content in the rutile no correction is required. Isoplot Ex 4.1  
20 (Ludwig 2004) and density plotter (Vermeesch 2012) are used to present U-Pb data on  
21 conventional Concordia diagrams and in kernel probability density plots.

22

### 23 **ID-TIMS Analyses**

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25 For U-Pb TIMS analysis rutile fragments were selected. The grains were brown-red to orange  
26 and translucent to transparent; some of the grains showed well-developed crystal faces. An  
27 initial set of three grains was processed without abrasion, whereas subsequent analyses were

1 done after air-abrasion of the grains (Krogh 1982; *Table 5*). The selected grains were cleaned  
2 in hot HNO<sub>3</sub>, followed by water and acetone combined with ultrasonication. After drying they  
3 were weighed, transferred to Krogh-type Teflon® bombs (Krogh 1973), with the addition of a  
4 mixed <sup>202</sup>Pb-<sup>205</sup>Pb-<sup>235</sup>U tracer, HF and HNO<sub>3</sub> (12:1), and dissolved for 5 days at 195 °C. The  
5 solutions were processed with a single-stage HCl-HBr ion exchange procedure to isolate U  
6 and Pb, which were then loaded on Re-filaments with Si-gel and H<sub>3</sub>PO<sub>4</sub> and measured on a  
7 MAT262 mass spectrometer. The Pb and U ratios were measured in static mode on Faraday  
8 cups except for the <sup>207</sup>Pb/<sup>204</sup>Pb ratios that were obtained with a secondary electron multiplier.  
9 The Pb fractionation was corrected either using the <sup>205</sup>Pb/<sup>202</sup>Pb ratio or an average value of 0.1  
10 %/amu based on repeated measurements of NBS982. The U isotope ratio was corrected with  
11 a value of 0.12 ± 0.06 %/amu based on measurements of U500. The data were also corrected  
12 for blanks of 2 pg for Pb and 0.1 pg for U. Initial common Pb was corrected using a  
13 composition calculated from the model of Stacey and Kramers (1975). Decay constants are  
14 those of Jaffey *et al.* (1971).

15

## 16 **Results**

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### 18 **Trace element data**

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20 A selection of trace elements were analysed using EPMA (44 spots in 20 grains): Cr (167±65  
21 µg g<sup>-1</sup>), Fe (2791±217 µg g<sup>-1</sup>), Zr (4366±128 µg g<sup>-1</sup>), Nb (260±40 µg g<sup>-1</sup>) (*Table 2; Fig. 2*);  
22 and with LA-ICP-MS technique (53 spot analyses in 27 grains): V (1179±64), Cr (212±23 µg  
23 g<sup>-1</sup>), Fe (3220±299 µg g<sup>-1</sup>), Zr (4294±196 µg g<sup>-1</sup>), Nb (630±28 µg g<sup>-1</sup>), Mo (18.2±1.2 µg g<sup>-1</sup>),  
24 Sn (289±12 µg g<sup>-1</sup>), Sb (1.30±0.11 µg g<sup>-1</sup>), Lu (0.012±0.018 µg g<sup>-1</sup>), Hf (107.7±5.5 µg g<sup>-1</sup>), Ta  
25 (37.9±3.2 µg g<sup>-1</sup>), and W (1235±88 µg g<sup>-1</sup>) where uncertainties are 1σ (*Table 3; Fig. 2*). The  
26 data was treated with a 2RSD filter as illustrated in *Fig. 2* and the final element  
27 concentrations and σ are calculated from the remaining data. Of the elements analysed with

1 both techniques, the Cr, Fe, and Zr concentrations agree while the measured Nb  
2 concentrations differ significantly. The obtained Lu concentrations are close to the detection  
3 limit for the LA-ICP-MS method, which explains the high uncertainty ( $0.012\pm 0.018$ ) and thus  
4 these concentration data are not used.

5

## 6 **Geochronology**

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8 A total of 42 U–Pb rutile age analyses were performed in three different laboratories using  
9 LA-ICPMS sector field MS (16 analyses), LA-ICPMS quadrupole (20 analyses), and ID-  
10 TIMS technique (8 analyses) techniques.

11

12 The LA-ICP-MS Mü dates define a Concordia age of  $496\pm 3$  Ma. The  $^{206}\text{Pb}/^{238}\text{U}$  dates spread  
13 between  $488\pm 10$  Ma and  $509\pm 15$  Ma (*Table 4*). The age distribution curve is slightly  
14 positively skewed with an  $\text{MSWD} = 1.3$  (*Fig. 3*). The sample signals obtained from the LA-  
15 ICP-MS Mü analyses show a stable signal with uniform element signal intensities as shown in  
16 *Fig. 4*, where five typical sample signals are presented. The Th and  $^{208}\text{Pb}$  intensities exceeded  
17 background levels slightly (*Fig. 4*) indicating common Pb contents of less than 1% ( $f_{206\%} <$   
18 1%) (*Table 4*). Intensity signals for  $^{238}\text{U}$ ,  $^{206}\text{Pb}$ , and  $^{207}\text{Pb}$  were stable over the whole length of  
19 the analyses indicating homogeneity within and between individual grains.

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21 The LA-ICP-MS St defines a Concordia age of  $493\pm 7$  Ma and the  $^{206}\text{Pb}/^{238}\text{U}$  dates spread  
22 between  $466\pm 31$  Ma and  $514\pm 36$  Ma (*Table 4*). The two discordant data points are excluded.  
23 The age distribution curve is slightly negatively skewed with an  $\text{MSWD} = 0.67$  (*Fig. 3*). No  
24 common Pb correction was applied as  $^{204}\text{Pb} < ^{202}\text{Hg}$ .

25

26 The ID–TIMS analyses (*Table 5*) reveal U concentrations of 350–400  $\mu\text{g g}^{-1}$  and Pb contents  
27 between 25 and 30  $\mu\text{g g}^{-1}$ , but with higher values observed in two grains (*Table 5*). All U

1 concentrations are much higher than for most rutiles presented in the literature. Initial Pb is  
2 mostly less than  $1 \mu\text{g g}^{-1}$ , and Th/U near zero. The lack of a straight correlation between  
3 apparent age and abrasion seems to argue against the scatter resulting from Pb-loss as the  
4 abraded grains would be expected to be older than the non-abraded grains. The age data plot  
5 on or close to the Concordia curve and the eight individual  $^{206}\text{Pb}/^{238}\text{U}$  dates range between  
6  $495\pm 1$  and  $507\pm 1$  Ma (*Fig. 3, Table 5*).

7

## 8 **Discussion**

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### 10 **Trace elements**

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12 To monitor the quality of the trace element analyses, R10/R10b was used as a secondary  
13 reference material and the results are presented in *Fig. 5* together with the published data for  
14 the same (Luvizotto *et al.* 2009) and the data agree well except for Sb. The Sb concentration  
15 for R10 from the LA-ICP-MS Mü is lower than, and does not overlap with, uncertainties with  
16 the published values for R10 (Luvizotto *et al.* 2009), although the difference is small ( $0.07 \mu\text{g}$   
17  $\text{g}^{-1}$ ). During the LA-ICP-MS analyses Sugluk-4, and PCA-S207 (Bracciali *et al.* 2013) were  
18 also used as secondary reference material and although they have larger uncertainties  
19 compared to sample R10, the measured concentrations and the published values (Bracciali *et*  
20 *al.* 2013) agree for most elements (V, Nb, Sn, Hf, W, Zr, Mo, Ta) while some discrepancies  
21 are observed for Cr, as well as V and Mo in PCA-S207 also.

22 Of the eleven trace elements determined in this study (*Fig 2.*, Tables 2 and 3), V, Fe, Zr, Nb,  
23 Mo, Sn, Sb, Hf, Ta, and W show the highest degrees of homogeneity in R632. All have  
24  $\text{RSD}\% < 10\%$  from the LA-ICP-MS Mü analyses. Of the elements that were also analysed  
25 with the EPMA technique, both methods provide Zr concentrations that agree within  
26 uncertainty, but Fe and Nb concentrations determined by EPMA are lower than those  
27 obtained using LA-ICP-MS. The phenomenon that Nb concentrations in rutile can appear

1 lower when determined by EPMA compared to LA-ICP-MS has been observed by Meinhold  
2 *et al.* (2010) and is most likely attributable to standardization problems associated with EMP  
3 analyses.

4  
5 The signal strengths remained stable over time for both the EPMA and LA-ICP-MS analytical  
6 sessions as illustrated in *Fig. 2* where the concentration is plotted against run number. The  
7 data spread for the analyses is lower for the LA-ICP-MS trace element results (RSD 4–9%)  
8 than for the EPMA (up to 39% for Cr). Although the data spread is larger for the EPMA  
9 analyses, the results overlap within error with the values obtained from the LA-ICP-MS  
10 analyses. The LA-ICP-MS trace element concentrations are considered as best estimates for  
11 the accurate concentrations. The higher uncertainty for the secondary reference materials  
12 Sugluk-4 and PCA-S207 reflects the heterogeneous nature of the material. The narrow range  
13 in measured trace element concentrations (as reflected in the scatter of the data), attests to the  
14 homogenous distribution of these elements in R10.

15  
16 In *Fig. 6* the core and rim concentrations from the LA-ICP-MS analyses of the same grain are  
17 plotted against each other to illustrate the degree of homogeneity of the R632 grains. A spread  
18 away from the 1:1 line would illustrate a within-grain concentration spread while a spread  
19 along the 1:1 line would illustrate a between-grain concentration spread. Of the data that pass  
20 through the 2RSD filter, all elements show a limited spread from the 1:1 line illustrating the  
21 intra and inter grain homogeneity of the R632 rutile. Compared to commonly utilized existing  
22 reference materials, R632 has a remarkably high content of Sn, Hf, W and Zr (*Fig. 5*).

23  
24 **Zr-in-Rutile Thermometry**

25  
26 The homogeneous and high Zr concentration,  $4294 \pm 196 \mu\text{g g}^{-1}$ , makes R632 suitable as a  
27 calibration reference material for quantitative EPMA Zr concentration analysis. As the *ZiR*

1 thermometer is more sensitive at lower Zr concentrations, an accurate calibration of the Zr  
2 peak is crucial, and is more easily obtained from material with high Zr concentrations. Metal,  
3 glass or zircon standards/reference materials are often used for the primary calibration of the  
4 Zr spectrum peak, but a high Zr content rutile as the R632 can also reduce possible errors  
5 induced due to matrix mismatch between the primary reference material and the rutile sample.

6

## 7 **U–Pb ages**

8

9 Although uncertainties of individual analyses vary with the methods used, the Concordia U-  
10 Pb ages obtained with three different experiments overlap within uncertainty, are relatively  
11 precise (Mü:  $496 \pm 3$  Ma; St:  $493 \pm 7$  Ma), and provide similar and robust Concordia ages (*Fig.*  
12 7). Individual high-precision ID-TIMS ages appear to reveal a small-scale heterogeneity in  
13 the U-Pb systematics of individual grains. This could be caused by minor differences in the  
14 closure temperature of the differently sized rutile grains or local alteration. However, this  
15 variation is not resolvable using any of the currently available microbeam techniques.

16 All ages from the three analytical methods are in broad agreement. Based on these estimates  
17 the “best U-Pb age” obtained for R632 is  $496 \pm 3$  Ma. The concordance of the U-Pb ages also  
18 confirms that possible Pb-loss is minor and does not affect LA-ICP-MS analyses since the  
19 amount of lost Pb is smaller than can be detected by the quadrupole and magnetic sector field  
20 single collector techniques. In the combined dataset the ages overlap, indicating good

21 reproducibility between different measurement techniques. The signal stability from the LA-  
22 ICP-MS analyses (*Fig. 4*) further displays inter- and intragrain stability in U–Pb analyses. A  
23 spot size of  $90 \mu\text{m}$  for LA-ICP-MS Mü analyses could be argued to homogenize the ages, but  
24 many facilities prefer a larger spot for rutile dating, particularly of young, low U unknowns.

25 For the LA-ICP-MS St analyses a smaller spot size of  $35 \mu\text{m}$  gives homogeneous data,  
26 although with a larger analytical uncertainty. Despite the large uncertainty, ca.  $\pm 30$  Ma, the

1 coupling of the U-Pb system in this grain and the accuracy of downhole fractionation  
2 corrections is reflected in the low MSWD and the precise U-Pb Concordia age of  $493 \pm 7$  Ma.  
3  
4 The relatively high U content of R632 ( $> 300 \mu\text{g/g}$ ) means that precise ages can be obtained  
5 on this reference material using LA-ICP-MS methods using standard spot sizes (ca. 30-  
6 50  $\mu\text{m}$ ) suitable for U-Pb analyses of natural rutiles. The relatively young ages combined with  
7 the very high U content ( $> 300 \mu\text{g g}^{-1}$ ) and negligible common Pb content make sample R632  
8 a highly suitable age reference material. Combining two reference materials of distinctly  
9 different ages allows for correct calibration of the analytical method over a larger age range  
10 of U-Pb ages and Pb isotope compositions. The R10/R10b reference material (for example)  
11 together with R632 provides the opportunity for multiple data reduction with reference  
12 materials that are better matched to unknowns isotopically.

13

#### 14 **Conclusion and Outlook**

15

16 Multi-element and isotope analyses of rutile R632 reveal that this material is very  
17 homogenous and thus highly suitable as reference material for calibration of analytical  
18 methods for microbeam U-Pb dating and Zr concentration measurement for *ZiR* thermometry  
19 on natural samples. The material yields consistent and precise U–Pb dates using three  
20 different techniques with different degrees of precision (LA-ICP-MS quadrupole, LA-ICP-  
21 MS magnetic sector field single collector, and ID-TIMS). The U-Pb ages obtained from  
22 different grains of the rutile fraction yielded indistinguishable ages when combined.

23

24 Rutile R632, in combination with an older reference material, can be used as a precise  
25 younger U–Pb age calibration sample and thus widens the range of well calibrated U-Pb rutile  
26 reference materials suitable for LA-ICP-MS technique. The best estimate for its U-Pb age is  
27  $496 \pm 3$  Ma. In addition, the Zr concentrations of  $4294 \pm 196 \mu\text{g g}^{-1}$  make R632 an excellent



1 reference material for evaluation of the Zr concentrations obtained in rutile from EPMA and  
2 thus for *ZiR* thermometry in natural samples.

3  
4 The R632 rutile complements the existing reference materials and can improve the data  
5 obtained from rutile thermochronological studies. With this new material there will be rutile  
6 references available spanning a significantly wider range of both age and temperature.

7  
8 Rutile R632 is available as a mineral separate in batches of ca. 20 mg each. It is available in  
9 the grain sizes 64-500  $\mu\text{m}$  and 500-1000  $\mu\text{m}$ . It can be provided to all interested laboratories  
10 that want to use it for calibrations or to develop new research methods. Request can be sent  
11 to: Emelie Axelsson (Stockholm, emelie.axelsson@geo.su.se) or Klaus Mezger (Bern,  
12 klaus.mezger@geo.unibe.ch).

13

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