Supplementary materials for

Millennial pulses of ore formation and an extra high Tibetan Plateau

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Samples and methods

Samples: Four quartz crystals from the Zhibula deposit (Figs. 1B-C and S1) were investigated in this study, from a current elevation of ~5260 m. Two grains (4919M and 4918M) were separated from sample ZBL10, which was collected from drill core ZK11805 (103 m below surface). One grain (4918B) was collected from sample ZBL07, which was collected from drill core ZK11806 (115.6 m below surface). The fourth grain (4928) was collected from an outcrop (ZBL03). Quartz grains are prismatic, terminating with six-sided pyramids, with grain sizes varying from 2 to 20 mm (Figs. 1B and S1). Quartz is closely associated with abundant pyrite, chalcopyrite, anhydrite and trace amounts of molybdenite (Fig. 1C), which is indicative of syn-mineralization quartz growth. These grains were cut into two halves along the c-axis. For each of the four quartz grains, the first half of each grain was mounted with NBS 28 and Qinghu quartz standards in a one-inch epoxy dish, and then fine-polished for petrographic investigation and SIMS/NanoSIMS analysis. The second half of each grain was prepared as a doubly polished wafer with thickness of ~200 μm for petrographic investigation and fluid inclusion study. This approach allows mirroring petrographic and geochemical data to fluid inclusion data.

Molybdenite Re-Os dating: Molybdenite grains (0.2 mm to 1 mm in size) were drilled from sample ZBL10 (Fig. 1B). Molybdenite digestion and sample-spike equilibrium was achieved through standard Carius tube technic following methods described previously (Li et al., 2017b). Re and Os were separated by anion column chromatography and solvent extraction method, respectively. Isotopic measurements were performed by on a Thermo Scientific TRITON mass spectrometer at Durham University. The high Re and Os abundances in the sample in comparison to the blanks (<2 pg for Re and <0.5 pg for Os) result in a negligible blank correction. The molybdenite Re-Os model date was calculated using the equation $t = \ln$

$(^{187}\text{Os}/^{187}\text{Re} + 1)/\lambda$, in which λ is the decay constant (Smoliar et al., 1996). Data are presented in Table S1; uncertainties including isotopic composition measurements, tracer calibration, weighting, reproducibility of standards were all propagated.

Fluid inclusion assemblages: Fluid inclusion studies were conducted following approaches similar to our previous studies (Li et al., 2017a; Li et al., 2017c). Doubly polished wafers were investigated by transmitted light microscopy to image distributions of fluid inclusion assemblages (FIAs) and to correlate FIAs with quartz growth history inferred from CL imaging. Here only primary FIAs were studied. The volumetric fraction of phases in fluid inclusions was estimated at room temperature. Fluid inclusion data were measured on a Linkham THMSG 600 heating-freezing stage mounted on a Zeiss transmitted light microscope at the institute of Geology and Geophysics, Chinese Academy of Sciences. Synthetic fluid inclusion standards (pure CO₂ and pure water) were used (Baumgartner et al., 2014) at -56.6, 0, 10.2, and 374 °C to correct the accuracy of the stage. Measurements below 31.1 °C, the critical point of CO₂, are accurate to ± 0.2 °C, and measurements above this temperature are accurate to ± 1 °C. The volumetric fraction of phases in fluid inclusions was estimated at room temperature by reference to the volumetric chart of Roedder (1984). Bulk salinity was calculated from the final ice melting temperature, or halite dissolution temperature (Bodnar and Vityk, 1994) for hypersaline fluid inclusions. Homogenization conditions and isochores of individual fluid inclusion assemblages (FIAs) have been calculated with HokieFlincs_H₂O-NaCl program based on fluid inclusion volumetric data (P-V-T-X) (Steele-MacInnis et al., 2012). Paleodepth is estimated from boiling fluid inclusion assemblages from stage 1 quartz, and pressure correction was applied to FIAs from the remaining stages to yield trapping temperatures following Steele-MacInnis et al. (2012). Data are presented in Table S2.

Cathodoluminescence (CL) imaging: The epoxy mounts were chromium coated, with cathodoluminescence (CL) images (Figs. 2A and S1) being acquired using a TIMA-X Mineral Analyzer at Peking University. The analyser is equipped with a TESCAN Colour CL detector, and was operated at an accelerating voltage of 20 kV and a beam current of 5 nA.

SIMS oxygen isotope analysis: SIMS oxygen isotope analysis was conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences with a CAMECA IMS-1280 SIMS following methods described previously (Tang et al., 2020). Data were presented in supplementary tables (Table S3). The Cs^+ primary ion beam was accelerated at 10 kV with a beam intensity of 4 nA. The spot size was $15 \times 10 \mu\text{m}^2$. Oxygen isotopes were measured using multi-collection mode on two Faraday cups for 40 cycles, with a ^{16}O intensity better than 2×10^9 cps. The instrumental mass fractionation factor (IMF) was corrected using NBS-28 standards. All data were presented in Table S3 and graphically illustrated in Figure S2. Accuracy and long-term drift of oxygen isotope analysis were monitored by analysing Qinghu quartz standard between samples, and analysis during this study yields a $\delta^{18}\text{O}$ value of $8.58 \pm 0.24 \text{ ‰}$ (2 SD, Table S3).

NanoSIMS mapping: Trace element mapping was conducted on a CAMECA 50L NanoSIMS at the institute of Geology and Geophysics, Chinese Academy of Sciences (Hao et al., 2016). A focussed ~ 80 pA oxygen beam in Gaussian model was used. The beam size is roughly 500 nm in diameter, as measured using the so-called “knife-edge” method. Six isotopes including ^7Li , ^{23}Na , ^{27}Al , ^{30}Si , ^{44}Ca and ^{49}Ti were measured with a mass resolution of 10000. We employed image profile mode analysis to further improve the spatial resolution (i.e., $\sim 0.1 \mu\text{m}$). In this mode, secondary ion images were acquired by rastering a $50 \times 50 \mu\text{m}^2$ area with the same oxygen beam (~ 80 pA), but for a much longer time period (~ 10 hours). Trace element compositions for a given region or profile in the ion images can be re-calculated. The regions

of interest (ROI) can be of any shape, and not confined to a square. Due to a lack suitable reference materials to correct matrix effect, only relative concentrations in counts per seconds are provided, which has no impact on diffusion modelling. Detection limit is defined as three times of background values, and are ~10 cps for most elements. High spatial resolution can be achieved at the expense of lower efficiency due to the longer period of data acquisition and image processing, which is necessary, and critical to provide a spatial resolution of ~0.1 μm for the purpose of this study. For SIMS analysis, yield may vary significantly between elements. Hence a higher relative content in cps for a given element does necessarily reflects a higher absolute content in ppm. Data for the studied profile are presented in Table S4.

Deriving $\delta^{18}\text{O}$ of meteoric water: In magmatic-hydrothermal systems, hydrothermal fluids are predominantly magmatic in origin, and experience variable degrees of mixing with meteoric water. Oxygen isotope compositions and temperatures of hydrothermal fluids can be quantified by a binary mixing model following Li et al. (2021). Here we briefly describe the principles as follows.

$$\delta^{18}\text{O}_f = \delta^{18}\text{O}_i \times R + \delta^{18}\text{O}_m \times (1-R) \quad (1)$$

$$T_f = T_i \times R + T_m \times (1-R) \quad (2)$$

Where the subscripts i , m and f stand for magmatic fluid, meteoric water and hydrothermal fluid (i.e., the mixture), respectively, and R is the percentage contribution of magmatic fluid.

Oxygen isotope composition and temperature ($\delta^{18}\text{O}_f$ and T_f) of hydrothermal fluid is also recorded by quartz grains crystallized from the fluid, and deriving $\delta^{18}\text{O}_f$ from $\delta^{18}\text{O}_q$ (measured quartz $\delta^{18}\text{O}$) is governed by equation 3 (Sharp et al., 2016).

$$\delta^{18}\text{O}_q - \delta^{18}\text{O}_f = 4.28 \times 10^6 / (T_f + 273.15)^2 - 3.5 \times 10^3 / (T_f + 273.15), \quad 34^\circ\text{C} < T_f < 800^\circ\text{C} \quad (3)$$

For a given magmatic-hydrothermal system, $\delta^{18}\text{O}_i$ and T_i of magmatic fluids can be given by oxygen isotope thermometry of zircon and magmatic quartz from the causative granite. Once T_f of the hydrothermal fluid is constrained (i.e., quartz formation), we obtain $\delta^{18}\text{O}_f$ following equation 3, and calculate $\delta^{18}\text{O}_m$ of meteoric water at any given T_m . We emphasize here that $\delta^{18}\text{O}_m$ values calculated using this approach are maximum values, hence elevations calculated below are minimum values.

With $\delta^{18}\text{O}_m$ being obtained, the relationship between $\Delta(\delta^{18}\text{O}_p)$ and elevation (h) in equation 4 (Rowley and Garzione, 2007) was used to calculate paleo-elevation,

$$h = -0.00614 \times A^4 - 0.6765 \times A^3 - 28.623 \times A^2 - 650.66 \times A \quad (4)$$

where A is the difference between $\delta^{18}\text{O}_m$ of meteoric water at a certain elevation and a reference site at low altitude (e.g., sea level). We use a $\delta^{18}\text{O}$ value of $-6 \pm 1.6\text{‰}$ for the reference site, which is consistent with previous studies (Rowley and Currie, 2006; Ding et al., 2014; Li et al., 2015; Ingalls et al., 2017).

Estimates on the temperature of quartz formation (T_f) are represented by trapping temperatures of FIAs from the specific stage of quartz growth.

Diffusion Chronometry: Sharp compositional gradients generated during quartz growth tend to homogenize at high temperatures, in which case elements diffuse out of regions with high contents to surrounding areas with low contents. This diffusion continues for as long as the crystal is hosted in hot magmatic-hydrothermal systems, but stops as soon as the crystal cools down. So the diffusive profile width together with the diffusion speed can be used to estimate the residence time of the crystal in the magmatic-hydrothermal system. The crystal is assumed not to grow or shrink during the diffusion process. This diffusion process can be computed using a one-dimensional numerical model using Fick's second law of diffusion in equation 5.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (5)$$

where C is the measured concentration of a given element, t is time, x is distance from the beginning of elemental profile, and D is diffusion coefficient. We used Diffuser software (Wu et al., 2021) to derive timescales.

List of supplementary tables

Table S1, Re-Os data for molybdenite from Zhibula

Table S2, Fluid inclusion data for hydrothermal quartz from Zhibula

Table S3, SIMS oxygen isotope data for hydrothermal quartz from Zhibula

Table S4, NanoSIMS trace element data for hydrothermal quartz from Zhibula

Table S5, Temperature vs timescale for Al diffusion in hydrothermal quartz from Zhibula

Table S6, Meteoric water $\delta^{18}\text{O}$ calculations and corresponding paleoelevation estimates.

Uncertainties for all input parameters are propagated using a Monte Carlo approach, the systematic uncertainties from the paleoaltimetric calibration of Rowley and Garzzone (2007) are also included.

List of supplementary figures

Figure S1, Backscattered electrons (BSE) and cathodoluminescence (CL) images of the four investigated Zhibula quartz grains. Also shown are transects of SIMS oxygen isotope measurements.

Figure S2, Measured $\delta^{18}\text{O}_q$ of Zhibula quartz along the transects shown in Figure S1.

Figure S3, Sensitivity test for input parameters on calculated paleo-elevations. A), quartz formation temperature; B), oxygen isotope composition of meteoric water for low altitude reference site; C), magmatic temperature; D), oxygen isotope composition of magmatic fluid.

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Figure S1

Figure S2

Figure S3