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Cassiterite oxygen isotopes in magmatic-hydrothermal systems: in situ microanalysis, fractionation factor and applications

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Abstract

Tin and tungsten are important metals for the industrializing society. Deciphering the origin and evolution of hydrothermal fluids responsible for their formation is critical to underpin genetic models of ore formation. Traditional approaches obtain isotopic information mainly from the bulk analysis of both ore and gangue minerals, or less frequently from in situ analysis of gangue minerals, which either bear inherited complexities and uncertainties or are indirect constraints. Hence directly obtaining isotopic information from ore minerals such as cassiterite by in situ techniques is critical, as this may significantly improve our understanding of fluid evolution and its controls on ore formation. However, this has been hampered by challenges from both analytical and applicational aspects. In this study, we first demonstrate a lack of crystallographic orientation effects during cassiterite ion microprobe oxygen isotope analysis. Along with our newly developed matrix-matched reference material, the Yongde-Cst, which has a recommended δ^{18}O value of 1.36 ± 0.16 ‰ (VSMOW) as defined by Gas-Source Isotope Ratio Mass Spectrometry, in situ oxygen isotope analysis of cassiterite now is possible. We further refine the oxygen isotope fractionation (1000 ln α) for quartz-cassiterite by first-principles calculations, which is given by the equation of $1.259\times10^6/T^2 + 8.15\times10^3/T - 4.72$ (T is temperature in kelvin). The 1000 ln α for quartz-cassiterite has a sensitive response to temperature, and makes cassiterite-quartz an excellent mineral pair in oxygen isotope thermometry, as described by the equation of $T\ (°C) = 2427 \times (\delta^{18}O_{qtz} - \delta^{18}O_{cst})^{-0.4326} - 492.4$. Using the well-established 1000 ln α of quartz-water, 1000 ln α of cassiterite-water is derived as $2.941\times10^6/T^2 - 11.45\times10^3/T + 4.72$ (T in kelvin), which shows a weak response to temperature. This makes cassiterite an ideal mineral from which to derive δ^{18}O of fluids as robust temperature estimates are not a prerequisite. We have applied oxygen isotope analysis to cassiterite samples from six Sn(-W) deposits in China. The results show considerable variability in δ^{18}O values both within a single deposit and among studied deposits. Combining the $\delta^{18}O$ of cassiterite samples and the equilibrium oxygen isotope fractionation, we find that the $\delta^{18}O$ values of ore-forming fluids show a strong magmatic affinity with variable but consistently low degree of involvements of meteoric water. This study demonstrates that in situ oxygen isotope analysis of cassiterite is a promising tool to refine sources of ore-forming fluids, and to decode hydrothermal dynamics controlling tin and tungsten mineralization.

Keyword

Cassiterite; SIMS; Oxygen isotope; 1000 ln α; Sn(-W) deposit; fluid source;

Introduction

Tin and tungsten are mostly sourced from magmatic-hydrothermal systems and bear a specific genetic association with peraluminous granites (Lehmann 1982; Blevin and Chappell 1995; Breiter et al. 2007). Formation of these deposits requires efficient scavenging of metals from their sources into hydrothermal fluids, and then their transport to sinks for mineralization (Wood and Samson 2000; Carr et al. 2020). In this process, aqueous fluids play a critical role in the mobilization, concentration, transportation and eventually deposition of tin and tungsten. In this regard, robust constraints on the sources, nature and evolution of hydrothermal fluids responsible for ore formation are essential for a better understanding of ore genesis. Oxygen is the most abundant element in aqueous fluids, and fluids from different origins typically bear diagnostic oxygen isotope compositions, which are a key proxy to directly decipher sources and track the evolution of ore-forming fluids (Cooke et al. 2014). Isotopic information of ore-forming fluids is predominantly obtained from two approaches. The first is bulk analysis of fluid inclusion assemblages (Bodnar et al. 2014). Fluid inclusions are remnants of paleo-fluids trapped during crystallization of gangue minerals (e.g., quartz) and ore minerals (e.g., cassiterite, wolframite). Extracting these ancient fluids for isotope analysis can give a direct measurement of the oxygen isotope composition of ore-forming fluids (Wilkinson 2001). On the other hand, both gangue minerals and ore minerals with oxygen in their crystal lattice can be analysed via bulk analysis to obtain δ^{18}O values of minerals, with δ^{18}O values of fluids being derived using the known oxygen isotope fractionation (1000 ln α) between mineral and water (Clayton et al. 1972). Due to almost unavoidable risks of mixing aliquots of fluids or domains of minerals from multiple stages of mineralization, which is inherent in the nature of bulk analysis, isotopic information obtained through these conventional approaches is subject to complexities and uncertainties, so interpretation from these data can be ambiguous.

In situ oxygen isotope analysis of ore minerals by ion microprobe (i.e., CAMECA SIMS and SHRIMP SI), such as cassiterite, the principal ore mineral of tin, is a promising method to directly obtain oxygen isotope compositions from ore minerals without mixing information from multiple stages of mineral growth. In comparison to analysing gangue minerals, analysing ore minerals also removes the fundamental assumption that gangue minerals and ore minerals are precipitated from the same aliquot of fluids. The ability of in situ techniques to overcome the drawbacks discussed above has been partly demonstrated in its applications to gangue minerals (D’Errico et al. 2012; Fekete et al. 2016; Li et al. 2018). An additional advantage of utilizing in situ techniques with high spatial resolution is that with detailed petrographic studies, texturally controlled information in mineral grains can be translated into temporal evolution patterns to reveal crystal growth history, and to reconstruct magmatic-hydrothermal processes during mineral precipitation. Such an approach is very beneficial for hydrothermal minerals with large grain sizes, such as cassiterite from Sn(-W) deposits, and it holds the promise to reveal fluid dynamics with unprecedented detail. Ion microprobes have been available to the geological community for more than half a century and have been routinely applied to the analysis of oxygen isotopes in silicates and carbonates. However, their applications to ore minerals are rare, and this is what we explore here.

An important consideration in ion microprobe analysis is the crystallographic orientation effect. When it is present, measured $\delta^{18}O$ values will strongly correlate with the crystallographic orientation of the analysed mineral relative to the incoming primary ion beam (Huberty et al. 2010). Previous studies have shown that rutile, an isostructural mineral with cassiterite, shows significant crystallographic orientation effects (Schmitt and Zack 2012; Taylor et al. 2012; Shulaker et al. 2015). As such, it is reasonable to expect that cassiterite might also show a crystallographic orientation effect, and rigorous evaluation is critical to making accurate oxygen isotope analyse. Carr et al. (2017) pioneered in situ cassiterite oxygen isotope analysis by SHRIMP SI. Using cassiterite grains from the Elsemore Granite in the New England Orogen, eastern Australia, they were able to achieve a reproducibility of ~2 ‰. Precision at this level limits its geological applications. With the potential presence of sample heterogeneity in the Elsemore cassiterite at the ~2 ‰ level, as highlighted by Carr et al. (2017), it is difficult to decipher whether the ~2 ‰ variation in their study was caused by true oxygen isotopic heterogeneity of the Elsemore cassiterite, or the presence of crystallographic orientation effects. An additional requirement for ion microprobe analysis is correcting for instrumental mass fractionation (IMF), which is matrix dependent. As such, to facilitate routine cassiterite oxygen isotope analysis, it is critical to conduct a rigorous evaluation of the crystallographic orientation effect, and to characterize matrix-matched reference materials.

Once the technique for cassiterite oxygen isotope analysis has been established, it is necessary to transfer δ^{18}O values of cassiterite to δ^{18}O values of fluids during cassiterite crystallization, for which knowing the temperature-dependent oxygen isotope fractionation (1000 ln α) between cassiterite and water is a prerequisite. Both experimental and computational approaches have been utilized to derive 1000 ln α (Zheng 1991; Zhang et al. 1994; Hu et al. 2005; Polyakov et al. 2005). Recent advances in first-principles calculations offer new chances to evaluate robustness of previous estimates from an independent perspective.

Once the analytical challenges and fractionation factors having been defined, it is necessary to demonstrate their application to cassiterite bearing deposits. As a response to these challenges, here we present a comprehensive and systematic investigation of cassiterite oxygen isotope in magmatic-hydrothermal systems. We first demonstrate a lack of crystallographic orientation effects in SIMS cassiterite oxygen isotope analysis, and then report the Yongde-Cst, the first cassiterite oxygen isotope reference material. We further calculate 1000 ln α between cassiterite and quartz using the density functional theory (DFT) method, with 1000 ln α between cassiterite and water being calculated using 1000 ln α between quartz and water from Sharp et al. (2016). We finally apply our methods to cassiterite samples from six well studied Sn(-W) deposits from a variety of geological settings. The results indicate that cassiterite oxygen isotope analysis is promising in ore-forming process studies.

Samples

The Yongde Cassiterite

Our Yongde cassiterite (Figs. 1A and 2A-C) was from a gem dealer. The original mega-crystal had been cut to make jewellery, leaving an irregular fragment that was investigated here (Fig. 2A). The cassiterite was collected from a granite-related Sn(-W) mine/outcrop in Yalian town (N24°11′, E99°36′), Yongde county, Yunnan province, but the exact sampling location is not known. The Yongde-Cst is transparent to semi-transparent with a milky grey colour (Fig. 2A), and has a weight of ~30 gram. The sample is reasonably clean with no fractures or cracks, except for the presence of wolframite inclusions in a limited area (~3 mm).

Cassiterite from six Chinese Sn(-W) deposits

The Xiaolonghe Sn deposit

The Xiaolonghe Sn deposit (N25°27′, E98°26′) is located in the Tengchong-Lianghe district, which is an important tin mineralization area in the Sanjiang Tethyan Metallogenic Domain of Southwest China. It comprises four mining sections from west to east, namely the Xiaolonghe, the Wandanshan, the Huangjiashan and the Dasongpo. Mineralization is genetically associated with a biotite monzogranite that has porphyritic, medium- to coarse-grained and fine-grained facies. The biotite monzogranite was emplaced at 71.4 ± 0.4 Ma as dated by LA-ICP-MS zircon U-Pb (Cao et al. 2016). Tin mineralization mainly developed as greisen and quartz veins in the contact zone between the biotite monzogranite and sedimentary wall rocks, and within the cupola of the granitic stock. The mineralization age (71.6 ± 2.4 – 73.9 ± 2.0 Ma) was defined by LA-ICP-MS cassiterite U-Pb dating (Chen et al. 2014). Fluid inclusion assemblages hosted in quartz, topaz and cassiterite mostly are liquid-rich with a salinity of ~15 wt% NaCl equiv., and a homogenization temperature of 423–450 °C (Cui et al. 2019). Samples XLH, RD and DSPK were collected from the Xiaolonghe, Huangjiashan and Dasongpo mining sections, respectively.

The Hehuaping Sn(-W) deposit

The Hehuaping Sn deposit (N25°45′, E113°06′) is located in southern Hunan province, Chinese Nanling Range. Tin mineralization is genetically associated with a hidden biotite granite pluton and granite porphyry dykes, which have emplacement ages of 157.1 ± 0.8–154.9 ± 0.5 Ma, as defined by LA-ICP-MS zircon U-Pb dating (Zhang et al. 2015). The tin deposit mainly consists of skarn, porphyry and greisen ores. Five main orebodies in the Hehuaping tin deposit were delineated. No. IV orebody is the largest and developed between dolomitic limestone of the Devonian Qiziqiao Formation and sandstone of the Tiaomajian Formation. It is related to a magnesian skarn system with a mineral assemblage of forsterite, spinel, diopside, tremolite, serpentine, talc and phlogopite (Yao et al. 2014). The cassiterite-magnetite orebody in the proximal skarn is 3.4 km long. Cassiterite grains coexisting with magnetite are very small (<100 μm). In the distal skarn, cassiterite–sulphide veins are common and crosscut the marble. The cassiterite has a relatively larger grain size (>100 μm) in comparison to those from the proximal skarn. Four paragenetic stages of skarn and ore formation have been recognized: I. prograde stage (spinel, forsterite and diopside), II. retrograde stage (serpentine, phlogopite, tremolite), III. cassiterite-sulphide stage (cassiterite, magnetite, galena, sphalerite, pyrrhotite, pyrite, chalcopyrite and arsenopyrite) and IV. carbonate stage (siderite, rhodochrosite, calcite and fluorite). Quartz and fluorite hosted fluid inclusion assemblages (Yao et al. 2014) revealed that the major ore-forming fluids from stage III are characterized by low temperature (170 °C to 240 °C) and low salinity (1 to 6 wt% NaCl equiv.). Sample IV was collected from the No. IV orebody.

The Tongkeng Sn(-W) deposit

The Tongkeng Sn(-W) deposit (N24°58′, E107°30′) from Dachang Sn district is located in the Youjiang Basin, South China. The Tongkeng-Changpo Sn(-W) deposit is the largest Sn deposit in this district. It lies at the northeast limb of the Dachang anticline, and approximately 4 km southwest of the Longxianggai granitic pluton (Cai et al. 2007). The deposit is hosted in the Upper Devonian limestone and siliceous rocks, and comprises cassiterite-bearing veins and stockworks in the upper part and stratiform Sn-Zn-Pb ores in the lower part (Fu et al. 1991). LA-ICP-MS U-Pb dating of cassiterite from the Tongkeng orebody yielded a mineralization age of 91.6 ± 2.4 Ma (Guo et al. 2018b), which is consistent with the zircon U-Pb age (96.6 ± 2.5 – 93.9 ± 0.9 Ma) of the Longxiangai granitic pluton (Liang et al. 2011). Three mineralization stages have been identified based on the mineral association and crosscutting relationships (Fu et al. 1991; Cai et al. 2007), i.e., stage I with cassiterite-pyrite/pyrrhotite-tourmaline-quartz, stage II with cassiterite-sphalerite-sulphosalt-quartz, and stage III with calcite-quartz ± sulphide ± sulphosalt. Cassiterite mainly formed during stages I and II, and is light yellowish in colour. Homogenization temperatures of quartz-hosted fluid inclusion assemblages from stages I, II and III are 270–365 °C, 210–240 °C and 140–190 °C, respectively (Cai et al. 2007). Sample TK was collected from a cassiterite vug in the Tongkeng deposit.

The Kafang Sn(-W) deposit

The Kafang Sn(-W) deposit (N23°22′, E103°09′) is in Gejiu Sn district. Located in the Youjiang Basin (Guo et al. 2018a), Gejiu is one of the largest tin district in the world. The Kafang Sn deposit is located in the southernmost part of the Gejiu ore district. Skarn type Cu-Sn ores mainly distribute at the contact between the Xinshan granite and carbonate. Stratiform Cu ores hosted by basalt and stratiform Cu-Sn ores hosted by carbonate also are well-developed in the mining area. Tin mineralization only is developed in the skarn type and stratiform orebodies hosted by carbonate (Cheng et al. 2012). Molybdenite from the skarn Cu-Sn ore yielded a Re-Os isochron age of 83.4 ± 2.1 Ma, which is coeval with the zircon U-Pb age (83.1 ± 0.4 Ma) of the Xinshan granite (Cheng et al. 2012). Homogenization temperatures of vapor-rich, vapor phase-moderate and vapor phase-poor types of fluid inclusion assemblages hosted by quartz are 279.3–452.0 °C, 161.6–342.4 °C and 105.2–227.8 °C, respectively (Cheng et al. 2012). Sample KF was collected from the skarn type Cu-Sn ore.

The Xishan Sn(-W) Deposit

The Xishan Sn(-W) deposit (N22°8′, E111°40′) is located in the western part of the Yangchun basin. Tin ore-bodies of the Xishan Sn(-W)deposit mainly occur in quartz veins, greisen and skarn (Cao et al. 2016). The quartz-vein type ore is the most important ore type in the mining area, which is mainly developed in the copula of the Xishan granitic pluton. Greisen mineralization lies in the copula of the Xishan pluton and consists mainly of quartz, muscovite and topaz, with minor cassiterite and fluorite. Skarn mineralization is formed in the contact zone between the limestone and the Xishan pluton. Ore minerals are cassiterite and wolframite. LA-ICP-MS zircon U–Pb dating of the Xishan granitic pluton defines an emplacement age of 79.3 ± 0.8 – 78.1 ± 0.9 Ma, which is consistent with the mineralization age of the Xishan Sn(-W) deposit, as constrained by molybdenite Re–Os isochron dating (79.4 ± 4.5 Ma) and LA-

ICP-MS cassiterite U–Pb dating (79.0 ± 1.2 – 78.1 ± 0.9 Ma) for the cassiterite-quartz veins (Zhang et al. 2017). Sample XS was collected from a quartz vein in a quarry.

The Lailishan Sn(-W)deposit

The Lalishan Sn deposit (N24°56′, E98°16′) is located in the Tengchong-Lianghe district. The ore bodies mainly developed as greisen lenses and cassiterite-sulphide veins in the contact zones between the granites and Carboniferous wall rocks, or the fractured zones surrounding the granitic intrusions. Cassiterite U-Pb and zircon U-Pb dating results show that the tin mineralization and granitic magmatism were broadly coeval at 50.0 ± 2.7 – 47.4 ± 2.0 Ma (Chen et al. 2014). The tin mineralization process can be divided into three successive mineralization stages, and homogenization temperatures of cassiterite-hosted fluid inclusions from these stages are 216–337 °C, 116–199 °C and 160–243 °C, respectively (Wang et al. 2020). Sample V109 was collected from the greisen orebody, whereas sample LLSK was from the cassiterite-sulphide veins in the breccia ore.

Analytical Methods

Sample preparation

The sharp end of the Yongde-Cst was cut by a wire saw to create a flat surface for further sample preparation. After the sharp end had been removed, the fragment was sliced into two halves along its vertical section. One vertical section was further cut along its horizontal section into two pieces. The sharp end, uncut vertical section and horizontal section were polished by 400-grit sandpaper, and then were cast into epoxy resin as standard 25-mm mounts. The vertical section was cast in mount A5243 (Fig. 2A), and the horizontal section and the sharp end were cast in A5244 (Fig. 2B). These mounts were firstly ground using 800-grit sandpapers, with further grinding by 10 µm diamond paste using an automatic polisher. To remove scratches from the surface of the grains, the mounts were further polished by 0.5 µm and 0.25 µm diamond paste successively. Between each grinding and polishing step, the mounts were cleaned in ethanol using an ultrasonic cleaner for 20 seconds to remove polishing materials from previous steps. With careful grinding and polishing, the mounts are expected to have a very small topography with a relief of less than 3 µm, which is critical for high quality SIMS oxygen isotope measurements (Tang et al. 2015).

The second horizontal section of the Yongde-Cst was crushed into aliquots with sizes ranging from 200 µm to 800 µm, then ~40 aliquots were randomly chosen and mounted together with cassiterite grains from six Sn(-W)deposits as mounts G855 and G856 (Fig. 1A). About 100 mg of the crushed Yongde-Cst was ground to 200-mesh for oxygen isotope measurements by Gas Source Isotope Ratio Mass Spectrometry.

Cathodoluminescence imaging

Cathodoluminescence (CL) imaging was conducted at Nanjing Hongchuang Geological Exploration Technology Service Company. Images were collected on a Tescan MIRA3 LM instrument equipped with a CL detector. Before analysis, mounts were cleaned by ethanol using an ultrasonic cleaner. Once dried, the mounts were carbon coated with a thickness of ~10 nm to improve electrical conductivity. For CL imaging, acceleration voltage and beam current during the course of study were 14 kV and 1.2 nA, respectively. Working distance between CL detector and sample surface was ~18.8 mm. Depending on grain size, magnification varied from 150 to 300. Each CL image was collected by an accumulation of 80 seconds.

Electron Backscatter Diffraction

Electron backscatter diffraction (EBSD) studies were performed using a ZEISS Crossbeam 540 Scanning Electron Microscope (SEM) with an EBSD unit from Oxford Instruments at the Institute of Geology and Geophysics, Chinese Academy of Sciences. For better EBSD measurements, a chemical polishing step using colloidal silicon was applied after our standard metallographic polishing procedures described above.

Sample mounts were cleaned in deionized water using an ultrasonic cleaner. Once dried, we applied a ~10 nm carbon coating on mount surface to improve its electrical conductivity. Using the same structure model of Carr et al. (2017) for cassiterite, diffraction patterns of cassiterite were obtained using a beam voltage of 20 kV, a beam current of 1–2 nA, and a spot size diameter of 10 nm. Orientation information was collected pixel by pixel with a pixel spacing of 100 nm. Inverse pole figure maps (Figs. 1B-C and 2A-C) of the analysed cassiterite grains were generated to illustrate the orientation of the cassiterite grains with respect to the major poles (111, 100, 110) of the stereographic triangle.

Secondary Ion Mass Spectrometry

SIMS oxygen isotope analysis for all cassiterite samples was conducted at the Beijing Research Institute of Uranium Geology (BRIUG) on a CAMECA IMS 1280HR SIMS. An exception was the horizontal section of the Yongde-Cst in mount A5244, which was measured at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) with a CAMECA IMS 1280 SIMS.

For mount A5243 and A5344, they were measured by SIMS with a 500 * 500 µm grid (Figs. 2A-B). There was a fracture in the middle of the grain in A5243 (Fig. 2A), which was generated during sample preparation, and that fractured area was avoided when selecting SIMS targets. For mount A5244 (Fig. 2B), a traverse was conducted across the horizontal section (big fragment in mount A5244) and the sharp end (small fragment in mount A5244) to assess isotopic homogeneity of the two fragments. To monitor instrumental drift during the measurements of mount A5244 at IGGCAS, NIST610 glass, which is expected to have a homogenous oxygen isotope composition, was measured twice after each 10 measurements of the Yongde-Cst. Please note that a few aliquots of NIST610 have very different oxygen isotope composition. At BRIUG, to monitor instrumental drift and to evaluate potential isotopic heterogeneity between the horizontal section (big fragment in mount A5244) and the sharp end (small fragment in mount A5244), a 900 * 200 μm area from the horizontal section was analysed with a 100 * 100 μm grid (Fig. 2C). The selected area was analysed twice after each 10 measurements of the sharp end of the Yongde-Cst.

Instrumental conditions, analytical procedure, and data reduction processes are the same in both laboratories after modification from previous studies (Li et al. 2009; Tang et al. 2020). Prior to analysis, mounts are cleaned by ethanol using an ultrasonic cleaner. Once dried, they are coated with a ~50 nm gold film to improve electrical conductivity. A normal incident electron flood gun is used to compensate for electrical charging. We use ~2 nA Cs^+ ions with an accelerating energy of +10 kV as the primary beam to liberate $^{16}O^-$ and $^{18}O^-$ from the samples. An accelerating voltage for secondary ions is set to –10 kV, so the total bombarding energy is 20 kV. The primary beam is focused in Gaussian mode, and the analytical spot as a square has a size of 10*15 μm. An energy window of 60 eV is used at the low energy band, and the mass resolution defined as $M/\Delta M$ at 50% peak height is set to 2500. A Nuclear Magnetic Resonance controller is applied at IGGCAS, but not at BRIUG. Prior to analysis, a 20-second sputtering with raster mode is applied to remove gold coating, and to clean the sample surface. After 60 seconds of automatic beam centering, oxygen isotope measurements are achieved through a 96-second integration, which are divided into 20 cycles, and each cycle contains 4-second isotope measurement plus 0.8-second waiting time. Each spot-measurement takes 176 seconds. Oxygen isotopes (^{16}O and ^{18}O) are measured simultaneously on two Faraday cups equipped with 10^{10} and 10^{11} Ω resistors, respectively, and a $^{16}O^{-}$ intensity of ~3.5×10^{9} counts per second (cps) is obtained in our routine measurements. Instrumental uncertainty from counting statistics for individual analysis (i.e., internal precision) is generally better than 0.2 ‰ (2σ).

Measured $^{18}O/^{16}O$ ratios are converted to raw $\delta^{18}O$ values ($\delta^{18}O_{measured}$) through normalizing the measured $^{18}O/^{16}O$ ratios to that of the Vienna Standard Mean Ocean Water (0.0020052, VSMOW) as outlined in Eq. 1,

$$\delta^{18}O_{measured} \text{ in per mil} = (^{18}O/^{16}O_{measured} \div 0.0020052 - 1) \times 1000 \qquad (1)$$

For mount 5243 and mount 5244, our primary concern is their homogeneity in terms of oxygen isotope composition. Hence only the measured $\delta^{18}O$ values are needed (see the discussion session for further details on this topic). This is also the case for the Yongde-Cst in mount G855 and mount G856 when evaluating crystallographic orientation effects.

For cassiterite samples from six Sn(-W) deposits, correction of instrumental mass fractionation is essential to yield true $\delta^{18}O$ values relative to the VSMOW scale. This is achieved through analysing the Yongde-Cst between samples, which has been developed as a matrix-match reference material in this study (see below for discussion). The IMF is quantified through replicated analysis of the Yongde-Cst following Eq. 2,

$$\text{IMF} = \delta^{18}O_{\text{measured value of RM}} - \delta^{18}O_{\text{true value of RM}} \qquad (2)$$

True δ^{18}O value of our Yongde-Cst relative to the VSMOW scale has been defined by Gas Source Isotope Ratio Mass Spectrometry (see below for discussion). Once IMF has been obtained, δ^{18}O values of cassiterite samples are calculated following Eq. 3,

$$\delta^{18}O_{sample}\ (VSMOW) = \delta^{18}O_{measured\ value\ of\ sample} - IMF \qquad (3)$$

Gas Source Isotope Ratio Mass Spectrometry

The oxygen isotope composition of the Yongde-Cst was obtained by the furnace fluorination method (Feng et al. 2020) at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Chinese national reference material GBW04409 (quartz) was analysed during the course of study for quality control purpose, and 5 analyses in the same period yield an average of 11.10 ± 0.09 ‰ (2 SD, VSMOW). Samples were fluorinated in a nickel reaction vessel and each analysis consumed about 6 mg of material. Samples were loaded under a positive pressure of pure nitrogen gas to prevent adsorption of atmospheric moisture in the nickel reaction vessel. After the initial overnight pumping and a 10-minute room-temperature fluorination with BrF_5, the vessel was evacuated and charged again with an aliquot of BrF_5. The nickel reaction vessel was heated to 750 °C with a resistance furnace for 4 hours. Generated gases were purified through a series of cryogenic traps which were chilled by liquid nitrogen. The purified oxygen gas was analysed on a viscous-flow mass spectrometer of Finnigan MAT252.

First-principles calculations

We obtained the equilibrium oxygen isotope fractionation between cassiterite and quartz using first-principles calculations based on the density functional theory. The equilibrium isotope fractionation factor of element X between two phases A and B, α_{A-B}, is the ratio of their isotope ratios in these two phases. According to the Bigeleisen-Mayer theory (Bigeleisen and Mayer 1947; Urey 1947), the isotope fractionation factor between the phase A and an ideal gas of X atoms is the reduced partition function ratio β_A of the element X. Within the harmonic approximation, the β_A can be expressed as:

$$\beta_A = \frac{Q_h}{Q_l} = \prod_i^{3N} \frac{u_{ih}}{u_{il}} \frac{e^{-\frac{1}{2}u_{ih}}}{1-e^{-u_{ih}}} \frac{1-e^{-u_{il}}}{e^{-\frac{1}{2}u_{il}}} \qquad (4)$$

where Q is the vibrational partition function, and index h and l refer to the heavy and light isotope, respectively. The running index i refers to the vibrational frequency mode and N is the number of atoms in the unit cell. Parameter u_{ih} or u_{il} is defined as:

$$u_{ih\ or\ il} = h\omega_{ih\ or\ il} \,/\, k_B T \qquad (5)$$

where h and k_B are the Planck and Boltzmann constants, respectively. T is temperature in kelvin, and $\omega_{ih\ or\ il}$ is the vibrational frequency of the i^{th} mode. Following Richet et al. (1977), the equilibrium isotope fractionation between two phases A and B can be rewritten in per mil as:

$$\triangle_{A-B} = 10^3 \ln \alpha_{A-B} = 10^3 \ln \beta_A - 10^3 \ln \beta_B \qquad (6)$$

The calculation processes in this study are similar to those in our previous work (Huang et al. 2013; Wang et al. 2017). We performed all calculations using an open-source software “Quantum Espresso” based on the DFT, plane wave and pseudopotential (Giannozzi et al. 2009). Local density approximation (LDA) was adopted for the exchange correlation functional (Perdew and Zunger 1981). The cut-off for plane-wave energy is 70 Ry. The pseudopotentials for oxygen and silicon were generated by the method of Troullier and Martins (1991) with a configuration of $2s^2 2p^4$ and a cut-off radius of 1.45 Bohr for oxygen and a configuration of $3s^2 3p^4 3d^0$ and a cut-off radius of 1.47 Bohr for silicon. The tin pseudopotential, sn_lda_v1.4.uspp.F.UPF, is an ultrasoft type generated using Vanderbilt method (Vanderbilt 1990), which is available in the online Quantum Espresso pseudopotential library (http://www.quantum-espresso.org/pseudopotentials/). Brillouin zone integrations over electronic states were performed with a 12×12×12 k-point grid for quartz and a 10×10×14 k-point grid for cassiterite. The crystal structures of quartz and cassiterite were optimized using variable cell shape molecular dynamics (Wentzcovitch 1991) and the residual forces converge within 10^{-4} Ry/Bohr. Their dynamical matrices were calculated on a regular q mesh of 2×2×2 for quartz and 3×3×4 for cassiterite using the density-functional perturbation theory and then interpolated on a dense q mesh to obtain the vibrational properties.

Oxygen isotope fractionation between cassiterite and water

Since the oxygen isotope fractionation between quartz and water has been well-established both experimentally and theoretically (Sharp et al. 2016 and references therein), oxygen isotope fractionation between cassiterite and water was obtained through using quartz as a bridge mineral. Specifically, with 1000 ln α of cassiterite and quartz being calculated from density functional theory method, we used 1000 ln α of quartz and water from Sharp et al. (2016) to calculate 1000 ln α of cassiterite and quartz using Eq. 7,

$$1000 \ln \alpha_{\text{cassiterite-water}} = 1000 \ln \alpha_{\text{quartz-water}} - 1000 \ln \alpha_{\text{quartz-cassiterite}} \quad (7)$$

A similar approach was utilized to calculate 1000 ln α of zircon and water, in which case 1000 ln α of zircon and quartz from Valley (2003) was used.

Results

Crystallographic orientations information

Crystallographic orientation information for the crushed aliquots of the Yongde-Cst in mounts G855 and G856 (Fig. 1A) was obtained by electron backscatter diffraction. The results are illustrated as inverse pole figures in Figs. 1B-C. As shown, the aliquots cast in mount G855 and G856 cover a variety of orientations as defined by three major crystallographic planes (i.e., 001, 110, 101). This was expected since the crushed aliquots were randomly cast during sample preparation. These aliquots were further measured by SIMS, and measured $\delta^{18}O$ values (i.e., raw data without IMF corrections) from both mounts show limited variation. For mount G855, measured $\delta^{18}O$ values define a gaussian distribution with two standard deviations of 0.29 ‰ (2 SD, n = 62, Fig. 1D); for mount G856, 55 analyses define a gaussian distribution with two standard deviations of 0.38 ‰ (2 SD, Fig. 1D).

SIMS oxygen isotope of the Yongde-Cst

All SIMS measurements of cassiterite oxygen isotope composition are presented in Table S1 in the appendix. For the vertical section of the Yongde-Cst in mount A5243 (Fig. 2A), the exposed sample surface has a uniform crystallographic orientation close to plane 010. In total, 256 analyses (mount A5243) were conducted continually for 19.7 hours at BRIUG, and measured $\delta^{18}O$ values define a distribution close to gaussian with two standard deviations of 0.54 ‰ (2 SD, n = 256). The measured $\delta^{18}O$ values show a pronounced correlation with their Y-coordinates (Fig. 2A) with a R^2 of 0.8 (Table S1 in appendix). A similar phenomenon has been investigated in detail during apatite oxygen isotope analysis (Li et al. 2021), and this artifact has been attributed to the presence of a slope on sample surface along the Y direction, which leads to an imperfect centering of the trajectory of secondary ions. In this regard, a correction was applied for this Y-coordinate related artifact following Li et al. (2021), and the corrected $\delta^{18}O$ values yield two standard deviations of 0.24 ‰ (n = 256, Fig. 2D).

For the horizontal section of the Yongde-Cst in mount A5244, the exposed sample surface also shows a uniform crystallographic orientation close to plane 110 (Fig. 2B). Analytical time for the traverse and the horizontal section were 2.5 hours and 32.75 hours, respectively. In total 438 analyses were conducted for the Yongde-Cst in mount A5244 at IGGCAS, and measured $\delta^{18}O$ values define a normal distribution with two standard deviations of 0.50 ‰ (2 SD, n = 438, Fig. 2E), and NIST610 yield two standard deviations of 0.35 ‰ (2 SD, n = 80). All analyses of NIST610 showed no time dependent drift, and this demonstrates that the instrument was stable at the 0.35 ‰ level during the course of study, hence no time drift correction was applied. These measurements also show no dependence on sample coordinates on the mount and instrumental tuning parameters (e.g., DTFA and DTCA, Table S1).

For the sharp end of the Yongde-Cst, exposed surface has a uniform crystallographic orientation close to plane 010 (Fig. 2C). The analysis lasted 8.5 hours, and 110 measurements from the sharp end of the Yongde-Cst define a normal distribution with two standard deviations of 0.20 ‰ (2 SD, n = 110, Fig. 2F).

IRMS oxygen isotope measurements of the Yongde-Cst

Six measurements of the Yongde-Cst by Gas Source Isotope Ratio Mass Spectrometry at IGGCAS are listed in Table 1. The results show limited variations in $\delta^{18}O$ values between 1.25 ‰ and 1.47 ‰, and give an average of 1.36 ± 0.16 ‰ (VSMOW, 2 SD, n = 6, Fig. 3,).

Oxygen isotope fractionation between quartz and cassiterite

Calculated oxygen isotope fractionation at 50–850 °C for quartz and cassiterite is given by Eq. 8 as follows,

$$1000 \ln \alpha_{\text{quartz-cassiterite}} = 1.259\times10^{6}/T^{2} + 8.15\times10^{3}/T - 4.72 \qquad (8)$$

where T is temperature in kelvin. The equation is plotted in Figs. 4A-B, with 1000 ln α from previous computational and experimental studies being graphically illustrated as well

(Zheng 1991; Zhang et al. 1994; Hu et al. 2005; Polyakov et al. 2005). Our calculation agrees remarkably well with recent computational and experimental studies, this convergency most likely results from advances in computing and improvements in experimental studies over the last decades. Using the well-established 1000 ln α of quartz and water (Fig. 4D) from Sharp et al. (2016), the oxygen isotope fractionation between cassiterite and water (Fig. 4C) is outlined in Eq. 9 as follows,

$$1000 \ln \alpha_{\text{cassiterite-water}} = 2.941\times10^6/T^2 - 11.45\times10^3/T + 4.72 \qquad (9)$$

We also derive oxygen isotope fractionation between zircon and water (Fig. 4E) using 1000 ln α of quartz-zircon and quartz-water from Valley (2003) and Sharp et al. (2016) respectively, and the 1000 ln α of zircon-water is described by equation of $1.56\times10^6/T^2 - 3.3\times10^3/T$ (T is temperature in kelvin). We note here that 1000 ln α of quartz-zircon reported in literature have considerable variations, and our preferred calibration from Valley (2003) is broadly consistent with those estimated from natural systems and a recent experimental study (Trail et al. 2009 and references therein).

When using 1000 ln α of mineral-water (i.e., cassiterite-water, quartz-water and zircon water) to derive oxygen isotope composition of fluids, uncertainties from both oxygen isotope measurements and temperature estimates have been propagated using a Monte Carlo approach (Li et al. 2019).

SIMS oxygen isotope analyses of cassiterite from Sn(-W) deposits

Nine cassiterite samples from six Sn(-W) deposits were measured by SIMS with an aim to constrain the oxygen isotope composition of the ore-forming fluids. Representative CL images of these samples are shown in Fig. 5A, with SIMS δ^{18}O data being illustrated in Fig. 5B. In general, the studied samples show well-developed oscillatory zonation in CL images. It should be noted that a few samples show alteration features with primary zonation being truncated by CL-bright bands.

To investigate the oxygen isotope composition of cassiterite samples with alteration, one sample (DSPK) showing a low degree of alteration was selected along with two fresh samples (XLH, RD) from the Xiaolonghe Sn(-W)deposit, Yunnan for SIMS analysis. Three samples yield similar $\delta^{18}O$ values with variations between 1.86 ‰ and 4.13 ‰, and average $\delta^{18}O$ values for XLH, RD and DSPK are 3.56 ± 0.51 ‰ (2 SD, n = 13), 2.81 ± 0.73 ‰ (2 SD, n = 21) and 3.25 ± 1.17 ‰ (2 SD, n = 31), respectively. The degree of alteration has had no measurable matrix-effects on the oxygen isotope composition.

Samples from the Hehuaping Sn(-W) deposit, Hunan province (IV), the Dachang Sn(-W) deposit, Guangxi province (TK), the Kafang Sn(-W) deposit, Yunnan province (KF) and the Xishan Sn(-W) deposit, Guangdong province (XS) all have well-developed oscillatory zonation with no sign of alteration. Samples from the same deposit show very limited variations in terms of $\delta^{18}O$ values, but vary significantly between deposits. Average $\delta^{18}O$ values for IV, TK, KF and XS are 3.27 ± 0.42 ‰ (2 SD, n = 32), 4.79 ± 0.75 ‰ (2 SD, n = 38), 1.46 ± 1.06 ‰ (2 SD, n = 18) and 3.02 ± 0.58 ‰ (2 SD, n = 20), respectively.

Two samples from the Lailishan Sn(-W) deposit, Yunnan province, show the highest degree of alteration among samples investigated in this study, though remnants of primary oscillatory zonation still can be seen from CL images (Fig. 5A). Measured $\delta^{18}O$ values show considerable variations for both samples, which range from –3.07 ‰ to 2.86 ‰. Average $\delta^{18}O$ values for V109 and LLSK are –0.20 ± 3.04 ‰ (2 SD, n = 27) and 1.42 ± 2.72 ‰ (2 SD, n = 21), respectively. Notably, zones with alteration consistently give low $\delta^{18}O$ values (peak at –1.3 ± 0.4 ‰), while zones with the least alteration have $\delta^{18}O$ values of 1.6 ± 0.4 ‰ (Fig. 5B).

Discussion

No crystallographic orientation effects on SIMS cassiterite oxygen isotope analyse

Crystallographic orientation effects pose serious challenges for robust SIMS isotope analysis, particularly of oxide minerals (Huberty et al. 2010; Taylor et al. 2012). Our oxygen isotope analysis of the Yongde-Cst has sampled a range of crystallographic orientations with almost all three major planes being covered (Figs. 1 B-C), but variations in $\delta^{18}O$ values are minimal (0.29–0.38 ‰, Figs. 1D-E). A previous attempt on cassiterite oxygen isotope analysis via SHRIMP SI revealed ~2 ‰ variation for grains with variable crystallographic orientations (Carr et al. 2017), although in that case sample heterogeneity was a possible problem. Our results from both sessions are at the same level with current analytical precision (e.g., ~0.2–0.3 ‰), hence the crystallographic orientation effects for CAMECA IMS 1280 SIMS cassiterite oxygen isotope analysis is negligible with current analytical precision. Since SHRIMP SI and CAMECA 1280 SIMS have very different instrumental designs, which have been shown to pose significantly and contrastingly different effects on the magnitude of matrix effect during oxygen isotope analysis of olivine (Isa et al. 2017; Scicchitano et al. 2018), it is reasonable to speculate that SHRIMP SI may also behave differently from CAMECA SIMS in crystallographic orientation effects. Carr et al. (2017) has documented an intra-grain variation of ~2 ‰ with a single crystallographic orientation in their SHRIMP SI analysis, which is the same with variation of analysis from a range of crystallographic orientations. As such, it is clear that crystallographic orientation effect does not add additional variations beyond sample heterogeneity in their study. Along with our new observations, we conclude that the crystallographic orientation effect is probably negligible for ion microprobe (i.e., CAMECA 1280 SIMS and SHRIMP SI) cassiterite oxygen isotope analysis. If indeed present, it should not be larger than current analytical precision (~0.2–0.3 ‰). This will pave the way for robust cassiterite oxygen isotope analysis, and facilitate geological applications in the study of ore-forming processes.

It is interesting to note that rutile shows significant crystallographic orientation effects during SIMS oxygen isotope analysis (Schmitt and Zack 2012; Taylor et al. 2012; Shulaker et al. 2015). Rutile is an isostructural mineral with cassiterite, so the contrasting behaviours between cassiterite and rutile makes it unlikely that there is a link between crystallographic orientation effects and mineral structures. A plausible hypothesis to explain this contrasting behaviour for isostructural minerals comes from the bonding element (e.g., Sn vs Ti) with oxygen, which could have an impact on focusing secondary ions as suggested previously (Huberty et al. 2010). Further investigation of possible mechanisms controlling crystallographic orientation effects is critical for SIMS analysis, but it is beyond the scope of this study and not discussed further.

The Yongde-Cst as a reference material for SIMS oxygen isotope analysis

Using matrix-matched reference materials to correct instrumental mass fractionation is fundamental for accurate SIMS isotope analysis. For the developments of oxygen isotope reference materials for microanalysis, a main concern is its isotopic homogeneity. Our evaluation on the vertical and horizontal sections as well as the sharp end using a grid approach (Figs. 2A-C) revealed variations in δ^{18}O values of 0.24 ‰, 0.50 ‰ and 0.20 ‰, respectively (Figs. 2D-F).

Both the selected 900 * 200 µm area from the horizontal section (Figs. 2C and F) and NIST610 analysed for monitoring instrumental drift show very limited variations (2 SD = 0.30 ‰, n = 26; 2 SD = 0.35 ‰, n = 80) in an extended period (8.5 hours and 32.75 hours) with no time dependence. These results suggests that instrumental drift in this study has been limited to less than 0.3 ‰ for a few tens of hours. As such, variations of 0.24 ‰ (2SD, n = 256) and

0.20 ‰ (2SD, n = 110) in $\delta^{18}O$ values observed here for the vertical section and the sharp end respectively are similar to instrumental noise, and we consider that they are homogeneous in terms of oxygen isotope composition. However, variations in $\delta^{18}O$ values of the horizontal section (2 SD = 0.50 ‰, n = 438) are apparently large for a homogenous sample. Other sources may account for this extra scatter are position effect and topography effect. It is well established that SIMS isotope analyses are subject to position effects (Kita et al. 2009; Peres et al. 2013), but no correlation has been observed between measured $\delta^{18}O$ values of the horizontal section and their position and renders position effect as an unlikely cause for the extra scatter. Hence the observed variations of the horizontal sections (0.50 ‰) are more likely arising from topography effect. This has been further supported by limited variation (0.29–0.38 ‰) in $\delta^{18}O$ values for crushed fragments in mounts G855 and G856 (Figs. 1D-E). To summarize, our SIMS analysis demonstrates that the Yongde-Cst has a homogeneous oxygen isotope composition at the micrometre level, and it meets the criteria as a reference material for microanalysis. Recommended $\delta^{18}O$ values of the Yongde-Cst relative to VSMOW have been defined by GS-IRMS as 1.36 ± 0.16 ‰ (Fig. 3, 2 SD, n = 6). Yongde-Cst is the first cassiterite reference material for oxygen isotope microanalysis, and it is available to the scientific community immediately via the corresponding author.

Cassiterite as a robust oxygen isotope record of ore-forming fluids

A diagnostic feature of the oxygen isotope fractionation between cassiterite and water is its insensitivity to temperature. The calculated $\delta^{18}O$ values of fluids only change by <3 ‰ over a wide temperature range (200–800 °C, Fig. 4C). This feature is very different from that of quartz-water, which changes by 11 ‰ (Fig. 4D) over the same temperature range (Sharp et al. 2016 and references therein).The oxygen isotope composition of ore-forming fluids can be used to decipher fluid sources and to evaluate evolutionary processes during ore formation, and minerals precipitated from these fluids are primary targets for deriving this information. However, calculating $\delta^{18}O$ values of fluids from $\delta^{18}O$ values of minerals requires knowledge of the temperature of isotope equilibrium between mineral and fluids. Independent temperature constraints for ore-forming fluids largely come from fluid inclusion studies. Obtaining temperatures from fluid inclusion studies is time consuming, and getting accurate and precise estimates has been shown to be challenging, even for experienced researchers (Bodnar et al. 2014; Chi et al. 2021). Large uncertainties in temperature estimates could be very problematic when quartz, the most explored mineral in ore-forming fluid studies, has been studied to derive $\delta^{18}O$ values of fluids. For example, a variation of 100 °C in temperature estimates will add an uncertainty of 2.5 ‰ to the calculated $\delta^{18}O$ values of co-existing fluids from quartz (Fig. 4D). An insensitivity between oxygen isotope fractionation and temperature for the cassiterite-water system (Fig. 4C), on the other hand, loosens the requirements for robust temperature constraints. As discussed above, over a wide range of reasonable temperatures (150 to 600 °C) of cassiterite crystallization (Wood and Samson 2000), calculated $\delta^{18}O$ values of fluids change only by 1.68 ‰, or a decrease of less than 0.57 ‰ when temperature increases 100 °C (Fig. 4C). Hence for situations where robust temperature constraints are difficult to obtain, a rough estimate in temperature does not include significant uncertainties in the calculated $\delta^{18}O$ values of fluids in cassiterite-water systems. An additional advantage in obtaining $\delta^{18}O$ of fluids from cassiterite over quartz is that cassiterite is a direct repository crystallized from metalliferous fluids, rather than assuming its precipitation from the same aliquots of metalliferous fluids when gangue minerals such as quartz is studied.

Quartz-Cassiterite as an oxygen isotope geothermometer

Over a reasonable temperature range (150 to 600 °C) during Sn(-W) mineralization (Wood and Samson 2000), 1000 ln α of quartz and cassiterite show a strong dependence on temperature (Fig. 4A), which shows a sharp decrease of ~15 ‰ when temperature increases from 150 to 600 °C (Fig. 4B). Since quartz is the most abundant gangue minerals in Sn(-W) deposits, and its co-precipitation with cassiterite is not uncommon, this makes quartz-cassiterite a very promising oxygen isotope thermometer. The theoretical calibration of quartz-cassiterite oxygen isotope thermometer is described by the equation of $T\ (°C) = 2427 \times (\delta^{18}O_{qtz} - \delta^{18}O_{cst})^{-0.4326} - 492.4$ (Fig. 4B). Current analytical precision for SIMS cassiterite and quartz oxygen isotope measurements is ~0.2–0.3 ‰, this corresponds to an uncertainty of 10 °C for temperature estimates from the analytical side. We have laid a firm ground for the application of quartz-cassiterite geothermometry, both data from natural samples and experimental work are required to validate, and to further calibrate our theoretical calibration.

The binary mixing model in magmatic-hydrothermal systems

Most Sn(-W) deposits are associated with granites, with ore-forming fluids being magmatic in origin, and then experienced variable degrees of mixing with meteoric water during ore precipitation (Legros et al. 2019; Harlaux et al. 2021). In addition to constraining temperatures of ore formation, estimating the proportion of meteoric water fluxing is also important to trace fluid evolutionary processes, and to decipher its role in metals deposition. This requires knowledge of the $\delta^{18}O$ values of meteoric water, but which is unknown in most cases, and in practice, an assumed value has been used.

For these systems, a binary mixing model can be used to quantify the proportional contribution of magmatic fluid and meteoric water (Fig. 4F). At the first order, temperature of the mixture (i.e., hydrothermal fluids) can be calculated from the binary mixing model using equation of $T_{hydrothermal} = T_{magmatic} \times p + T_{meteoric} \times (1–p)$, where p is the proportional contribution of meteoric water. Oxygen isotope composition of the hydrothermal fluid also can be estimated following the binary mixing model in a similar fashion using equation of $\delta^{18}O_{hydrothermal} =$

$\delta^{18}O_{magamatic} \times p + \delta^{18}O_{meteoric} \times (1–p)$. It is reasonable to assume that the temperature of primary magmatic fluids is approaching or slightly lower than the solidus of granitic magma (e.g., ~650 °C), and the $\delta^{18}O$ values of primary magmatic fluids also can be estimated with confidence from equilibrium zircon-water oxygen isotope fractionation (Fig. 4E). With temperatures of hydrothermal fluids being estimated from the quartz-cassiterite oxygen isotope thermometer, or independent fluid inclusions studies, $\delta^{18}O$ values of ore-forming fluids could be calculated from $\delta^{18}O$ values of cassiterite. To this end, a unique solution for the $\delta^{18}O$ values of meteoric water can be obtained following the binary mixing model. Hence proportional contributions of magmatic fluids and meteoric water also can be calculated. Principles of this binary mixing model has been illustrated in Fig. 4F. The beauty of this method is that only $\delta^{18}O$ values of zircon, cassiterite and quartz are needed, and the outcomes (e.g., ore-forming temperatures) could be validated by fluid inclusion studies. We also would like to emphasis here that the predicted $\delta^{18}O$ values of meteoric water is most likely represent the $\delta^{18}O$ values of meteoric water experienced water-rock interaction, which may lead to significantly overestimated values. To decode the $\delta^{18}O$ values of primary meteoric water, it is critical to use samples recorded the highest proportional contribution of meteoric water, and using in situ techniques such as SIMS to target specific domains under a robust petrographic framework will be a prerequisite.

Applications in Sn(-W) deposits

We apply our analytical technique and newly calculated 1000 ln α of cassiterite-water to nine samples from six Chinese Sn(-W) deposits (Fig. 5A). Obtained $\delta^{18}O$ values of cassiterite show significant variations both within a single deposit and among deposits (Fig. 5B), which may reflect variable degrees of fluid mixing for Sn(-W) mineralization. We first investigate samples from two individual deposits and the most altered ones in detail, and then discuss samples from all six deposits to yield general trends. For the Xialonghe Sn(-W) deposit, Yunnan, mineralisation is genetically associated with the Xiaolonghe pluton composed of medium-grained to coarse-grained granites. The pluton has a zircon $\delta^{18}O$ value of 7.80 ± 0.83 ‰ (Chen et al. 2015). Large variations in the zircon $\delta^{18}O$ values potentially indicate the presence of inherited zircons, but since it is not expected to bias our estimated $\delta^{18}O$ values of magmatic fluids significantly, we do not discuss the overdispersion of zircon $\delta^{18}O$ values further. Assuming primary magmatic fluids reached oxygen isotope equilibrium with the granitic melts during zircon crystallization, it is expected to have a $\delta^{18}O$ value of 9.54 ± 0.83 ‰ at 600 ± 50 °C (Fig. 6A). Cassiterite samples from the main mineralization stage have $\delta^{18}O$ values (Fig. 5A) of 3.56 ± 0.51 ‰ (XLH), 2.81 ± 0.73 ‰ (RD) and 3.25 ± 1.17 ‰ (DSPK). Using the temperature (420 ± 55 °C) estimated from cassiterite-hosted fluid inclusion assemblages (Cui et al. 2019), the oxygen isotope composition of ore-forming fluid during cassiterite precipitation is estimated as 9.23 ± 0.61 ‰ for sample XLH (Fig. 6B). We would like to highlight here that the accuracy of ore-forming temperatures has very limited effects on estimated $\delta^{18}O$ values of ore-forming fluids, as expected from the insensitivity between isotope fractionation of cassiterite-water and temperature discussed above. For instance, using temperatures of 520 °C and 320 °C, calculated $\delta^{18}O$ values of ore-forming fluids are 8.60 ± 0.62 ‰ and 9.73 ± 0.56 ‰, respectively, which still are overlap within uncertainties. For another two samples (RD and DSPK, Figs. 5A-B), estimated $\delta^{18}O$ values of ore-forming fluids at 420 ± 55 °C are 8.47 ± 0.80 ‰ and 8.91 ± 1.22 ‰ respectively. Within uncertainties, the calculated $\delta^{18}O$ values of fluids from cassiterite-water systems are essentially the same, and show an excellent agreement with $\delta^{18}O$ values of primary magmatic fluids. Therefore, meteoric water is unlikely to have played a significant role in cassiterite mineralization at the Xiaolonghe deposit.

For the Kafang Sn(-W) deposit, Yunnan, $\delta^{18}O$ values of cassiterite are 1.46 ± 1.06 ‰, which are the lowest among all investigated samples except the two altered ones (Figs. 5A-B). Mineralization at Kafang is genetically linked with the Xinshan biotite granite, which has a zircon $\delta^{18}O$ value of 7.80 ± 0.83 ‰ (Cheng et al. 2012). The oxygen isotope composition of primary magmatic fluids at Kafang is estimated as 10.28 ± 0.88 ‰ at 600 ± 50 °C (Fig. 6C). With ore formation temperatures (331 ± 44 °C) being constrained by quartz-hosted fluid inclusion assemblages from the main mineralization stage (Cheng et al. 2012; Zhang et al. 2012), the oxygen isotope composition of ore-forming fluids during cassiterite precipitation is estimated as 7.63 ± 1.08 ‰ (Fig. 6D). This estimated $\delta^{18}O$ value is slightly lower than that of primary magmatic fluids, and requires the involvement of external fluids bearing a depleted oxygen isotope signature. Using the binary mixing model in Fig. 4F, the $\delta^{18}O$ value and proportional contribution of external water are estimated as 4.81 ± 2.72 ‰ and 50 ± 8 %, respectively. A potential source for this external water is meteoric water which has experienced water-rock interaction with wall rocks with high $\delta^{18}O$ value (e.g., sedimentary rocks). If we assume the primary meteoric water has a $\delta^{18}O$ value of –10 ‰, then estimated proportional contribution of primary meteoric water is ~12 %.

We further investigate samples (V109 and LLSK) from the Lailishan Sn(-W) deposit, Yunnan, which show a high degree of alteration (Fig. 5A). Measured $\delta^{18}O$ values show considerable variations for both samples, which range from –3.07 to 2.86 ‰. While zones with alteration consistently give low $\delta^{18}O$ values (peak at –1.1 ± 0.4 ‰), areas with low degree of alteration have $\delta^{18}O$ values of 1.6 ± 0.4 ‰ (Fig. 5B), and remnants of primary zones have $\delta^{18}O$ values of up to 3 ‰. These features are best explained by a two-stage process, where cassiterite grains were firstly formed with a magmatic affinity, and then experienced alteration by fluids bearing low $\delta^{18}O$ values. This highlights that cassiterite could preserve primary oxygen isotope signature, and using in situ techniques with detailed petrographic study is critical.

Individual deposits having been discussed, now we consider general trends of cassiterite $\delta^{18}O$ values from all studied deposits. Pooling the data together, 221 oxygen isotope analyses of cassiterite by SIMS define three distinct peaks at 4.6 ± 0.6, 3.3 ± 0.8 and –1.1 ± 0.4 ‰ (Fig. 7A). We use 300 ± 100 °C as the best estimated temperature (Fig. 7B), and calculated $\delta^{18}O$ values of ore-forming fluids also have considerable variations with peaks at 10.6 ± 1.2 , 9.3 ± 1.2 and 4.9 ± 1.1 ‰ (Fig. 7C). As discussed above, 1000 ln α between cassiterite and water is insensitive to temperature over a wide range of temperatures (Fig. 4C), hence the calculated $\delta^{18}O$ values of ore-forming fluids are robust despite of temperature fluctuations. Our results indicate that most cassiterite, and by inference, tin mineralization, was crystallized from fluids with a magmatic affinity (e.g., 11–9 ‰, Fig. 7C), with variable but consistently low degrees (~0–10 %) of involvement of meteoric water. Mixing magmatic fluids and meteoric water has been proposed as a primary driver to promote metals deposition in Sn(-W) deposits. While mixing induced cooling certainly could play a significant role in this regard (Legros et al. 2019; Xiong et al. 2019; Liu et al. 2020; Harlaux et al. 2021), but most samples studied here do not require the involvement of meteoric water, hence our cassiterite oxygen isotope analysis call for an reassessment for this hypothesis.

Since the oxygen isotope fractionation between cassiterite and water is not sensitive to temperature (Fig. 4C), the observed variations in cassiterite $\delta^{18}O$ values are best explained by fluctuations in $\delta^{18}O$ values of ore-forming fluids. Possible mechanisms could account for this variable $\delta^{18}O$ values of ore-forming fluids include fluid mixing and water-rock interaction. Taking advantage of the high spatial resolution of ion microprobe analysis, it is possible to reveal a more complete picture of the interaction between magmatic fluid and meteoric water during ore formation, and we expect to achieve a deeper and more detailed understanding of how hydrothermal fluids control Sn(-W) mineralization.

Conclusion

Our robust evaluation demonstrates a lack of crystallographic orientation effect on cassiterite oxygen isotope analysis by ion microprobe given the current analytical precision (e.g., ~0.2–0.3 ‰). Along with the Yongde-Cst, a mega-crystal of cassiterite from Yalian town, Yongde county, Yunnan province, which has been developed as a matrix-matched reference material for oxygen isotope analysis, we have paved the way for cassiterite oxygen isotope analysis by ion microprobe. The recommended $\delta^{18}O$ value for the Yongde-Cst is 1.36 ± 0.16 ‰, as determined by Gas-Source Isotope Ratio Mass Spectrometry. We further calculated the temperature-dependent isotope fractionation between quartz and cassiterite, which is given by the equation of $1.259\times10^6/T^2 + 8.15\times10^3/T - 4.72$ (T is temperature in kelvin), hence the fractionation between cassiterite and water is given by $2.941\times10^6/T^2 - 11.45\times10^3/T + 4.72$ (T is temperature in kelvin). A sensitive response of the oxygen isotope fractionation between quartz and cassiterite to temperature makes cassiterite-quartz an excellent oxygen isotope thermometer, as described by the equation of $T\ (°C) = 2427 \times (\delta^{18}O_{qtz} - \delta^{18}O_{cst})^{-0.4326} - 492.4$. Current analytical precision of SIMS $\delta^{18}O$ is ~0.2–0.3 ‰, this will bring an uncertainty of ±10 °C for temperatures estimated from the quartz-cassiterite oxygen isotope thermometer. We further developed a conceptual model to derive $\delta^{18}O$ and temperature of ore-forming fluids, as well as the $\delta^{18}O$ and proportional contribution of meteoric water in magmatic-hydrothermal systems, with the $\delta^{18}O$ values of zircon, cassiterite and quartz as inputs. We eventually applied SIMS oxygen isotope analysis to cassiterite samples from six deposits, which revealed significant fluctuations in $\delta^{18}O$ values both within a single deposit and between deposits. The predicted $\delta^{18}O$ of ore-forming fluids bears a strong magmatic affinity, with variable and mostly low degree (~0–10 %) involvements of meteoric water. Our results presented here highlight the fact that in situ oxygen isotope analysis of cassiterite is a very promising tool for tracing the sources and evolutionary processes of ore-forming fluids.

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Figure captions

Fig. 1 SIMS oxygen isotope composition and crystallographic orientation information of cassiterite fragments of the Yongde-Cst. A), CL imaging of cassiterite fragments from the Yongde-Cst; fragments with sizes ranging from ~300 μm to ~1 mm were cast in two epoxy resin mounts (G855 and G856); B), Inverse pole figure map of cassiterite fragments on mount G855; a stereographic triangle is used to represent the crystallographic orientation with respect to three major planes (i.e., 111, 100, 110). C), Inverse pole figure map of cassiterite fragments on mount G856. D), Histogram of SIMS δ^{18}O values of cassiterite fragments on mount G855. E), Histogram of SIMS δ^{18}O values of cassiterite fragments on mount G856.

Fig. 2 SIMS δ^{18}O values of the Yongde-Cst. A), Horizontal section of the Yongde-Cst cast in epoxy resin as mount A5243; pits of SIMS δ^{18}O analysis are illustrated with a color scheme to represent their measured δ^{18}O values; there is a gradual increase in measured $\delta^{18}O$ values along the Y axis, which is an artifact and has been corrected (Li et al. 2021); also presented is an inverse pole figure map of the studied cassiterite surface; a inserted photo shows the Yongde-Cst studied here before cutting. B), Vertical section (fragment on top) of the Yongde-Cst cast in epoxy resin as mount A5244, also shown are pits of SIMS $\delta^{18}O$ analysis and an inverse pole figure map of the exposed surface; a traverse was conducted across the horizontal section (big fragment in mount A5244) and the sharp end (small fragment in mount A5244) to assess isotopic homogeneity of the two fragments; NIST610 glass was analyzed to monitor instrumental drift. C), A small tip (the sharp end) of the Yongde-Cst cast in epoxy resin together with the vertical section as mount A5244, also shown are pits of SIMS $\delta^{18}O$ analysis and an inverse pole figure map of the exposed surface; A 900 * 200 μm area from the horizontal section was analyzed with a 100 * 100 μm grid to monitor instrumental drift. D), Histogram of SIMS $\delta^{18}O$ values of the horizontal section of the Yongde-Cst after correcting the Y-coordinate related artifact following Li et al. (2021). E), Histogram of SIMS $\delta^{18}O$ values of the vertical section of the Yongde-Cst. F), Histogram of SIMS $\delta^{18}O$ values of the small tip (the sharp end) of the Yongde-Cst.

Fig. 3 Oxygen isotope composition of the Yongde-Cst determined by Gas Source Isotope Ratio Mass Spectrometry.

Fig. 4 Oxygen isotope exchange in the cassiterite, quartz, zircon and water systems. A), oxygen isotope fractionation between quartz and cassiterite as a function of temperature from previous studies (Zheng 1991; Zhang et al. 1994; Hu et al. 2005; Polyakov et al. 2005) and recalculated in this study. B), a sensitive response between 1000 ln α of quartz-cassiterite and temperature, as quantified by $1.259\times10^6/T^2 + 8.15\times10^3/T - 4.72$ (T is temperature in kelvin), makes quartz-cassiterite very promising for oxygen isotope thermometry. C), Oxygen isotope fractionation of cassiterite-water as a function of temperature, as quantified by the equation of $2.941\times10^6/T^2 - 11.45\times10^3/T + 4.72$, where T is temperature in kelvin; it shows a weak and negative response to temperature; such a weak temperature dependence makes it possible to predict the $\delta^{18}O$ values of ore-forming fluids without robust prior knowledge of the mineralization temperatures. D), Oxygen isotope fractionation of quartz-water as a function of temperature, and the corresponding equation is $4.2\times10^6/T^2 - 3.3\times10^3/T$, where T is temperature in kelvin; it shows a sensitive response to temperature, and the positive response gets more sensitive at low temperature regions, which highlights the importance of getting accurate temperature-estimates when calculating $\delta^{18}O$ values of fluids from quartz. E), Oxygen isotope fractionation of zircon-water as a function of temperature, and the corresponding equation is $1.56\times10^6/T^2 - 3.3\times10^3/T$, where T is temperature in kelvin. F), A conceptual model to derive the nature of ore-forming fluids in magmatic-hydrothermal systems from an oxygen isotope perspective; using a binary mixing model, oxygen isotope composition of magmatic water, ore-forming fluids and meteoric water as well as temperatures of ore formation all can be constrained with the $\delta^{18}O$ values of zircon, quartz and cassiterite as inputs. In this model, temperature of the mixture (i.e., hydrothermal fluids) can be calculated using the equation of $T_{hydrothermal} = T_{magmatic} \times p + T_{meteoric} \times (1–p)$, where p is the proportional contribution of meteoric water. Similarly, oxygen isotope composition of the hydrothermal fluid also can be estimated as $\delta^{18}O_{hydrothermal} = \delta^{18}O_{magamatic} \times p + \delta^{18}O_{meteoric} \times (1–p)$. Assuming primary magmatic fluids have a temperature of ~600 °C, its oxygen isotope composition can be calculated from equilibrium isotope fractionation of zircon-water. Both temperature and oxygen isotope composition of hydrothermal fluids can be obtained using quartz-cassiterite thermometer (or fluid inclusion studies) and 1000 ln α of cassiterite-water, respectively. See text for details.

Fig. 5 SIMS oxygen isotope analyses of cassiterite from six Sn(-W) deposits. A), CL imaging of representative cassiterite grains from the studied Sn(-W) deposits. Note that most cassiterite grains show well-developed oscillatory zonation, while a few samples have alteration features with primary zonation being truncated by bright bands. B), $\delta^{18}O$ values of cassiterite from the studied Sn(-W) deposits. Samples with no sign of alteration show limited variation in terms of $\delta^{18}O$ values, while samples with a high degree of alteration show considerable variation in $\delta^{18}O$ values.

Fig. 6 Constraining the oxygen isotope composition of primary magmatic fluids and ore-forming fluids by analyzing the $\delta^{18}O$ values of zircon and cassiterite, respectively. A), predicting $\delta^{18}O$ values of primary magmatic fluids at the Xiaolonghe Sn(-W) deposit, Yunnan province; zircon $\delta^{18}O$ values from SIMS analysis (Chen et al. 2015) are illustrated with 1000 ln α of zircon-water vs temperature; uncertainties are shown at the 2 sigma level as the shaded area; predicted $\delta^{18}O$ values (at 2 sigma level) of magmatic fluids at 600 ± 50 °C are shown as vertical rectangles at the left side. B), predicting $\delta^{18}O$ values of ore-forming fluids at the Xiaolonghe deposit from cassiterite oxygen isotope analysis; 1000 ln α of cassiterite and water vs temperature with known $\delta^{18}O$ values of cassiterite from SIMS analysis are illustrated, with uncertainties shown at the 2 sigma level as the shaded area; predicted $\delta^{18}O$ values (at 2 sigma level) of ore-forming fluids at 420 ± 55 °C are shown as vertical rectangles at the left side; ore-forming temperatures are from cassiterite-hosted fluid inclusion assemblages (Cui et al. 2019); Using a Monte Carlo approach, simulated $\delta^{18}O$ values of magmatic and ore-forming fluids at the Xiaolonghe deposit are shown at the right side of panel B, which are broadly the same. C), in a similar fashion to Fig. 4A, predicting $\delta^{18}O$ values of primary magmatic fluids (600 ± 50 °C) at the Kafang Sn(-W) deposit, Yunnan province; zircon oxygen isotope data is from Cheng et al. (2012). D), in a similar fashion to Fig. 4B, predicting $\delta^{18}O$ values of ore-forming fluids at the Kafang deposit from cassiterite oxygen isotope analysis at 331 ± 44 °C; homogenization temperatures of cassiterite-hosted fluid inclusion assemblages are from previous studies (Cheng et al. 2012; Zhang et al. 2012). Using a Monte Carlo approach, simulated $\delta^{18}O$ values of magmatic and ore-forming fluids at the Kafang deposit are shown at the right side of panel C, which indicates a low degree involvement of external fluids with low $\delta^{18}O$ values; See text for details.

Fig. 7 Oxygen isotope composition of cassiterite and corresponding ore-forming fluids of six Sn(-W) deposits investigated in this study. A), Histogram of $\delta^{18}O$ values of the six Sn(-W) deposits analyzed in this study; the red curve is the kernel density curve which highlights the three major peaks of $\delta^{18}O$ values of cassiterite at 4.6 ± 0.6, 3.3 ± 0.8 and –1.1 ± 0.4 ‰. B), 1000 ln α of cassiterite-water vs temperature, with three major peaks of $\delta^{18}O$ values of cassiterite from the six Sn(-W) deposits being illustrated as shaded areas (uncertainties at 2 sigma level). C), at a temperature of 300 ± 100 °C (as shaded in Fig. 7B), predicted $\delta^{18}O$ values (10.6 ± 1.2 , 9.3 ± 1.2 and 4.9 ± 1.1 ‰) of ore-forming fluids are shown as rectangles at the left side; these estimates predominately show a magmatic affinity (11–9 ‰) but limited contribution of fluids with low $\delta^{18}O$ values (e.g., meteoric water, ~0–10 %); we would like to highlight here that obtaining the $\delta^{18}O$ values of fluids from cassiterite is not sensitive to temperature estimates, see text for further discussion.

List of tables

Table 1 Oxygen isotope composition of the Yongde-Cst determined by Gas Source Isotope Ratio Mass Spectrometry.

Supplementary materials

Table S1, SIMS cassiterite oxygen isotope composition of the Yongde-Cst;

Table S2, SIMS cassiterite oxygen isotope composition from six Chinese Sn(-W) deposits.