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ADDITIONAL INFORMATION

South China is one of the important W–Sn metallogenic provinces in the world, particularly the Nanling Range. Numerous studies led to Nanling W–Sn metallogenic events occurring during 160 to 150 Ma (Mao et al. 2007; Yuan et al. 2008). Recently, a new phase of W–Sn polymetallic mineralization linked with 145–135 Ma granites have been recognized in the Southeastern Coastal Metallogenic Belt (SCMB) of China, such as the Feie’shan W–Sn, Jinkeng Sn–Cu, Taoxihu Sn, Lianhuashan W and Xiling Sn deposits (Fig. S1). The Xiling deposit is in the southwestern domain of the SCMB, and it has long been regarded as a volcanic or subvolcanic rock–related Sn mineralization (Chen et al., 1986). However, our recent geochronological and fluid inclusion data suggested a new genetic model of mixing of magmatic brine from a hidden granitic intrusion with meteoric water (Liu et al., 2018, 2019). Five hydrothermal stages were recognized: cassiterite + feldspar + quartz (Stage I), cassiterite + quartz ± muscovite (Stage II), sulfide + cassiterite (Stage III), quartz + sulfide + chlorite (Stage IV), and calcite + chlorite + quartz (stage V) (Liu et al., 2018). Stages I and II are the major Sn depositional stages at Xiling.

METHODS

SEM–CL

The internal structure of the analyzed cassiterite was studied by cathodoluminescence

(CL) microscopy. CL images of cassiterite were taken using the TESCAN MIRA 3LMH SEM with a cathodoluminescence detector at the Nanjing Hongchuang Technology Co., Ltd., China.

***In-situ* LA–ICP–MS cassiterite analysis**

All laser ablation ICP-MS analyses (single spot and mapping) were performed in Ore Deposit and Exploration Center (ODEC), Hefei University of Technology (China), using an Agilent 7900 ICP–MS equipped with a Photon Machines Analyte HE 193nm ArF excimer laser. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP (Wang et al., 2017).

Each analysis was performed by a uniform spot size diameter of 30 μm at 7 Hz with energy of $\sim 3 \text{ J/cm}^2$ for 40s after measuring the gas blank for 20s. The following basic set of isotopes for cassiterite were monitored: ^7Li , ^{23}Na , ^{25}Mg , ^{27}Al , ^{29}Si , ^{39}K , ^{44}Ca , ^{45}Sc , ^{49}Ti , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{72}Ge , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{95}Mo , ^{97}Mo , ^{118}Sn , ^{125}Te , ^{133}Cs , ^{137}Ba , ^{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 , ^{209}Bi , ^{208}Pb , ^{232}Th , ^{238}U . Standard reference materials NIST 610, NIST 612 and BCR-2G were used as external standards to plot calibration curve. The preferred values of element concentrations for the USGS reference glasses are from the GeoReM database (<http://georem.mpch-mainz.gwdg.de/>). Standard reference materials were run after each 10-15 unknowns; detection limits were calculated for each element in each spot analysis. The off-line data processing was performed using a program called ICPMSDataCal (Liu et al., 2008). Trace element compositions of oxide minerals were

calibrated against multiple-references materials without applying internal standardization. The sum of all element concentrations expressed as oxide is considered to be 100% m/m for a given anhydrous silicate mineral.

Element maps were created by ablating sets of parallel line rasters in a grid across the sample. The laser beam was 15 μ m and the scanning speed was 15 μ m/s. A laser repetition of 10Hz was selected at a constant energy output of 80mJ, resulting in an energy density of ~ 2 J/cm² at the target. Reference material GSE-1g was analyzed at both the start and the end of each mapping for data calibration. Major and trace element compositions were calibrated by references without applying internal standardization. The sum of all element concentrations expressed as oxide is considered to be 100% m/m for a given anhydrous mineral. Images were compiled and processed using LIMS (Wang et al., 2017). For a single element, the average background was subtracted from its corresponding raster, and the rasters were compiled into a 2-D image displaying combined background/drift corrected intensity (Wang et al., 2017).

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