Prolonged mantle residence of zircon xenocrysts from the western Eger rift

Wolfgang Siebel1*, Axel K. Schmitt2, Martin Danišák3, Fukun Chen4, Stefan Meier5, Stefan Weiß5 and Sümeyya Eroğlu1

Zircon is a common mineral in continental crustal rocks. As it is not easily altered in processes such as erosion or transport, this mineral is often used in the reconstruction of geological processes such as the formation and evolution of the continents. Zircon can also survive under conditions of the Earth’s mantle, and rare cases of zircons crystallizing in the mantle significantly before their entrainment into magma and eruption to the surface have been reported1,2. Here we analyse the isotopic and trace element compositions of large zircons of gem quality from the Eger rift, Bohemian massif, and find that they are derived from the mantle. (U–Th)/He analyses suggest that the zircons as well as their host basalts erupted between 29 and 24 million years ago, but fragments from the same xenocrysts reveal U–Pb ages between 51 and 83 million years. We note a lack of older volcanism and of fragments from the lower crust, which suggests that crustal residence time before eruption is negligible and that most rock fragments found in similar basalts from adjacent volcanic fields equilibrated under mantle conditions. We conclude that a specific chemical environment in this part of the Earth’s upper mantle allowed the zircons to remain intact for about 20–60 million years.

Zircon (ZrSiO4) is a common accessory mineral in continental crustal rocks, and the earliest witness for the formation of continents. For crustal zircons, the U–Pb decay system is known to remain isotopically closed through high-grade metamorphism, partial melting or deep burial of crustal material3–5. In recent years, there has also been a rise in interest in studying mantle-derived zircons, including mafic xenoliths, alkali basalts and kimberlites (as reviewed by refs 6–9). Experimental data on lead diffusion10, however, predict open behaviour for the U–Pb isotopic system over protracted crystal storage at mantle temperatures, suggesting little alluvial transport from their source(s). The zircons are rounded to subrounded (Fig. 1c) and show magmatic surface corrosion textures owing to incipient melt reaction with the basaltic host lava. Some zircons contain inclusions of magnesium-rich ilmenite (MgO = 2–8 wt%) typical for mafic-ultramafic rocks or high-pressure assemblages in kimberlites. Fragments of individual xenocrysts, between 1 and 3 mm in diameter and free from cracks or visible inclusions, were selected for whole-grain or grain-fragment analysis (U–Pb, (U–Th)/He, Sm–Nd) and high-spatial-resolution isotopic (Lu–Hf, oxygen) and trace element analysis of grain subdomains. We grouped the samples according to colour from white (sample 1) to yellow (sample 3), pink (sample 2) to red–brown (sample 4) (Fig. 1b).

Oscillatory zonation is visible in cathodoluminescence images of pink and red–brown xenocrysts (samples 2 and 4) (Fig. 2a,b), whereas white and yellow xenocrysts (samples 1 and 3) reveal only faint zonation patterns or are featureless in cathodoluminescence. Oscillatory zonation in mantle zircons is generally interpreted to result from crystallization from a melt11,12. Under cold-cathode luminescence, most zircon crystals show distinct bluish cathodoluminescence colours (Fig. 2a), a characteristic feature of mantle zircons12. Cathodoluminescence brightness correlates positively with rare-earth elements (REEs), uranium and thorium concentrations (Fig. 3; Supplementary Table S1) and the difference in element content between the four types of zircon xenocrystal probably reflects variable chemical conditions during their growth. The colourless and yellow zircons (samples 1 and 3) contain the lowest amounts of uranium, thorium and REEs, whereas the pink and red–brown populations (samples 2 and 4) have higher abundances of these trace elements. This finding suggests that the colour is a function of zircon’s response to radiation-induced structural damage after the eruption. From the preservation of chemically distinct growth domains in these zircons (Fig. 2a,b), we infer that diffusion length scales for REEs and the tetravalent cations uranium and thorium (and by analogy hafnium) are smaller than the tens to hundreds of micrometres of oscillatory zoning visible in cathodoluminescence.

Trace element analyses (Fig. 3; Supplementary Table S1) indicate steep chondrite-normalized REE patterns with variable enrichment and concavity of the heavy REEs as well as positive cerium and lack of europium anomalies in all analysed xenocrysts, similar to mantle-affinity zircons13. In a garnet-bearing source, we would expect a higher retention of heavy REEs (and yttrium) by residual garnet, whereas in the presence of plagioclase, europium (as Eu2+) under

1Institute of Geosciences, University of Tübingen, 72074 Tübingen, Germany, 2Department of Earth and Space Sciences, University of California, Los Angeles, California 90095, USA, 3Department of Applied Geology/John de Laeter Centre of Mass Spectrometry, Curtin University of Technology, Perth WA6845, Australia, 4CAS Key Laboratory of Crust-Mantle Material and Environment; School of Earth and Space Sciences, University of Science and Technology of China, 230026 Hefei, China, 5Zweigstraße 22, 95615 Marktredwitz, Germany, 6Redaktion Lapis, Orleanstr. 69, 81667 Munich, Germany.

*e-mail: wolfgang.siebel@uni-tuebingen.de.
low-oxidizing and reducing conditions) would fractionate from the other REEs (ref. 4). Hence, the REE patterns are compatible with zircon crystallization from a garnet- and plagioclase-free mantle source in the spinel-facies peridotite field.

Uptake of titanium in zircon is sensitive to temperature\(^\text{12}\). On the basis of in situ titanium analyses (6.6–18 ppm Ti), model Ti-in-zircon temperatures at TiO\(_2\) in situ the basis of other REEs (ref. 4). Hence, the REE patterns are compatible with low-oxidizing and reducing conditions) would fractionate from the source in the spinel-facies peridotite field.

The average values are consistent with \(\delta^{18}O\) values of 5.3 ± 0.3‰ (refs 9, 16) found for zircons that crystallized in equilibrium with the mantle. Fragments from the different zircon groups were analysed for hafnium isotopes by laser-ablation multiple-collector inductively coupled plasma source mass spectrometry\(^\text{17}\) and for neodymium isotopes by whole-grain isotope-dilution thermal ionization mass spectrometry (ID-TIMS) (Supplementary Tables S2 and S3). The \(^{176}\text{Hf}/^{177}\text{Hf}\) and \(^{144}\text{Nd}/^{144}\text{Nd}\) ratios are denoted as \(\varepsilon_{\text{Nd}}(t)\) and \(\varepsilon_{\text{Hf}}(t)\) relative to bulk Earth at \(t = 0\) Myr. In all of the grains, positive \(\varepsilon_{\text{Hf}}(t)\) values were found, but differences exist between the four different zircon xenocrysts (ten spots on each xenocryst) with values of 5.6 ± 1.3 (sample 1), 6.0 ± 1.2 (sample 2), 3.6 ± 1.3 (sample 3) and 7.4 ± 1.0 (sample 4) (mean ± standard error). Three of the four zircon populations have bulk neodymium contents (0.2–2 ppm) sufficiently elevated to permit isotope analysis at uncertainties <0.3 \(\varepsilon_{\text{Nd}}\) units. Initial \(\varepsilon_{\text{Nd}}(t)\) values are positive, with values of 1.5 (sample 1), 3.8 (sample 4) and 4.5 (sample 2).

Nineteen zircon fractions from the four different zircon xenocryst types were dated by the U–Pb ID-TIMS method (Table 1). The zircons have low uranium and lead concentrations (8–121 ppm and 0.19–1.45 ppm, respectively). Most fractions cluster on or near the concordia curve at 73–51 Myr (Fig. 2c), but minor discordance is evident in four zircon fragments from the same grains with \(^{206}\text{Pb}/^{238}\text{U}\) age as old as 83 Myr. All four zircon xenocryst populations show U–Pb age variability without any discernible trends in U–Pb ages from one population to another. Three different zircon xenocrysts (fragments from the same grains used for U–Pb geochronology and other isotope analyses) were analysed by the (U–Th)/He dating technique (Supplementary Table S4). Samples 2 and 4 give results consistent within 1σ, with weighted mean ages of 25.7 ± 1.5 Myr (sample 2, \(n = 2\)) and 24.9 ± 1.5 Myr (sample 4, \(n = 2\)), whereas the two fragments of sample 3 yield ages of 23.8 ± 1.1 and 28.7 ± 2.4 Myr. The larger age uncertainty of the latter analysis mainly results from very low total amounts of uranium (0.082 ng) and thorium (0.001 ng) encountered in this zircon fragment. The alkali-basaltic fields of
the western Eger rift formed 29–19 Myr ago\(^1\); the largest volume of lava erupted during a narrow time interval 26–23 Myr ago. Zircons will retain helium at temperatures below 170–190 °C (ref. 19) and the lack of evidence for volcanism older than 29 Myr ago in this rift segment provides no support for the possibility that the (U–Th)/He zircon ages represent a reheating age of older eruption(s). We conclude that the (U–Th)/He ages correspond to the time of eruption of zircon-bearing host basalts in the Late Oligocene epoch, whereas U–Pb dating marks a minimum time for zircon crystallization. Hence, the combined U–Pb and (U–Th)/He data supply strong evidence that zircon crystallization preceded volcanic entrainment and eruption by > 20–60 Myr.

Neodymium isotopes in zircons are slightly more enriched compared with Eger rift alkali basalts by about 2–3 \(\epsilon\)\textsubscript{Nd} units\(^2\), yet they are clearly indicating depleted source(s) for the zircons\(^3\). The lack of older volcanism (> 29 Myr) and the absence or extreme scarcity of lower crustal xenoliths (for example, granulites) in basalts of the western Eger rift\(^1\) provide support for the conclusion that the zircons resided in the mantle before entrainment in the host basalts and eruption. Frequently erupted mantle xenoliths comprise spinel, spinel lherzolites, spinel harzburgites, olivine pyroxenites and pyroxenites, that is, rocks of lithospheric mantle origin. The equilibration pressure and temperature estimates of mantle xenoliths from mid-European volcanic fields are equivalent to \(\sim 30–50 \text{ km depth} \) and \(> 900–1,000 ^\circ\text{C}\) (refs 22, 23). During eruption the zircons were heated by their host basaltic magma. Rapid transfer from depth to surface is indicated by the preservation of mineral equilibria for mantle conditions in xenoliths from other European volcanic fields\(^22,23\), which allows us to infer that entrainment in basaltic magma during ascent and eruption occurred over short timescales that left U–Pb isotopic compositions unaltered. U–Pb zircon age variability, however, suggests that some Pb loss occurred during residence in the lithospheric mantle at temperatures of possibly 1,000 °C or more, consistent with diffusion data\(^10\) and the partial loss of intra-crystalline zonation in white and yellow xenocrysts. For concordant zircon fragments in Fig. 2c, it is impossible to decide whether they represent newly crystallized zircon, or complete Pb loss of older crystals. Regardless of the zircon crystallization age, the spread of zircon compositions along concordia (Fig. 2c) is inconsistent with a single Pb-loss event, and requires either multiple or protracted zircon growth events, or
resetting at different times before eruption. The data provide no
evidence that this occurred shortly before the eruption because of
the significant gap between (U–Th)/He and U–Pb ages, but
we emphasize that our interpretation does not require isotopic
closure. The survival of zircons in a mantle that was affected by
asthenospheric upwelling processes25 and the Hf–Nd isotope
composition of the grains calls for a locally enriched chemical
composition

Methods

Oxygen isotope ratios in concert with trace element compositions were determined using the Cameca ims 1,270 high-resolution ion microprobe at UCLA. Analytical procedures on oxygen isotopes and trace elements were those outlined in refs 14 and 15, respectively. 20O/18O ratios are expressed as δ18O and reported versus the Vienna Standard Mean Ocean Water (VSMOW) standard: [(18O/16O)sample/(18O/16O)VSMOW – 1] × 10^3.

For hafnium laser-ablation multiple-collector inductively coupled plasma source mass spectrometry measurements (Finnigan Neptune, State Key Laboratory of Continental Dynamics, Northwest University Xi’an), we used the analytical techniques and interference corrections that have recently been described elsewhere27. 141 analyses of zircon 91500 standard yielded a 176Hf/177Hf-weighted mean value of 0.282307±0.000025 (2σ a.d.), Hafnium isotope ratios are reported relative to a 18O/15O/Hf value of 0.282306. εHf(t) represents the deviation of the 176Hf/177Hf ratio (in parts per 10,000) from this ratio for the bulk Earth, which is modelled on the composition of chondritic meteorites (CHUR): εHf(t) = [176Hf/177Hf]sample/(176Hf/177Hf)CHUR – 1] × 10^4. εHf(t) values, where t is time, show this deviation for a given time in the past and were calculated using chondritic hafnium data of 176Hf/177Hf = 0.282785 and 176Hf/177Hf = 0.0336 (ref. 28). A value of 1.865 × 10^-11 yr^-1 was used for the decay constant of 178Lu.

For Sm–Nd isotope analyses, zircon powder (<10 μm, 40–90 mg) was dissolved in 29 M hydrofluoric acid for one week at 220 °C in a pressure bomb. Samarium and neodymium were separated from other elements by standard ion-exchange chromatography. All isotopic measurements were made by ID-TIMS, on a Finnigan MAT 262 mass spectrometer on a rhenium double-filament assembly. 143Nd/144Nd ratios were measured with 7–10 ppm internal precision and total procedural blanks were 20 pg for samarium and 30 pg for neodymium.

For U–Pb analysis, zircons were loaded into Teflon perfluoroalkoxy microcapsules, spiked with a mixed 206Pb and 207Pb, and 238U/206Pb date of the sample.

Table 1: U–Pb isotope composition (ID-TIMS data) of four different zircon xenocrysts (samples 1–4).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Weight (mg)</th>
<th>206Pb/238U</th>
<th>U (ppm)</th>
<th>Pb/207Pb</th>
<th>Pb* a/Dbc</th>
<th>Th/U</th>
<th>Isotopic ratios</th>
<th>Apparent age (Myr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–1A</td>
<td>0.337</td>
<td>52.9</td>
<td>8.3</td>
<td>0.192</td>
<td>0.55</td>
<td>0.39</td>
<td>0.0801</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>1–5A</td>
<td>0.087</td>
<td>58.3</td>
<td>9.0</td>
<td>0.278</td>
<td>0.63</td>
<td>0.39</td>
<td>0.0115</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>1–1S</td>
<td>0.041</td>
<td>49.9</td>
<td>13.3</td>
<td>0.406</td>
<td>0.50</td>
<td>0.35</td>
<td>0.0100</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>1–2S</td>
<td>0.032</td>
<td>45.3</td>
<td>11.1</td>
<td>0.346</td>
<td>0.43</td>
<td>0.48</td>
<td>0.0091</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>1–4S</td>
<td>0.047</td>
<td>43.0</td>
<td>13.9</td>
<td>0.514</td>
<td>0.39</td>
<td>0.42</td>
<td>0.0102</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>2–3A</td>
<td>0.183</td>
<td>202</td>
<td>29.8</td>
<td>0.536</td>
<td>3.03</td>
<td>0.56</td>
<td>0.0129</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>2–4A</td>
<td>0.093</td>
<td>91.5</td>
<td>25.1</td>
<td>0.442</td>
<td>1.20</td>
<td>0.54</td>
<td>0.0092</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>2–6A</td>
<td>0.203</td>
<td>157</td>
<td>21.8</td>
<td>0.356</td>
<td>2.33</td>
<td>0.61</td>
<td>0.0106</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>3–1A</td>
<td>0.699</td>
<td>90.0</td>
<td>6.7</td>
<td>0.102</td>
<td>1.14</td>
<td>0.41</td>
<td>0.0079</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>3–2A</td>
<td>0.122</td>
<td>88.8</td>
<td>27.0</td>
<td>0.489</td>
<td>1.17</td>
<td>0.58</td>
<td>0.0091</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>3–5A</td>
<td>0.066</td>
<td>43.7</td>
<td>26.0</td>
<td>0.838</td>
<td>0.40</td>
<td>0.38</td>
<td>0.0090</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
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<tr>
<td>4–3A</td>
<td>0.111</td>
<td>107</td>
<td>52.3</td>
<td>0.988</td>
<td>1.44</td>
<td>0.52</td>
<td>0.0106</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>4–4A</td>
<td>0.052</td>
<td>65.9</td>
<td>52.2</td>
<td>1.399</td>
<td>0.76</td>
<td>0.43</td>
<td>0.0113</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>4–5A</td>
<td>0.437</td>
<td>310</td>
<td>50.3</td>
<td>0.665</td>
<td>4.83</td>
<td>0.56</td>
<td>0.0103</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>4–1S</td>
<td>0.034</td>
<td>141</td>
<td>34.1</td>
<td>0.540</td>
<td>2.02</td>
<td>0.55</td>
<td>0.0100</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>4–2S</td>
<td>0.157</td>
<td>1178</td>
<td>52.1</td>
<td>0.599</td>
<td>18.97</td>
<td>0.51</td>
<td>0.0106</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>4–3S</td>
<td>0.031</td>
<td>1284</td>
<td>121</td>
<td>1.259</td>
<td>21.64</td>
<td>0.68</td>
<td>0.0092</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
<tr>
<td>4–5S</td>
<td>0.092</td>
<td>599</td>
<td>67.2</td>
<td>0.811</td>
<td>9.53</td>
<td>0.53</td>
<td>0.0104</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
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<tr>
<td>4–6S</td>
<td>0.030</td>
<td>243</td>
<td>94.5</td>
<td>1.453</td>
<td>3.76</td>
<td>0.60</td>
<td>0.0112</td>
<td>206Pb* 0.02% 207Pb* 0.12%</td>
</tr>
</tbody>
</table>

*Samples analysed were small pieces from larger fragments (>2 mm) of four different megacryst xenocrysts (samples 1–4).
†Weight and concentration error better than 20%.
‡Corrected for mass discrimination and isotopic tracer contribution.
§Corrected for mass discrimination, isotopic tracer contribution, U and Pb blank with 206Pb/207Pb = 18.70, 207Pb/204Pb = 15.63, 208Pb/204Pb = 38.64 and initial common Pb with 206Pb/204Pb = 18.61, 207Pb/204Pb = 15.62, 208Pb/204Pb = 38.53.
∥Errors (in %) reported at 2σ confidence level.
**Correlation coefficient between errors at 206Pb/207Pb and 207Pb/205Pb ratios.
Degassed zircons were dissolved following ref. 29 and analysed by isotope dilution for uranium and thorium on an Agilent 7500 CS mass spectrometer.

Received 13 May 2009; accepted 21 October 2009; published online 22 November 2009

References

Acknowledgements
Y. Hong, Lin, Northwest University, Xi’an, and W. Fang, CAS Beijing. assisted with microprobe work at UCLA was supported by a grant from the Instrumentation and Facilities Program, NSF. We thank J. C. Harvey (Caltech Pasadena, USA) for revising the English and I. Williams (ANU Canberra, Australia) for his valuable comments on an earlier version of the manuscript.

Author contributions
S.M. and S.W. provided the zircons and valuable background information. Experiments were carried out by A.K.S. (oxygen, trace elements), F.C. (Lu–Hf analyses, oxygen isotopes, and multiple-collector ICP-MS). N. Evans and B. McDonald, Curtin University of Technology, Perth, with U and Th analyses. Ion microprobe work at UCLA was supported by a grant from the Instrumentation and Facilities Program, NSF. We thank J. C. Harvey (Caltech Pasadena, USA) for revising the English and I. Williams (ANU Canberra, Australia) for his valuable comments on an earlier version of the manuscript.

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