Supplementary Material, American Mineralogist, October 2014
Cottle: Geochronology of (U)ThSiO4

AM-14-1008

Appendix

Analytical methods

XRD. Single-crystal X-ray diffraction (XRD) patterns were made with a Kappa Apex II X-ray diffractometer in the Chemistry Department at the University of California, Santa Barbara.

EPMA. Elemental maps and quantitative major and trace element analyses were made using a Cameca SX-100 Electron Probe MicroAnalyzer (EPMA) housed at the University of California, Santa Barbara. X-ray maps of U (LPET, Mα), Th (LPET, Mα), Y (LTAP, Lα), and P (LPET, Kα) were made in beam scan mode using 15 keV accelerating voltage, 200 nA beam current (equating to a ~1 μm^3 interaction volume), and a dwell time of 25 ms. Quantitative analyses were performed on the same instrument. Operating conditions were 40 degrees takeoff angle, accelerating voltage of 20 keV, 200 nA beam current and a beam diameter of 5 μm. Elements were acquired using analyzing crystals LLIF for La Lα, Nd Lα, Pr Lα, Eu Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα, Fe Kα, Sm Lα, LPET for Pb Mα, U Mα, Ce Lα, Ca Kα, Y la, Th Mα, and TAP for P Kα, Si Kβ, Al Kα.

The standards were ThO2 for Th Mα, U-2 (10.00% UO_2 in diopside glass) for U Mα, Anorthite (Grass Valley) U.C. no. 16706 for Al Kα, Diopside (Chesterman) for Si Kβ, Ca Kα, Magnetite U.C. no. 3380 for Fe Kα, $CePO_4$ (USNM 168484) for Ce Lα, DyPO4 (USNM 168485) for Dy Lα, ErPO4 (USNM 168486) for Er Lα, $EuPO_4$ (USNM 168487) for Eu Lα, $GdPO_4$ (USNM 168488) for Gd Lα, HoPO4 (USNM 168489) for Ho Lα, LaPO4 (USNM 168490) for La Lα, P Kα, $LuPO_4$ (USNM 168491) for Lu Lα, $NdPO_4$ (USNM 168492) for Nd Lα, $PrPO_4$ (USNM 168493) for Pr Lα, $SmPO_4$ (USNM 168494) for Sm Lα, $TbPO_4$ (USNM 168496) for Tb Lα, $TmPO_4$ (USNM 168497) for Tm Lα, $YbPO_4$ (USNM 168498) for Yb Lα, YPO_4 (USNM 168499) for Y Lα, and Pyromorphite (Cameca) for Pb Mα.

The counting time was 40 s for La Lα, Ce Lα, Nd Lα, Th ma, Pr Lα, Eu Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα, Fe Kα, Si Kβ, Sm Lα, 100 s for Al Kα, Pb Mα, 120 s for U Mα, 160 s for Y Lα, and 200 s for P Kα, Ca Kα. The off peak counting time was 40 s for La Lα, Ce Lα, Nd Lα, Th Mα, Pr Lα, Eu Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα, Fe Kα, Si Kβ, Sm Lα, 100 s for Al Kα, Pb Mα, 120 s for U Mα, 160 s for Y Lα, and 200 s for P Kα, Ca Kα. Off Peak correction method was Linear for La Lα, Ce Lα, Nd Lα, Th Mα, P Kα, Pr Lα, Gd Lα, Ho Lα, Tm Lα, Yb Lα, Si Kβ, Ca Kα, Y Lα, Sm Lα, and Multi-Point for Lu Lα, Pb Mα, U Mα, Fe ka, Eu Lα, Al Kα, Er la, Tb Lα, Dy Lα.

Unknown and standard intensities were corrected for deadtime. Standard intensities were corrected for standard drift over time. Interference corrections were applied to La for interference by Nd, and to Nd for interference by Ce, and to Pr for interference by La, Y, and to Eu for interference by Nd, Pr, and to Gd for interference by Nd, Ce, La, and to Dy for interference by Eu, and to Ho for interference by Gd, Lu, and to Er for interference by Tb, and to Tm for interference by Dy, Gd, and to Yb for interference by Eu, Dy, Tb, and to Lu for interference by Dy, Ho, and to Pb for interference by Y, and to U for interference by Th, and to Fe for

interference by Dy, and to Al for interference by Tm, Yb, Th, and to Ca for interference by Pb and Yb. See Donovan et al. (1993) for detail.

Oxygen was calculated by cation stoichiometry and included in the matrix correction. The matrix correction method was ZAF or Phi-Rho-Z Calculations and the mass absorption coefficients data set was LINEMU Henke (LBL, 1985) < 10KeV/CITZMU > 10KeV. The ZAF or Phi-Rho-Z algorithm utilized was Armstrong/Love Scott (Armstrong 1988). Accuracy of unknown analyses was checked routinely using in house natural monazite reference materials, synthetic ThO_2, and NIST SRM 610.

LA-MC-ICPMS. In situ U-Th/Pb geochronology analyses were performed using a laser ablation multi-collector inductively coupled plasma mass spectrometer (LA-MC-ICPMS) at the University of California Santa Barbara (UCSB). Analytical methods follow Cottle et al. (2012, 2013); and Kylander-Clark et al. (2013) and are briefly described here. Instrumentation consists of an Analtye 193 nm ArF excimer laser (Photon Machines, San Diego, U.S.A.) equipped with a HelEx two-volume sample cell (Eggins et al. 1998) attached to a Nu Plasma HR MC-ICPMS (Nu Instruments, Wrexham, U.K.). The collector array on the Nu Plasma is configured to simultaneously measure ^{238}U and ^{232}Th on two high-mass side Faraday cups and ^{208}Pb, ^{207}Pb, ^{206}Pb, and ^{204}X (where X includes ^{204}Pb and ^{204}Hg) on four low-mass side secondary electron multipliers. Ablations were conducted for 20 s each at 1.2 J/cm^2 or 1.5 J/cm^2 fluence (thorite, zircon), a frequency of 4 Hz, and a pit diameter of 5 or 20 μm yielding craters ~3, or 9 μm deep (as assessed by optical microscopy). Utilizing a sample–standard bracketing technique, analyses of reference materials (RMs) with known isotopic composition were measured before and after each set of seven unknown analyses. Data reduction, including corrections for baseline, instrumental drift, mass bias, down-hole fractionation as well as age calculations were carried out using Iolite v. 2.1.2 (Paton et al. 2010). Background intensities and changes in instrumental bias were interpolated using a smoothed cubic spline while down-hole inter-element fractionation was modeled using an exponential function. Statistics for baselines, on peak intensitie, and isotopic ratios were calculated using the mean with a 2 S.D. outlier rejection.