

Nature and timing of Sn mineralization in southern Hunan, South China: Constraints from LA-ICP-MS cassiterite U-Pb geochronology and trace element composition

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SM 1 ANALYTICAL METHODS

Cassiterite analysis

BSE images and mapping. The cassiterite grains were extracted using conventional heavy liquid and magnetic separation techniques. Separated cassiterite grains were handpicked under a binocular microscope, mounted in epoxy resin, and polished in order to expose the center of each grain. Cathodoluminescence (CL) and backscattered electron (BSE) imaging were carried out at Sample Solution Analytical Technology Co., Ltd. (Wuhan, China) using a scanning electron microscope equipped

with an energy-dispersive spectroscopy (EDS) system and a CL^{3+} detector, operated at 15 kV and 20 nA.

Geochronology analyses. Currently, isotope dilution thermal ionization mass spectrometry (ID-TIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) are the main U-Pb dating methods for cassiterite. ID-TIMS is a well-established and widely used method for U-Pb dating of various U-rich minerals, including cassiterite (Gulson et al. 1992), that guarantees high accuracy and reproducibility (Carr et al., 2020). However, direct U-Pb isotope dating of cassiterite by ID-TIMS requires a costly and lengthy procedure in a clean-lab (including sample cleaning, dissolution, and U-Pb separation), which is time-inefficient and can result in large errors for cassiterites with high common Pb content (Tu et al. 2016). Considering these shortcomings, LA-ICP-MS provides an attractive alternative for in situ determination of U-Pb isotopes in cassiterite. The use of LA-ICP-MS not only eliminates the lengthy pre-treatment processes such as sample dissolution and U-Pb separation inherent to the ID-TIMS method, but also allows resolution of isotopic heterogeneities at a scale of tens of microns. Moreover, using LA-ICP-MS to determine the U-Pb isotopic age of cassiterite allows the selection of the most suitable crystals (i.e. those with high U-Th contents), while avoiding those with high inclusion content that may contain large amounts of common Pb (Neymark et al. 2018, 2021).

In situ U-Pb dating and trace element analyses of cassiterite were completed at the Sample Solution Analytical Technology Co., Ltd. (Wuhan, China) using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Laser sampling was

performed using the GeolasPro HD laser ablation system, which combines a COMPexPro 102 ArF excimer laser (wavelength 193 nm, maximum energy 200 mJ) and a MicroLas optical system. The ion signal intensity is obtained using an Agilent 7700e ICP-MS instrument. Helium was used as a carrier gas in the ablation cell and combines with argon (makeup gas) behind ablative cells (Günther and Heinrich, 1999; Luo et al., 2018a). In this study, all analyses were performed with a laser spot size of 44 μm , a repetition rate of 50 Hz, and a fluence of 5.5 J/cm². A signal-smoothing and mercury-removing device were used in this laser ablation system to obtain smooth signals and reduce mercury signal (Hu et al., 2014). A small amount of water vapor (4.1 mg min⁻¹) was added to the ablation cell to improve analytical accuracy and precision (Luo et al., 2018b). Each analysis consisted of a 20-second background measurement followed by a 30-second data acquisition interval. Zircon 91500 (Wiedenbeck et al., 1995) was used as an external standard for correction of Pb-U fractionation during ablation and instrument mass discrimination. To check measurement accuracy, cassiterite AY-4 (Yuan et al., 2011) was analyzed as an unknown. Zircon 91500 was analyzed twice and AY-4 once or twice after testing of every four to six cassiterite grains to ensure high accuracy throughout the test session. The weighted average ²⁰⁶Pb/²³⁸U age of AY-4 obtained in this study is 157.4 ± 2.3 Ma (1 σ , n = 30, MSWD = 1.3, Table 1), consistent with the reference age of 158.2 ± 0.4 Ma (Yuan et al., 2011). Offline selection and integration of background and analyte signals, as well as time-drift correction and quantitative calibration for trace element analysis and U-Pb dating were

performed by ICPMSDataCal (Liu et al., 2010a). Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 (Ludwig, 2003). Tera-Wasserburg concordia plots of cassiterite were generated with IsoplotR (isoplotr.es.ucl.ac.uk, 2021/11, Database hosting in Beijing).

Trace element analyses

Trace element analysis of minerals was conducted by LA-ICP-MS at the Wuhan SampleSolution Analytical Technology Co., Ltd., Wuhan, China. Detailed operating conditions for the laser ablation system and the ICP-MS instrument and data reduction follow those of Zong et al. (2017). 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 7900 ICP-MS instrument was used to acquire ion-signal intensities. Helium was used as the carrier gas and argon as the make-up gas, being mixed with the carrier gas via a T-connector before entering the ICP. A “wire” signal smoothing device is included in this laser ablation system (Hu et al., 2015). The spot size and frequency of the laser were set to 44 μm and 50 Hz, respectively. Analyzed masses were ^{29}Si , ^{31}P , ^{43}Ca , ^{49}Ti , ^{55}Mn , ^{57}Fe , ^{89}Y , ^{91}Zr , ^{93}Nb , ^{118}Sn , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{182}W , ^{208}Pb , ^{232}Th , and ^{238}U . The trace element compositions of cassiterite were calibrated against NIST 610 glass as an external standard (Liu et al., 2010b). Each analysis incorporated a background acquisition interval of approximately 20-30 s followed by a data acquisition interval of 50 s. The 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 (Liu et al., 2010a).

Statistical analysis

Two chemometric methods were used to show the variability of trace elements in cassiterite between different deposits: unsupervised principal component analysis (PCA) and supervised orthogonal projection to latent structures discriminant analysis (OPLS-DA). Prior to OPLS-DA, the data were automatically adjusted and normalized to balance differences in stable isotope ratios and elemental contents. All data analysis was done by MetaboAnalyst 5.0 (<https://www.metaboanalyst.ca/>, 2022/08).

Principal component analysis (PCA). Principal component analysis is a commonly used linear-transformation dimensionality-reduction method that involves the characterization of covariance matrices obtained from training data and can be used to reduce the complexity of input variables when a large amount of information is present to facilitate identification and interpretation of key variables. It is frequently applied to process geochemical and other types of geological data on the following principles: (1) to reduce the number of relevant variables to a small number of uncorrelated principal components that represent most of the variability carried by multiple original variables; and (2) to enhance the interpretability of these components as a combination of multiple variables (Cheng et al., 2011; Frenzel et al., 2016).

Orthogonal projection to latent structures-discriminant analysis (OPLS-DA). This technique is a further step in PCA that is helpful in extracting information related to specific samples and variables of a dataset. The principal component score of the OPLS-DA model can be used to assess the differentiation of trace elements in cassiterite between two deposits, as it maximizes covariance between the measured variable X and the response of variable Y within the group. Overall, OPLS-DA is well suited for the classification of data with multiple covariates and noisy variables.

The evaluation parameters of the OPLS-DA results are cumulative R^2X , R^2Y , and

Q^2 . R^2X_{cum} is the explanatory power of variation in the X variables, and R^2Y_{cum} is the explanatory capacity of changes in the Y variables consisting of the predictor and orthogonal components. In OPLS-DA, the predictor variables denote between-class variables, whereas the orthogonal variables are intraclass variables, also known as uncorrelated variables. Based on cross-validation of the specified component, the fraction Q^2_{cum} of the Y variation predicted by the X model in that component indicates the predictive power of the developed discriminant, and the two are positively correlated. $Q^2 > 0.5$ can be considered as a valid model, and $Q^2 > 0.9$ is an excellent model. In OPLS-DA, the closer the indicators R^2X_{cum} , R^2Y_{cum} and Q^2_{cum} are to 1, the more stable and reliable the model is.

Table OM1. U–Pb dating results of standard cassiterites

Spot No.	Pb (ppm)	Th (ppm)	U (ppm)	²⁰⁷ Pb	1σ	²⁰⁶ Pb	1σ	²⁰⁷ Pb/	1σ
				²³⁵ U		²³⁸ U		²⁰⁶ Pb	
AY-4-1	2	0	93	0.1759	0.0115	0.0257	0.0006	0.0513	0.0037
AY-4-2	2	0	87	0.1743	0.0086	0.0247	0.0005	0.0552	0.0035
AY-4-3	2	0	94	0.1724	0.0135	0.0255	0.0008	0.0523	0.0053
AY-4-4	1	0	63	0.1789	0.0130	0.0250	0.0007	0.0572	0.0053
AY-4-5	1	0	22	0.1891	0.0210	0.0256	0.0012	0.0662	0.0102
AY-4-6	1	0	15	0.1654	0.0193	0.0248	0.0012	0.0571	0.0110
AY-4-7	2	0	84	0.1559	0.0101	0.0240	0.0006	0.0503	0.0038
AY-4-8	2	0	80	0.1615	0.0117	0.0237	0.0006	0.0523	0.0045
AY-4-9	2	0	84	0.1656	0.0093	0.0246	0.0005	0.0518	0.0037
AY-4-10	2	0	62	0.1722	0.0133	0.0254	0.0007	0.0518	0.0043

AY-4-11	3	0	111	0.1522	0.0079	0.0244	0.0006	0.0476	0.0029
AY-4-12	2	0	95	0.2051	0.0124	0.0248	0.0006	0.0635	0.0046
AY-4-13	1	0	21	0.3162	0.0343	0.0244	0.0011	0.1058	0.0136
AY-4-14	1	0	36	0.2353	0.0185	0.0251	0.0009	0.0744	0.0073
AY-4-15	3	0	97	0.1898	0.0108	0.0257	0.0006	0.0549	0.0033
AY-4-16	3	0	114	0.1800	0.0111	0.0252	0.0006	0.0541	0.0039
AY-4-17	2	0	76	0.1701	0.0128	0.0249	0.0007	0.0519	0.0044
AY-4-18	2	0	82	0.1751	0.0111	0.0254	0.0005	0.0514	0.0038
AY-4-19	3	0	122	0.1708	0.0087	0.0251	0.0005	0.0508	0.0029
AY-4-20	3	0	93	0.1911	0.0121	0.0259	0.0006	0.0566	0.0042
AY-4-21	2	0	59	0.1912	0.0117	0.0243	0.0006	0.0510	0.0041
AY-4-22	1	0	44	0.1867	0.0166	0.0250	0.0008	0.0522	0.0055
AY-4-23	1	0	42	0.3187	0.0222	0.0248	0.0010	0.1010	0.0089

AY-4-24	2	0	93	0.1888	0.0128	0.0252	0.0006	0.0561	0.0042
AY-4-25	3	0	114	0.1735	0.0116	0.0252	0.0006	0.0518	0.0040
AY-4-26	3	0	107	0.2040	0.0129	0.0269	0.0006	0.0580	0.0043

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