Nuerkanati Madayipu, Huan Li, Safiyanu Muhammad Elatikpo, Michael W. Förster, Hou-Xiang Zhou, Han Zheng, and Qian-Hong Wu, 2022, Magmatic-hydrothermal evolution of long-lived Nb-Ta-(Sn) mineralization in Lianyunshan, NE Hunan, South China: GSA Bulletin, https://doi.org/10.1130/B36591.1.

Supplemental Material

Text. EMS 1 Analytical methods.

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Magmatic-hydrothermal evolution of long-lived Nb-Ta-(Sn) mineralization in Lianyunshan, NE Hunan, South China

Nuerkanati Madayipu[a], Huan Li[a,*], Safiyanu Muhammad Elatikpo[a], Michael W. Förster[b], Hou-Xiang Zhou[c], Han Zheng[a], Qian-Hong Wu[a]

[a] *Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment Monitoring, Ministry of Education, School of Geosciences and Info–Physics, Central South University, Changsha 410083, China*

[b] *School of Natural Sciences, Macquarie University, NSW 2109, Sydney, Australia*

[c] *Hunan Provincial Institute of Land and Resources Planning, Changsha 410007, China*

*Corresponding authors' email: lihuan@csu.edu.cn (H., Li)

EMS 1 Analytical methods

Coltan analyses

BSE images and mapping

Chemical mapping of single crystals using backscattered electron (BSE) images was carried out at the School of Geosciences and Info–Physics, Central South University, China. A scanning electron microscope equipped with an energy-dispersive spectrometer (EDS) and a CL+ detector was used for imaging and element mapping. The operating conditions included an accelerating voltage of 15 kV, an electron beam current of 20 nA, and a beam diameter of 2 μm.

Major element analyses

The major elements of columbite-tantalite grains were determined using a JEOL JXA 8230 electron probe microanalyzer (EPMA) equipped with four wavelength dispersive-type spectrometers at Yanduzhongshi Geological Analysis Laboratories Ltd.,

China. The operating conditions were 15 kV accelerating voltage, a 20 nA beam current, and an electron beam with a diameter of 5-μm. The standards used were as follows: $LiTaO_3$ (Ta), Fe_2O_3 (Fe), $KNbO_3$ (Nb), UO_2 (U), $MnTiO_3$ (Mn), $RbTiOPO_4$ (Ti), Cal-STD (Y), ThO_2, (Th), SiO_2 (Si), $ZnWO_4$ (W), zircon (Si Kα, Zr Lα, Hf Lα), and SnO_2 (Sn). Spectral lines, peak time(s), and off-peak background time(s) used for the wavelength dispersive spectrometry (WDS) analyses are as follows: Ta (K*α*, 40, 5), Fe (K*a*, 10, 5), Nb (L*a*, 40, 20), U (M*a*, 20, 10), Mn (Ka, 10, 5), Ti (K*a*, 40, 20), Y (L*a*, 10, 5), Th (M*a*, 10, 5), Si (K*a*, 10, 5), W (M*a*, 10, 5), and Sn (K*a*, 10, 5).

Geochronology

Coltan grains were separated from sample 18RL-28, mounted in epoxy, and polished. The trace elements (including rare earth elements) and U–Pb isotopic compositions of coltan were determined at the Institute of Geology and Geophysics, Chinese Academy of Sciences, China, by using a GeoLas PLUS 193 nm excimer ArF LA system coupled to an Agilent 7500a quadrupole-based ICP–MS (Q–ICP–MS) instrument. Samples and standards were ablated using a 35 μm laser spot size with a repetition rate of 4 Hz. Eight sample analyses were bracketed by one NIST610 and two coltan standards (Coltan 139). Nb was used as the internal standard for the trace element content and NIST 610 as the external reference material. Data reduction, including off-line integration of background and analytical signals, time-drift correction and quantitative calibration for trace-element analyses and U–Pb ages, were carried out using GLITTER 4.0 software. Details of the analytical procedures are described by Che et al. (2015).

Zircon analyses

Geochronology

Zircons were separated from three samples (20-23S1, and 20-11S1 from the MFSC, respectively) using standard techniques involving individual grains hand-picked under a binocular microscope, then mounted in epoxy resin and polished to expose the grain centres. Cathodoluminescence (CL) imaging was performed at Beijing Geo Analysis Co., Ltd. (Beijing, China), using a scanning electron microscope attached to an energy dispersive spectroscopy (EDS) system and a CL3+ detector. This was operated at an acceleration voltage of 15 kV and a current of 20 nA. The CL images of zircon grains were used to examine their internal structures and aided the choice of suitable sites without cracks and inclusions prior to *in situ* U–Pb dating, trace element and Hf isotope analyses.

Zircon U–Pb dating and trace element analyses were conducted using a quadrupole ICP–MS equipped with a 193 nm excimer laser in pulse energy of 70 mJ and a repetition rate of 5 Hz. The analysis was performed at the School of Geosciences and Info–Physics of Central South University, China. Helium was used as a carrier gas to provide efficient aerosol transport to the ICP-MS and minimize aerosol deposition. Argon was used as a make–up gas and mixed with the carrier gas. Nitrogen was added to the central gas flow (Ar+He) of the Ar plasma to reduce the detection limit and improve precision (Hu et al., 2008; Liu et al., 2010b). A background acquisition of 20–30 seconds and a data acquisition of 40 seconds were used for each sample analysis, with spot size and laser ablation depth of 32 μm and 20–40 μm, respectively. Laser-induced fractionation was corrected by the SSB (Sample Standard Bracket) method. External standard zircon 91500 was used to normalize isotopic fractionation during analysis and was analyzed twice for every five samples. GJ–1 and Plešovice zircon standards were used for quality control, and NIST SRM 610 was applied as an external standard for concentration calculations, analyzed once for every 60 samples. ^{204}Pb was monitored during the

analytical process, and zircon grains with high ^{204}Pb intensities compared to the gas blank were excluded. Common Pb correction was processed following the method given by Stacey and Kramers (1975). More detailed descriptions of analytical instrumentation and procedures can be found in Yuan et al. (2008) and Liu et al. (2010a).

Trace element compositions of zircon grains were simultaneously measured with zircon U–Pb dating. Combined with the external standard NIST SRM610, 29Si was used as an internal standard to correct the trace element concentrations of unknowns. The reference values of trace element compositions for the standard sample NIST SRM610 glass are from the GeoReM database (http://georem.mpch–mainz.gwdg.de/). GLITTER 4.4.4 developed by GEMOC was used during data reduction. Concordia diagrams and weighted mean age calculations were made by using the Isoplot R program (Vermeesch, 2020).

Hf isotopes

Zircon in situ Hf isotope analysis was carried out at the Beijing Geo Analysis Co., Ltd. (Beijing, China) using a laser-ablation system NWR 193nm, attached to a Neptune Plus multiple collector MC-ICP-MS. All analyses were conducted on the same zircon grains previously analyzed for U-Pb isotopes, using a beam diameter of 40 μm, an energy density of 7-8 J/cm2, an ablation time of 26 seconds, and a laser pulse frequency of 10 Hz. During the analysis, helium was used as the carrier gas. International standard zircon sample GJ-1 was used as reference material. Wu et al. (2007) gave a detailed description of instrumental conditions and test procedures. The initial $^{176}Lu/^{177}Hf$ ratios and εHf(t) values were calculated using the measured U-Pb ages and are referenced to the chondritic reservoir [present-day $^{176}Hf/^{177}Hf = 0.282772$ and $^{176}Lu/^{177}Hf = 0.0332$] (Bruguier et al., 1997). The decay constant for ^{176}Lu of 1.865×10^{-11} $year^{-1}$ (Scherer et al., 2001) was adopted. Two-stage model ages (T_{DMC}) were calculated for the source

rock of magma by assuming that the parental magma was produced from average continental crust ($^{176}Lu/^{177}Hf = 0.015$) that was originally derived from depleted mantle (Griffin et al., 2000).

Cassiterite analyses

In situ U-Pb dating of cassiterite was conducted using LA-ICPMS in Beijing GeoAnalysis CO., Ltd microanalysis lab, Beijing. The Resolution SE model laser ablation system (Applied Spectra, USA) was equipped with ATL (ATLEX 300) excimer laser and a Two Volume S155 ablation cell. The laser ablation system was coupled to an Agilent 7900 ICPMS (Agilent, USA).

Detailed tuning parameters can be seen in Thompson et al. (2018). LA-ICPMS tuning was performed using a 50 micron diameter line scan at 3 μm/s on NIST 612 at ~3.5 J/cm^2 with repetition rate 10 Hz. Adjusting the gas flow to get the highest sensitivity (^{238}U~6*10^5 cps) and the lowest oxide ratio(ThO/Th ＜ 0.2%). P/A calibration was conducted on the NIST 610 using a line scan with a diameter of 100μm. Other laser parameters are identical to those during tuning. Analyzed masses were ^{27}Al, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{66}Zn, ^{69}Ga, ^{90}Zr, ^{93}Nb, ^{118}Sn, ^{121}Sb, ^{137}Ba, ^{178}Hf, ^{181}Ta, ^{182}W, ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, and ^{238}U, with a total sweep time of ~ 0.26 seconds. Samples were mounted in epoxy discs, polished to expose the grains, ultrasonicated in ultrapure water, and then cleaned again prior to the analysis using AR grade methanol. Pre-ablation was conducted for each spot analysis using 5 laser shots (~0.6 μm in depth) to remove potential surface contamination. The analysis was performed using 50 μm diameter spot at 5 Hz and a fluence of 4 J/cm^2.

Data reduction was performed by using the Iolite software package（Paton et al., 2010). Cassiterite AY-4 was used as primary reference material（Yuan et al., 2011). Double AY-4 were bracketed between multiple groups of 10 to 12 sample unknowns. Typically, 35-40 seconds of the sample signals were acquired after 20 seconds gas background measurement. Using the exponential function to calibrate the downhole fractionation (Paton et al., 2010). NIST 610 and ^{118}Sn were used to calibrate the trace element concentrations as external reference material and internal standard element, respectively. The internal standard content of Sn was determined by assuming stoichiometry.

Monazite analyses

Monazite isotopic compositions were investigated by LA-ICP-MS at the Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Laser sampling was performed using a GeolasPro laser ablation system that consists of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7700e ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. A "wire" signal smoothing device was included in the laser ablation system, by which smooth signals were produced even at very low laser repetition rates down to 1 Hz (Hu et al., 2015). This is useful for *in-situ* U-Pb dating of high-U minerals (Zong et al., 2015). The spot size and frequency of the laser were set to 44/60 μm and 5/6 Hz, respectively. Monazite standard 44069 and glass NIST610 were used as external standards for U-Pb dating and trace element calibration, respectively. Each analysis incorporated a background acquisition of approximately 20-30 s followed by 50 s of

data acquisition from the sample. An Excel-based software ICPMSDataCal was used to perform off-line selection and integration of background and analyzed signals, time-drift correction and quantitative calibration for trace element analysis and U-Pb dating (Liu et al., 2008; Liu et al., 2010a). Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 (Ludwig, 2003).

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