

Supplement

Hydrothermal experiments

Three hydrothermal experiments have been carried out at 200, 400, and 600°C. The reactive solution was 1M HCl-0.2M HF containing 300 ppm non-natural Hf (98.2% ^{180}Hf) and 970 ppm Yb. The isotopic composition of the solution was $^{180}\text{Hf}/^{177}\text{Hf} = 377.5$, $^{176}\text{Hf}/^{177}\text{Hf} = 0.2389$, and $^{176}\text{Yb}/^{177}\text{Hf} = 157$, which is quite different from that of the starting zircon (Table 1). For the 400 and 600°C experiments, four to five grains ($\sim 3 \times 10^{-4}$ g) were placed into a gold capsule (3 mm i.d.). The capsules were then filled with 0.0388 g (400°C experiment) and 0.0176g (600°C experiment) of the solution, sealed by laser welding, weighed, and placed in cold-seal hydrothermal vessels, which were then heated to 400 °C and 600 °C for 120 h and 72 h, respectively. The uncertainty in the temperature was estimated to be $\pm 10^\circ\text{C}$. The pressure was set to 1.00 ± 0.05 kbar using water as the pressure medium. At the end of the experiments, the vessels were quenched in an air stream for 10 - 15 min. The gold capsules were re-weighed to check for any loss of solution. The 200 °C experiment was carried out under autogenous pressure in a 3 ml, cold-seal Teflon[®] reactor with five grains and 0.5183 g of the same solution as used in the high-temperature experiments. The Teflon[®] reactor was then placed in a preheated oven for 1018 h.

Analytical methods

Six ion microprobe analyses for Y and the REE of the starting material (sample CZ25) were performed at the Max-Planck-Institut für Chemie in Mainz, Germany, with a modified Cameca IMS 3f ion microprobe using a ~ 1 nA O^+ primary ion beam (17 keV) of ~ 10 μm diameter. The analyses were done with energy filtering (100 eV energy offset relative to low-energy edge of $^{16}\text{O}^+$ secondary ions) to suppress molecular interferences with the Y and REE signals. Secondary ion signals for ^{16}O , ^{30}Si , Y, and the REE were acquired in six measurement cycles, and the concentrations were calculated using a procedure similar to that of Zinner and Crozaz (1986).

The U-Pb measurements were carried out by laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) with a Thermo-Scientific Element2 coupled to the New Wave Research UP-193HE Laser at Westfälische Wilhelms-Universität Münster, Germany. For the U-Pb zircon analyses, the masses ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{238}U were measured. The ^{202}Hg count rates were also measured to correct the interference of ^{204}Hg on ^{204}Pb , which is necessary to correct for common Pb. The repetition rate was 10 Hz, and an energy of ~ 5 J/cm² was used. The laser spot size was set to 35 μm . The helium flow varied between 0.5 and 0.6 l/min. Five measurements of the zircon samples were bracketed with two measurements on the calibration standard GJ1 (Jackson et al. 2004) to monitor and correct for any instrumental mass bias. Age calculations were performed with an in-house Excel[®] spreadsheet using the intercept method (e.g., Košler and Sylvester 2003) to correct for elemental fraction during laser analysis. The standard zircon 91500 was measured as an unknown along with samples to monitor the accuracy of the analyses. Eight analyses of the standard zircon 91500 yielded a concordia age of 1068 ± 12 Ma, which agrees well with the reference age of 1065 Ma (Wiedenbeck et al. 1995).

Hafnium isotope measurements were performed with a Thermo-Scientific Neptune multi-collector ICP-MS coupled to the New Wave Research UP-213 laser system (LA-MC-ICPMS) at Goethe-Universität in Frankfurt, Germany. A teardrop-shaped, low volume laser cell was used. Data were collected in static mode (^{172}Yb , ^{173}Yb , ^{175}Lu , ^{176}Hf -Yb-Lu, ^{177}Hf , ^{178}Hf , ^{179}Hf , ^{180}Hf) during 29 to 58 seconds of laser ablation. Analyses were performed mostly as single spots having a diameter of 20 or 40 μm . Thin rims were analyzed by moving the laser spot ($\sim 20\mu\text{m}$) at 8 $\mu\text{m/s}$ along the rim, resulting in line scans of ~ 200 μm length. Nitrogen (~ 0.005 l/min) was introduced via a Cetac Aridus into the Ar sample carrier gas to enhance sensitivity by $\sim 20\%$ and to reduce

oxide formation to below $< 0.1\%$ (e.g., HfO/Hf). The signals of ^{172}Yb , ^{173}Yb , and ^{175}Lu were simultaneously monitored during each analysis step to allow for correction of isobaric interferences of Lu and Yb isotopes on mass 176. The ^{176}Lu and ^{176}Yb were calculated using $^{176}\text{Lu}/^{175}\text{Lu}$ of 0.02658 and $^{176}\text{Yb}/^{173}\text{Yb}$ of 0.795015 (both in-house values; Gerdes and Zeh, 2009). The use of the Cetac Aridus system allowed bracketing of laser ablation analyses with solution mode analyses of JMC 475, which were used for tuning the Neptune and monitoring accuracy of Hf isotope analyses including interference corrections. For all laser ablation Hf isotope data, the instrumental mass bias was corrected using an exponential law with a fixed βHf and a $^{179}\text{Hf}/^{177}\text{Hf}$ value of 0.7325 (Patchett et al. 1981). This was necessary because the non-natural Hf isotopic composition of the tracer solution used for the experiments did not allow the application of an internal mass bias correction. The fixed βHf value (-0.9374 ± 0.0067 ; $n=10$) was inferred from repeated analyses of the GJ-1 reference zircon during the analytical session. This value is identical to the mean βHf value (-0.9341 ± 0.0102) of 35 analyses on zircon domains where the Hf isotope composition has not been modified during the experiments. A fixed βYb of about 12% lower than the βHf ($\beta\text{Hf}/\beta\text{Yb} = 1.012 \pm 0.003$) was used for correcting Lu and Yb isotope ratios for mass bias. This is the mean value of all analyses with a ^{173}Yb signal above 80 mV. The external reproducibility (2SD; $n > 50$), estimated from analyses of reference zircon 91500, GJ-1, and Plešovice ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282298 \pm 0.000026$, 0.282003 ± 0.000018 and 0.282482 ± 0.000015 , respectively) over six months, is about 0.005-0.009% (< 1 epsilon unit).

Micro-Raman measurements have been carried out with a high-resolution Jobin Yvon HR800 Raman system using a Nd-YAG (532 nm) laser. The scattered Raman light was collected in 180° backscattering geometry and dispersed by a grating of 1800 grooves/mm after having passed a 150 μm entrance slit. A 100 \times objective (N.A. = 0.9) was used for all measurements. The backscattered Raman signal was collected two times for 10 to 100s.

References

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Table S1. Average REE concentration ($n = 6$) of the starting material (zircon CZ25) as measured by ion microprobe.

	ppm	$\pm 2\sigma_m$
La	0.160	0.007
Ce	18.9	0.5
Pr	0.13	0.02
Nd	1.82	0.05
Sm	4.99	0.09
Eu	0.40	0.05
Gd	36.4	0.8
Tb	13.5	0.3
Dy	166	3
Ho	61.4	1.4
Er	309	7
Tm	68.2	1.4
Yb	682	13
Lu	144	3

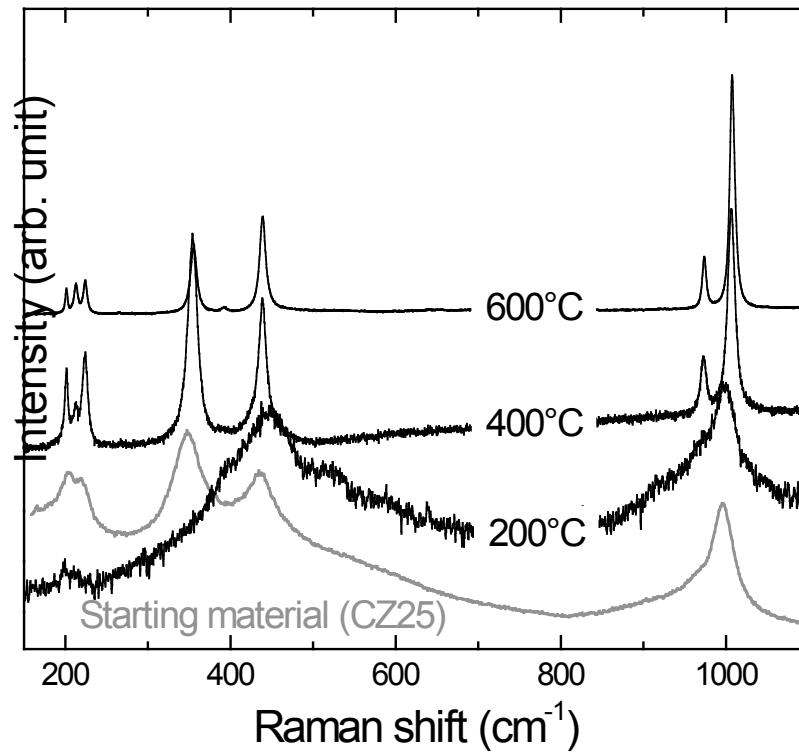


FIGURE S1. Representative Raman spectra of the experimentally altered domains in comparison with a typical spectrum of the starting material (zircon CZ25). Structural recovery in the altered domains is reflected by a decrease of the widths and an increase of the frequency (wavenumber) of the fundamental Raman bands. Note the temperature-dependent degree of structural recovery.