

Supplementary information:

**Table S1:** Major oxide composition (wt%) of cassiterite used in this study from the Zinnwald deposit, Germany (n = 124), determined by EMPA.

**Table S2:** Isotope composition of the NIST SRM 3161a and calibrated double spike.

**Table S3:** Effects of double spike proportion on measured  $\delta^{122}\text{Sn}/^{118}\text{Sn}$  of NIST 3161a.

**Table S4:** Recovery yields (%) of Sn during evaporation-re-dissolution and subsequent column chemistry.

**Table S5:**  $\delta^{122}\text{Sn}/^{118}\text{Sn}_{3161a}$  values and Sn recovery yields of NIST SRM 3161a after evaporation at different temperatures.

**Table S6:** Effect of concentration mismatch on  $\delta^{122}\text{Sn}/^{118}\text{Sn}_{3161a}$ .

**Table S7:** Long-term reproducibility of Sn isotope measurements.

**Figure S1.** Experimental dissolution of cassiterite in NaOH conducted within different container materials. (a) Outer Pt crucibles containing inner MgO (left) and Al oxide (right) crucibles inside the muffle furnace; (b) powdery reaction products observed in the MgO crucible; (c) products adhering to the bottom of the Al oxide crucible.

**Figure S2.** A contour plot illustrates the propagation of uncertainties on the natural fractionation factor  $\alpha$  (1SD) for the  $^{117}\text{Sn}$ ,  $^{118}\text{Sn}$ ,  $^{122}\text{Sn}$ , and  $^{124}\text{Sn}$  inversion. The diagram explores how the error varies as a function of both the proportion of double spike added to the sample mixture and the relative contribution of  $^{117}\text{Sn}$  in the  $^{117}\text{Sn}$ - $^{122}\text{Sn}$  double spike, based on calculations with the Double Spike Toolbox. The optimal configuration, indicated by red cross, corresponds to ~ 40 % double spike in the spike-sample mixture. Contours denote.

**Figure S3.** Optimization and validation of the  $^{117}\text{Sn}$ - $^{122}\text{Sn}$  double spike. Predicted error in  $\alpha$  (1 SD) as a function of the proportion of double spike in the double spike-sample mixture, calculated for the inversion of  $^{117}\text{Sn}$ ,  $^{118}\text{Sn}$ ,  $^{122}\text{Sn}$ , and  $^{124}\text{Sn}$ . increments of 1% in the error relative to the minimum value.