**In situ U-Pb Dating of Calcite from the South China Antimony Metallogenic Belt**

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**HIGHLIGHTS**
- The syn-ore calcite yielded an in situ U-Pb age of 115.3 ± 1.5 Ma.
- The South China antimony mineralization occurred during the early Cretaceous.
- Calcite in situ U-Pb dating can determine the timing of hydrothermal mineralization.

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SUMMARY
Accurately determining the age of hydrothermal ore deposits is difficult, because of lack of suitable mineral chronometers and techniques. Here we present the first LA-MC-ICPMS U-Pb age of carbonates from hydrothermal Sb deposits. Three stages of hydrothermal carbonates from the giant South China Sb metallogenic belt were identified: (1) pre-ore dolomite (Dol-I), (2) syn-ore calcite (Cal-II), and (3) post-ore calcite (Cal-III). The U and Pb isotopic data show that Cal-II yielded a lower intercept age of 115.3 ± 1.5 Ma (MSWD = 2.0), suggesting a Sb mineralization that corresponds to an extension event occurred during the early Cretaceous in South China. Although Cal-III yielded an age of 60.0 ± 0.9 Ma (MSWD = 1.5), indicating a potential tectonothermal event occurred in this belt during the early Cenozoic. Hence, in situ U-Pb dating of calcite offers a new way to determine the age of hydrothermal ore deposits.

INTRODUCTION
Dissolution-based carbonate U-Pb dating has been successfully applied to diagenesis of marine carbonate (Israelson et al., 1996; Cole, 2003), coral (Denniston, 2008), fossils (Walker et al., 2006) as well as speleothems (Richards et al., 1998; Woodhead et al., 2006; Victor et al., 2008; Pickering et al., 2010). However, previous bulk analysis using isotope dilution has limited application for most hydrothermal ore deposits. The limitations include: (1) the scarce of spike (e.g. 233U-205Pb) (Moorbath et al., 1987; Pickering et al., 2010; Engel et al., 2020); (2) low U and Pb contents (<1 ppm) within single hydrothermal carbonate minerals (Branon et al., 1996; Grandia et al., 2000; Coveney et al., 2000; Meinhold et al., 2020); and (3) a small spread of 238U/206Pb due to the average of isotopic zonation within the analytical volume (Li et al., 2014; Guillong et al., 2020; Roberts and Walker, 2016). Recently, in situ U-Pb isotopic analysis using laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) equipped with ion counters provides the potential to date these carbonates (Coogan et al., 2016; Methner et al., 2016; Roberts and Walker, 2016; Roberts et al., 2017). Such method can help to identify high U/Pb ratios regions in a sub-mm scale and enable high spatial resolution (less than ca. 100 μm) and low detection limits (ca. 1 ppb Pb) (Woodhead et al., 2006; Li et al., 2014; Roberts and Walker, 2016; Goodfellow et al., 2017; Nuriel et al., 2017; Salih et al., 2020). It potentially targets and utilizes endmember μ 238U/204Pb domains, along with high-n datasets (Shen et al., 2019; Roberts et al., 2020), leading to an improvement in precision on the regressed age, and thus offers a new way to date hydrothermal ore deposits.

Antimony (Sb) is one of the critical metals and commonly found in epigenetic hydrothermal ore deposits (Seal et al., 2017). Precisely determining the age of Sb deposits can help to understand their origin and further prospecting (Scratch et al., 1984; Maheux, 1989; Lu, 1994; Wang, 2008; Tran et al., 2016; Xie et al., 2017). However, dating is a challenging work because of low radioisotope contents in their minerals (stibnite, carbonates, and quartz ± fluorite) (Gumiel and Arribas, 1987; Wu, 1993; Murao et al., 1999; Shen et al., 2011, 2013). Although there are some successful examples of calcite/fluorite Sm-Nd dating (e.g. Peng et al., 2003b), such method has certain limiting factors, such as high cost, low efficiency, unfavorable Sm/Nd ratios, and unavailability to differentiate multiple ore-forming generations (Uysal et al., 2007; Zhu et al., 2017).

The giant South China Sb metallogenic belt has supplied >50% of the world’s Sb metal resource (e.g. Wu, 1993; Fu et al., 2019b). Despite of much attention received (e.g. Xiao, 2014; Fu et al., 2019a, 2019b), the...
timing of Sb mineralization is still not well constrained. In this contribution, we use the Weizhai Sb deposit in the giant South China Sb metallogenic belt as a case study for LA-MC-ICPMS in situ U-Pb dating. The syn-ore calcite was identified by field mapping, mineralogy, in-situ elements, and C-O-Sr isotopic compositions. The aim of this study is to (1) establish a new and precise dating technique of hydrothermal ore deposits and (2) solve the currently challenging problem of timing and geodynamic setting of the South China Sb metallogenic belt.

**Geological Setting**

The giant South China Sb metallogenic belt covers an area between the Yangtze Block and the Cathaysia Block and is a part of the South China low-temperature metallogenic domain (Figure 1A; Hu et al., 2017). This belt hosts more than 500 Sb deposits accounting for 87% of the proven reserves in China and 55% of the world (Figure 1B; Wu, 1993; Fu et al., 2019b) and constitutes an important part of the circum-Pacific Sb metallogenic domain (Wu, 1993; Jin and Dai, 2007; Xiao, 2014). Antimony deposits in this belt are hosted in Proterozoic to Permian sedimentary rocks and structurally controlled by NE-trending folds and faults. The formation of these deposits was generally considered to be genetically related to large-scale extensional tectonics (e.g. Peng et al., 2003b; Hu et al., 2017; Li et al., 2018; Yang and Sun, 2018).

In the southwestern part of the South China Sb metallogenic belt, the Dushan Sb ore district hosts >30 Sb deposits (~287,000t Sb), including the Weizhai, Banpo, Banian, and Jiabai deposits (Figure 1C). These deposits are controlled by folds and faults, including (1) the NE-trending Dushan anticline formed in the Caledonian; (2) the NE-trending Dushan normal fault (29 km in length, 3–10m in width, and dipping SE with an angle of 50–80°); (3) the NNE-trending Lantu normal fault (35km in length, 1–5m in width, and dipping NW with an angle of >70°), and (4) numerous secondary folds and normal faults (Figures 1B and S1; e.g. Wang and Jin, 2010; Shen et al., 2013). These fractures underwent multiple transitions from compression to tension. Strong silicification, carbonatization, and pyritization occur in these faults, accompanying with large amounts of hydrothermal Sb, Hg, As, Pb, and Zn deposits.

The Sb ore bodies normally occur as veinlets defined by these faults (e.g. the Weizhai and Banpo deposits), or stratiform and lens-shaped ore bodies controlled by anticline and bedding fractures (e.g. the Banian and Jiabai deposits) (Figure S1). Among them, the Weizhai deposit (~21,000t Sb @ 4.18 wt. %) is hosted in argillaceous limestone and siltstone of the Lower Silurian. Sb mineralization is almost entirely constituted of stibnite occurring mainly columnar in texture. Field observations identified two modes of occurrence of the Sb ores, including brecciated and veined. Gangue minerals are quartz and carbonate minerals associated with sulfides (Figure 2A). The wall rock alteration includes silicification and carbonatization. The mineral assemblage and wall rock alteration can be compared with those of many other Sb deposits in the South China Sb metallogenic belt (Figures 2B and 2C).

Hydrothermal carbonate minerals in the Weizhai deposit are formed by three stages: pre-ore dolomite (Dol-I), syn-ore calcite (Cal-II), and post-ore calcite (Cal-III). Dol-I enclosing breccia of organic-rich carbonate wall rocks is featured by fine-grained, light yellow Fe-Mn-dolomite with local recrystallization and several to tens of centimeters in width (Figures 2A, 2D, and 2E). Cal-II is characterized by gray thick veins with coarse-grained stibnite, organic matters (Figure 7), and minor pyrite (Figures 2A and 2F). This stage of calcite occurs irregularly in several to tens of meters in length. Cal-III occurs as relatively thinner veins crosscutting all of the early stage carbonate minerals (Figures 2D–2F).

**RESULTS**

**In Situ Trace Elements**

Trace element contents of carbonates from the Weizhai deposit are listed in Table 1. Cal-II has an average 842 ppm Mg, 64.1 ppm Sr, 532 ppm Mn, 1927 ppm Fe, 0.07 ppm Pb, and 0.35 (0.04–0.88 ppm) ppm U (n = 44), whereas fifty-seven spot analyses of Cal-III have average 1241 ppm Mg, 146 ppm Sr, 970 ppm Mn, 2931 ppm Fe, 0.24 ppm Pb, and 0.27 (0.03–0.99) ppm U (n = 57), respectively. This is consistent with elemental mapping results, which shows that images of Ca are almost uniform, but Mg, Fe, and Mn are highly varied with a marked contrast between Cal-II and -III. Furthermore, U and Pb are heterogeneously distributed on the micrometer scale (Figures 3C and 4F).

**Figure 5 shows** the chondrite-normalized rare earth elements (REE) patterns for these carbonates. Dol-I is characterized by a light rare earth elements (LREE) enrichment with a mean LREE/HREE ratio of 4.66
Figure 5B), which is similar to those of carbonate wall rocks (avg. 7.49) (Figure 5A). In contrast, Cal-II and Cal-III are enriched in HREE with mean La$_N$/Yb$_N$ ratios of 0.07 and 0.15, respectively (Figures 5C and 5D).

Carbon and Oxygen Isotopic Compositions

$\delta^{13}$C and $\delta^{18}$O values of hydrothermal carbonates from the Weizhai deposit are listed in Table 2. Pre-ore dolomite has $\delta^{13}$C and $\delta^{18}$O values ranging from $-2.8$ to $-1.9\%_{oo}$ and $+17.8$ to $+18.4\%_{oo}$, respectively, as compared with those of syn-ore calcite ranging from $-0.6$ to $+0.4\%_{oo}$ and $+14.4$ to $+17.4\%_{oo}$, respectively (Figure 6).
Strontium Isotopic Ratios

Table 2 lists $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of hydrothermal carbonates from the Weizhai deposit, ranging from 0.714688 to 0.718653 (2σ). The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decrease from Dol-I (0.718413), to Cal-II (0.715714) and Cal-III (0.714688).

Calcite In Situ U-Pb Age

Among the pre-screened hydrothermal carbonates of three stages from the Weizhai deposit, Cal-II and -III has datable U/Pb ratios (0.05–70; Figure S2; Table 3) with 133–1281 ppb U (mean 475 ppb) and 11–215 ppb Pb (mean 58 ppb), compared with Dol-I of U/Pb ratios (0.03–0.12) with 81–504 ppb U (mean 183 ppb) and 1614–7110 ppb Pb (mean 3895 ppb). As shown in Figure 7, Cal-II has 27 spots with U-Pb data falling on well-defined lines in the isochron plot (2σ analytical and propagated uncertainty) and yields an age of 115.3 ± 1.5 Ma (MSWD = 2.0) (Table 3). Cal-III has an isochron defined by 16 U-Pb data points with a highly radiogenic lower intercept and a significantly younger age of 60.0 ± 0.9 Ma (MSWD = 1.5).

DISCUSSION

Reliability of Calcite In Situ U-Pb Age

Sampling technique using the laser ablation system help to exploit the potential for micro-scale heterogeneity in carbonates and obtain high $\mu (^{238}\text{U}/^{204}\text{Pb})$ values and a large spread of U-Pb ratios (U/Pb = 0.05–70; Table 3). However, concentrations of U and Pb in calcites from the Weizhai Sb deposit range down to tens of ppb, compared with traditional U-bearing accessory minerals often with $>100$ppm U in zircon and $>1$ppm U in meteoric-water-sourced carbonates (e.g. speleothem and tufas) (Woodhead et al., 2006). Such extremely low U and Pb contents in calcites cannot be sufficiently measured by conventional Q-ICP-MS or MC-ICP-MS (Kylander-Clark, 2020).

Accordingly, at the highest mass end of collector array of the Nu Plasma II MC-ICPMS, we employ an ETP (electron multiplier) discrete dynode multiplier dedicated to static measurement of low signal $^{238}\text{U}$. Such discrete dynode multiplier is characterized by higher sensitivity (100 μm, 3 J/cm², 10 Hz, $^{238}\text{U} > 500000$ cps/ppm, $^{207}\text{Pb}$ blank = 10–100 cps) with ~3–10 times higher than that of Q-ICP-MS (Liu et al., 2019; Shen et al., 2019; Cheng et al., 2020).
| Stage     | Mg    | Ca    | Sr    | Mn    | Fe    | La    | Ce    | Pr    | Nd    | Sm    | Eu    | Tb    | Gd    | Dy    | Ho    | Er    | Tm    | Yb    | Lu    | Pb    | Th    | U     | LREE/HREE | LaN/YbN |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Wall rock | Max   | 145500| 404500| 2780  | 7010  | 182000| 270   | 499   | 50.9  | 169   | 20.5  | 2.65  | 1.94  | 10.1  | 11.6  | 2.05  | 5.27  | 0.83  | 5.91  | 0.87  | 316   | 41.2  | 9.10  |
| (n = 26)  | Min   | 38200 | 380600| 321   | 2714  | 34600 | 2.34  | 5.37  | 0.67  | 3.39  | 2.14  | 0.64  | 0.67  | 3.91  | 4.36  | 0.79  | 2.11  | 0.28  | 1.78  | 0.25  | 1.15  | 0.89  | 0.61  |
|           | Mean  | 95836 | 397896| 1036  | 4552  | 79128 | 39.8  | 80.1  | 8.90  | 33.8  | 6.88  | 1.32  | 1.09  | 6.83  | 6.54  | 1.20  | 3.22  | 0.46  | 3.03  | 0.43  | 56.2  | 11.1  | 2.01  | 7.49  | 9.42  |
| Dol-I     | Max   | 165700| 402800| 869   | 3519  | 99500 | 23.3  | 59.0  | 6.98  | 27.6  | 6.05  | 1.17  | 1.56  | 7.77  | 9.64  | 1.66  | 4.16  | 0.55  | 3.49  | 0.48  | 7.11  | 0.75  | 0.50  |       |
| (n = 43)  | Min   | 87500 | 396400| 212   | 2481  | 71920 | 6.30  | 13.5  | 1.52  | 6.50  | 1.69  | 0.38  | 0.37  | 2.77  | 2.23  | 0.43  | 1.07  | 0.12  | 0.57  | 0.08  | 1.61  | 0.02  | 0.08  |       |
|           | Mean  | 137751| 400142| 505   | 2946  | 89831 | 14.4  | 34.2  | 3.92  | 15.5  | 3.46  | 0.70  | 0.71  | 4.18  | 4.64  | 0.43  | 1.07  | 0.12  | 0.57  | 0.08  | 1.61  | 0.02  | 0.08  |       |
| Cal-II    | Max   | 1139  | 404700| 218   | 896   | 2680  | 0.51  | 1.81  | 0.32  | 1.96  | 1.18  | 0.38  | 1.20  | 4.26  | 10.8  | 2.57  | 7.72  | 1.03  | 5.67  | 0.72  | 0.58  | 0.44  | 0.88  |       |
| (n = 69)  | Min   | 424   | 396400| 15.0  | 206   | 856   | 0.01  | 0.03  | 0.01  | 0.07  | 0.09  | 0.05  | 0.16  | 0.65  | 1.03  | 0.17  | 0.40  | 0.04  | 0.22  | 0.03  | 0.00  | 0.02  | 0.04  |       |
|           | Mean  | 842   | 400362| 64.1  | 532   | 1927  | 0.11  | 0.41  | 0.08  | 0.58  | 0.47  | 0.18  | 0.46  | 1.93  | 3.35  | 0.65  | 1.69  | 0.21  | 1.17  | 0.15  | 0.07  | 0.19  | 0.35  | 0.19  | 0.07  |
| Cal-III   | Max   | 2650  | 407700| 1060  | 1700  | 4170  | 2.52  | 7.26  | 1.10  | 6.43  | 3.86  | 1.27  | 2.35  | 10.5  | 17.6  | 3.57  | 9.49  | 1.20  | 6.37  | 0.78  | 1.84  | 1.51  | 0.99  |       |
| (n = 19)  | Min   | 466   | 395700| 15.1  | 568   | 1244  | 0.0007| 0.0013| 0.0011| 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 |
|           | Mean  | 1241  | 400488| 146   | 970   | 2931  | 0.25  | 0.77  | 0.14  | 0.95  | 0.80  | 0.27  | 0.47  | 2.25  | 3.30  | 0.64  | 1.69  | 0.21  | 1.22  | 0.16  | 0.24  | 0.17  | 0.27  | 0.32  | 0.15  |

Table 1. LA-ICP-MS In Situ Element Composition (ppm) of Carbonates from the Weizhai Sb Deposit

Note: LREE/HREE = (La + Ce + Pr + Nd + Sm + Eu)N/(Gd + Dy + Ho + Er + Tm + Yb + Lu)N, δEu = 2Eu/(Sm + Gd).
Taking the advantage of high sensitivity and static analysis, our employment of LA-MC-ICPMS could achieve superior internal error (i.e. <1% 2σ) for U and Pb isotopic compositions with good signal intensity for samples as those in this study. As shown in plot of $^{238}\text{U}/^{206}\text{Pb}-^{207}\text{Pb}/^{206}\text{Pb}$ (Figure 7), the scatters (mean standard weighted deviation (MSWD = 2.0 & 1.5)) of U and Pb isotopic compositions are sufficiently small and less than 2.5, suggesting a precise regression due to well-behaved closed system behavior (Brooks et al., 1972). Besides, through cross-calibration by AHX-1a (Figure S3; Table S1), the matrix-matched carbonate reference materials ASH-15D (3.001 ± 0.012 Ma; Mason et al., 2013; Vaks et al., 2013; Nuriel et al., 2017) attained the expected age within uncertainty (ASH-15D: 2.957 ± 0.033 Ma, MSWD = 1.7; the data have been shown in Figure S4 and Table S1), confirming that the derived ages are accurate.

In this study, therefore, the ages of 115.3 ± 1.5 Ma (MSWD = 2.0) and 60.0 ± 0.9 Ma (MSWD = 1.5) obtained from two types of calcites from the Weizhai Sb deposit (Figure 7) are meaningful and can represent significant geological events.
Determination of Syn-Ore Calcite

Since calcite often has multi-stage generation in hydrothermal systems, its relationship with Sb mineralization cannot be easily established using conventional optical microscope (Morishita, 2012; Zhu et al., 2017). In this study, CL petrography, major, minor, and trace elements, C-O and Sr isotopes, further help to characterize the syn-ore calcite.

The high spatial resolution of CL can be an useful tool for identifying micrometer-scale calcite grain growth zonation and alteration and characterizing different generations formed from different fluids (e.g. Barnaby and Rimstidt, 1989; Tullborg et al., 2008; Milodowski et al., 2018). Figure 2D shows that pre-ore Dol-I with a

Figure 4. Element Mapping of Different Stages of Carbonates from the Weizhai Sb Deposit
Transmitted light image (A) and element mapping of Ca (B), Mg (C), Mn (D), Fe (E), and U (F) of hydrothermal carbonates, showing U concentration heterogeneity in Cal-II and Cal-III.

Figure 5. Chondrite-Normalized REE patterns of Different Stages of Carbonates from the Weizhai Sb Deposit
Carbonate wall rock (A), pre-ore Dol-I (B), syn-ore Cal-II (C), and post-ore Cal-III (D). The chondrite values are from Sun and Mcdonough (1989).
dark-grey CL color is cemented by calcite of two late stages. Syn-ore Cal-II filling in fissures of Dol-I is typically high in the CL intensity and forms a bright orange luminescent. Post-ore Cal-III gray calcite veinlets crosscut both Dol-I and Cal-II crystals with an immediate contact, which rules out the alteration and reprecipitation during the latest hydrothermal event (Roberts et al., 2020). Because of Fe²⁺ serving as the dominant luminescence quencher (Peyrotty et al., 2020), Cal-II with lower Fe concentration exhibits bright CL responses in calcite as being different from that of Cal-III, which is supported by the in situ element data (Table 1).

Other elements, such as Mg, Sr, Ba, Mn, and Fe, can be used to distinguish between syn-ore and post-ore calcites (e.g. Alexandre, 2010; Wang et al., 2018). Data of carbonates from the Weizhai deposit, which were plotted, form two distinct clusters in the Sr/Ca versus Ba/Ca (Figure 3A) and Fe versus Mn (Figure 3B) diagrams, supplemented by different REE patterns (Figure 5), indicating that Cal-II and Cal-III may have different origin from Dol-I and carbonate wall rocks (Scholle and Ulmer-Scholle, 2003; Uysal et al., 2007). Lower Mg, Sr, Mn, and Fe contents of Cal-II are unlikely to be attributed to less fluid-rock interaction, demonstrated by the inconsistent liner relationship of Fe versus Mn between Cal-II and Cal-III (Figure 3B; Bau and Dulski, 1995; Hori et al., 2013). Instead, such elemental signature may reflect separate fluid source with contrasting elemental compositions (e.g. Sb).

δ¹³C and δ¹⁸O values of Cal-II and Cal-III from the Weizhai deposit well overlap with those of calcites from other regional Sb deposits in South China (Figure 6A). Such calcites have slightly lower δ¹⁸O values than those of Dol-I. The ⁸⁷Sr/⁸⁶Sr ratios of Cal-II and -III ranging from 0.7147 to 0.7166 are also similar to those of the Xujiashan (0.7109–0.7154) and Banxi (0.7112–0.7176) Sb deposits but higher than ⁸⁷Sr/⁸⁶Sr ratios of Phanerozoic marine carbonates (0.7068–0.7092; Figure 6B; Veizer and Compston, 1974). The Cal-II and –III Sr isotopic values can be compared with those of the Mesoproterozoic strata in South China (⁸⁷Sr/⁸⁶Sr120Ma ranges from 0.7127 to 0.7261; Figure 6C; Ma et al., 2003; Peng et al., 2003b). This probably indicates that the Sb-bearing fluid derived or flowed through radiogenically ⁸⁷Sr-enriched rocks, e.g. the Mesoproterozoic Banxi Group (Peng et al., 2003b).

Table 2. C, O, and Sr Isotopic Compositions of Carbonates and Strata Units from the South China Sb Metallogenic Belt

| Deposit/Strata     | Sample No. | Stage | δ¹³C_{PDB} (‰) | δ¹⁸O_{SMOW} (‰) | ⁸⁸Sr | ⁸⁷Sr/⁸⁶Sr | ± 2σ | Ref. |
|--------------------|------------|-------|---------------|----------------|------|----------|------|------|
| Weizhai WZ05-4 Dol-I | –1.9       | +17.8 | 14.9          | 0.718653    | 0.000007 | This study |
| WZ05-5             | –2.8       | +18.4 | 15.3          | 0.718173    | 0.000007 |                    |
| WZ05-2 Cal-II      | –0.4       | +17.2 | 16.8          | 0.714795    | 0.000006 |                    |
| WZ05-3             | –0.6       | +17.4 | 16.1          | 0.716632    | 0.000006 |                    |
| WZ05-1 Cal-III     | –0.3       | +16.1 | 15.3          | 0.714688    | 0.000007 |                    |
| WZ02               | +0.4       | +14.4 |              |              |         |         |      |      |
| Banpo              | –2.4––0.5  | +10.9––14.7 |          |              |         |         |      | Xiao, 2014 |
| Xujiashan Syn-ore calcite | –3.9––2.1 | +11.5––15.3 | 0.7109–0.7154 | Shen et al. (2007) |
| Pre-ore calcite    | –0.7––2.0  | +18.6––19.6 | 0.7096–0.7097 |                     |
| Xikuangshan Syn-ore calcite | –7.0––2.1 | +11.0––17.9 | 0.710198–0.714435 | Peng and Hu (2001) |
| Banxi              |            |       |              |              |         |         |      | Li et al., 2018 |
| Qinglong Fluorite  |            |       |              |              | 0.70766–0.70932 | Peng et al. (2003a) |
| Phanerozoic marine carbonates |            |       |              |              | 0.7068–0.7092 | Veizer and Compston, 1974 |
| Mesoproterozoic Banxi Group |            |       |              |              | 0.7127–0.7261 | Ma et al., 2003; Peng et al. (2003b) |

Note: Ore-forming age of 120 Ma was used to calculate initial ⁸⁷Sr/⁸⁶Sr ratios of metamorphism rocks, the Mesoproterozoic Banxi Group, which has ⁸⁷Sr/⁸⁶Sr ranging from 0.7131 to 0.7287.
Therefore, the above geochemical evidence, supported by field observations, establishes a set of complementary criteria for confirming the syn-ore calcite.

Implications for Sb Mineralization of the South China Sb Metallogenic Belt

Due to the lack of suitable minerals for reliable radiometric dating, the age of Sb mineralization in South China is still under debate. A few conventional methods such as Rb-Sr and Ar-Ar dating of fluid inclusion of quartz/calcite, quartz electron spin resonance (ESR), and fluorite/calcite Sm-Nd dating have been employed in an attempt to constrain the timing of Sb mineralization, but yielded a large range of ages (mostly ca. 435–402 Ma and 156–101 Ma; Table 4). These ages were often questionable because of the isochron...
| Stage | $^{238}$U/$^{206}$Pb | Int2SE | $^{207}$Pb/$^{206}$Pb | Int2SE | Approx. U_ppb | Approx. Pb_ppb | U/Pb |
|------|---------------------|--------|-----------------------|--------|--------------|--------------|------|
| Cal-II | 43.44 | 1.795 | 0.2340 | 0.0160 | 448 | 11 | 41 |
| | 46.78 | 1.017 | 0.1640 | 0.0140 | 807 | 12 | 70 |
| | 45.18 | 0.6398 | 0.2029 | 0.0082 | 1281 | 25 | 52 |
| | 33.29 | 0.6829 | 0.3871 | 0.0095 | 807 | 41 | 20 |
| | 39.60 | 0.6271 | 0.2838 | 0.0088 | 693 | 22 | 32 |
| | 43.68 | 1.176 | 0.2310 | 0.0140 | 781 | 18 | 13 |
| | 36.95 | 0.4132 | 0.3412 | 0.0074 | 1079 | 43 | 25 |
| | 38.29 | 1.379 | 0.3230 | 0.0160 | 676 | 26 | 26 |
| | 45.44 | 0.6917 | 0.2020 | 0.0120 | 977 | 19 | 53 |
| | 16.44 | 0.3799 | 0.6682 | 0.0089 | 210 | 38 | 5.5 |
| | 19.63 | 2.457 | 0.5980 | 0.0220 | 434 | 60 | 7.3 |
| | 25.38 | 2.158 | 0.5120 | 0.0290 | 311 | 28 | 11 |
| | 22.74 | 1.733 | 0.5550 | 0.0310 | 156 | 19 | 8.1 |
| | 15.64 | 0.4495 | 0.6840 | 0.0110 | 133 | 27 | 4.9 |
| | 19.91 | 1.114 | 0.6130 | 0.0170 | 171 | 25 | 6.8 |
| | 16.56 | 0.5925 | 0.6570 | 0.0100 | 288 | 52 | 5.6 |
| | 19.35 | 1.376 | 0.6280 | 0.0160 | 298 | 46 | 6.5 |
| | 13.76 | 0.7777 | 0.6970 | 0.0100 | 475 | 111 | 4.3 |
| | 10.12 | 1.008 | 0.7349 | 0.0080 | 359 | 119 | 3.0 |
| | 12.56 | 0.7678 | 0.7070 | 0.0110 | 285 | 79 | 3.6 |
| | 10.36 | 1.055 | 0.7310 | 0.0120 | 208 | 67 | 3.1 |
| | 5.723 | 0.0970 | 0.8140 | 0.0056 | 245 | 153 | 1.6 |
| | 9.599 | 0.5165 | 0.7499 | 0.0098 | 283 | 101 | 2.8 |
| | 6.115 | 0.4351 | 0.8169 | 0.0044 | 348 | 215 | 1.6 |
| | 8.240 | 1.365 | 0.7820 | 0.0120 | 279 | 121 | 2.3 |
| | 7.203 | 0.2030 | 0.8032 | 0.0095 | 152 | 72 | 2.1 |
| Cal-III | 37.28 | 0.9314 | 0.5642 | 0.0091 | 855 | 56 | 15 |
| | 61.42 | 1.305 | 0.3930 | 0.0110 | 703 | 19 | 37 |
| | 71.73 | 1.557 | 0.3280 | 0.0110 | 1018 | 19 | 53 |
| | 42.19 | 1.924 | 0.5260 | 0.0170 | 460 | 26 | 18 |
| | 70.99 | 2.560 | 0.2890 | 0.0180 | 289 | 7 | 44 |
| | 24.28 | 0.5099 | 0.6709 | 0.0072 | 396 | 50 | 8.0 |
| | 8.800 | 0.5441 | 0.7990 | 0.0110 | 132 | 54 | 2.5 |

Table 3. LA-MC-ICP-MS U-Pb Dating of Hydrothermal Calcite from the Weizhai Sb Deposit

(Continued on next page)
precision or the multi-stage presence of dating minerals and abundant non-primary fluid inclusions. For example, the Qinglong Sb deposit in the western South China Sb metallogenic belt was dated at quite different ages (ca. 146 Ma, 125 Ma, and 104 Ma) by using different dating minerals/methods (Zhu, 1998; Peng et al., 2003b).

The newly obtained ca. 115 Ma may indicate the Sb mineralization event between the Yangtze Block and the Cathaysia Block, corresponding to the large-scale Early Cretaceous (ca. 125–100 Ma) extension after the Yanshanian orogenic period (ca. 180–125 Ma) (Mao et al., 2010; Wang, 2012; Wang, 2013; Hu, 2015). Despite the poor timing constraints, the Yanshanian movement (ca.180–100 Ma) is generally considered to be the main driving force for the widespread low-T hydrothermal Hg, Sb, and Au mineralization in South China (Table 4; Wang and Wen, 2015; Su et al., 2009a; Hu et al., 2017). These hydrothermal mineralization are predominantly located in Jurassic NE trending folds and thrusts, and Early Cretaceous NE trending normal faults (Wan, 2010), which is in good agreement with NE-trending trap structures the Dushan Sb ore district featured in this study (Figure 1C).

The younger age (ca. 60 Ma) may reflect a tectonothermal event during the early Cenozoic in the region. This age is within previously published age range of 66.4–51.6 Ma through ESR dating of quartz from

| Stage | 238U/206Pb | Int2SE | 207Pb/206Pb | Int2SE | Approx._U_ppb | Approx._Pb_ppb | U/Pb |
|-------|------------|--------|-------------|--------|---------------|---------------|------|
| 22.63 | 1.550      | 0.6940 | 0.0140      | 179    | 23            | 7.8           |
| 68.51 | 3.855      | 0.3440 | 0.0280      | 781    | 17            | 45            |
| 36.99 | 3.402      | 0.5660 | 0.0250      | 414    | 33            | 13            |
| 58.30 | 4.408      | 0.3880 | 0.0330      | 420    | 13            | 32            |
| 5.228 | 0.4047     | 0.8110 | 0.0100      | 145    | 109           | 1.3           |
| 0.1770| 0.0030     | 0.8510 | 0.0017      | 88     | 1925          | 0.05          |
| 0.1964| 0.0045     | 0.8519 | 0.0014      | 107    | 2150          | 0.05          |
| 9.724 | 0.3800     | 0.7771 | 0.0076      | 241    | 87            | 2.8           |
| 10.70 | 0.2905     | 0.7780 | 0.0110      | 126    | 40            | 3.2           |

Table 3. Continued

Figure 7. Tera-Wasserburg Concordia Diagrams (238U/206Pb versus 207Pb/206Pb) of LA-MC-ICPMS U-Pb Data of Syn-ore and Post-ore Calcites from the Weizhai Sb Deposit Error ellipses are at 2σ.
| Ore Deposit       | Host Strata              | Host Rock                | Ore-Type | Dating Method      | Results (Ma) | Ref.          |
|-------------------|--------------------------|--------------------------|----------|--------------------|--------------|--------------|
| Weizhai           | Devonian-Silurian        | Limestone, siltstone     | Sb       | Calcite in situ U-Pb| 115.3 ± 1.5  | This study   |
| Banpo             | Devonian                 | Sandstones               | Sb       | Quartz Fls K-Ar    | 145          | Wang, 1994   |
|                   |                          |                          |          | Calcite Sm-Nd      | 130.5 ± 3.0  | Xiao, 2014   |
|                   |                          |                          |          |                    | 128.2 ± 3.2  | J.S. Wang (2012) |
|                   |                          |                          |          |                    | 126.4 ± 2.7  |              |
| Maxiong           | Cambrian, Devonian       | Dolostones, sandstones   | Sb       | Quartz Fls Ar-Ar   | 141          | Wei (1993)   |
|                   |                          |                          |          | Quartz Fls Rb-Sr   | 156          |              |
| Muli              | Devonian                 | Carbonates               | Sb       | Quartz Fls Ar-Ar   | 165          | Hu et al. (2007) |
| Qinglong          | Permian                  | Marine volcanic rocks    | Sb (Au)  | Quartz Fls Rb-Sr   | 101.0 ± 2.9  | Xiao, 2014   |
|                   |                          |                          |          | Fluorite ESR       | 104          | Zhu (1998)   |
|                   |                          |                          |          | Quartz ESR         | 125.2        |              |
|                   |                          |                          |          | Fluorite Sm-Nd     | 148 ± 8      | Peng et al., 2003b |
|                   |                          |                          |          |                    | 142 ± 16     |              |
|                   |                          |                          |          |                    | 141 ± 20     | Wang (2013)   |
|                   |                          |                          |          | Calcite Sm-Nd      | 148 ± 13     | J.S. Wang (2012) |
|                   |                          |                          |          |                    | 142.3 ± 7.9  |              |
| Xujiashan         | Upper Ediacaran          | Carbonates, clastic rocks| Sb       | Calcite Sm-Nd      | 402          | Shen, 2008   |
| Pingcha           | Lower Ediacaran          | Carbonates, clastic rocks| Sb       | Quartz Fls Rb-Sr   | 435 ± 9      | Peng and Dai, 1998 |
| Woxi              | Neoproterozoic Banxi Group| Low-grade metamorphic rocks| Sb-Au | Scheelite Sm-Nd    | 402 ± 6      | Peng et al., 2002 |
|                   |                          |                          |          | Quartz Fls Ar-Ar   | 423.2 ± 1.2  |              |
|                   |                          |                          |          |                    | 416.2 ± 0.8  |              |
| Zhazixi           | Neoproterozoic Banxi Group| Low-grade metamorphic rocks| W-Sb   | Scheelite Sm-Nd    | 227.3 ± 6.2  | Y.L. Wang (2012) |
| Banxi             | Neoproterozoic Banxi Group| Low-grade metamorphic rocks| Sb    | Stibnite Rb-Sr     | 129.4 ± 2.4  | Li et al. (2018) |
|                   |                          |                          |          | Stibnite Sm-Nd     | 130.4 ± 1.9  |              |
|                   |                          |                          |          | Zircon (U-Th)/He   | 130–120      | Fu et al. (2019a) |
|                   |                          |                          |          |                    | 123.8 ± 3.8  | Li et al. (2020) |
|                   |                          |                          |          | Zircon (U-Th)/He   | 156–117      | Fu et al. (2019b) |
| Xikuangshan       | Devonian                 | Carbonates, clastic rocks| Sb       | Calcite Sm-Nd      | 155.5 ± 1.1  | Peng et al., 2003b |
|                   |                          |                          |          |                    | 124.1 ± 3.7  |              |
|                   |                          |                          |          |                    | 156.3 ± 12   | Hu et al. (1996) |
|                   |                          |                          |          | Zircon (U-Th)/He   | 156–117      | Fu et al. (2019b) |
| Lannigou          | Triassic                 | Clastic rocks, carbonates| Au      | Quartz Fls Rb-Sr   | 105.6 ± 4.5  | Su et al. (1998) |
|                   |                          |                          |          |                    | 142 ± 2      | Liu et al. (2006) |
| Shuiyindong       | Permian                  | Clastic rocks, carbonates| Au      | Calcite Sm-Nd      | 134 ± 3      | Su et al., 2009a |
| Zimudang          | Permian, Triassic        | Clastic rocks            | Au      | Calcite Sm-Nd      | 148.4 ± 4.8  | Wang (2013)   |
| Jialing-La’e      | Ordovician               | Carbonates               | Hg      | Calcite Sm-Nd      | 129 ± 20     | Wang and Wen (2015) |

Table 4. Age Summary of Major Hydrothermal Ore Deposits in the South China Low-T Metallogenic Domain
Abbreviations: Fls, fluid inclusions; ESR, electron spin resonance.
the giant Xikuangshan Sb deposit in the South China Sb metallogenic belt (Jin, 2002). At the same time, it is temporally consistent with the apatite fission track age (61.5 ± 5.9 Ma; Wang et al., 2018), indicating an uplift event in South China. This is probably attributed to a change in the direction and speed of the subduction (ca. 60–40 Ma) of the Pacific Plate beneath the Eurasian Plate (Li et al., 2005; Tang et al., 2014).

Furthermore, compared with enrichment of LREE signature of pre-ore stage (Figures 5A and 5B), enriched HREE signatures were observed in both stage-II and -III calcites (Figures 5C and 5D). The HREE enrichment may reflect a source of (bi) carbonate-rich ligands in an evolving and cooling hydrothermal fluid, which preferentially mobilize HREE in near neutral to basic waters in basinal environments (Wood, 1990; Bau and Dulski, 1995; Rolland et al., 2003; Middleton et al., 2015). This REE signature can also be found in many other hydrothermal Sb and Au deposits in South China (e.g. the Qinglong and Xikuangshan Sb deposits, the Paiting, Miaolong, and Shuiyindong Au deposits; Figure 1B; Peng et al., 2003a, Xie et al., 2013; Peng et al., 2014, Su et al., 2009b).

Therefore, our new calcite in situ U-Pb ages indicate that the Sb mineralization of the giant South China Sb metallogenic belt occurred during the early Cretaceous, followed by a significant tectono thermal event during the early Cenozoic.

**Conclusion**

1. The calcite LA-MC-ICPMS in situ U-Pb dating is recommended for future use in age determination of hydrothermal ore deposits with extremely low U and Pb contents and a large spread of U/Pb ratios.
2. The new U-Pb age of 115.3 ± 1.5 Ma represents the timing of main-stage Sb mineralization during the early Cretaceous; 60.0 ± 0.9 Ma probably indicates a tectono thermal event occurred during the early Cenozoic.

**Limitations of the Study**

More in situ U-Pb ages of calcites from the giant South China antimony metallogenic belt are required. Future systematic studies would shed light on this issue.

**Resource Availability**

**Lead Contact**
Further information and requests for resources should be directed to and will be fulfilled by the Lead Contact, Prof. Jia-Xi Zhou (email: zhoujiaxi@ynu.edu.cn).

**Materials Availability**
This study did not generate new unique reagents.

**Data and Code Availability**
This study did not generate code. The published article contains all datasets generated in this study.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101575.

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AUTHOR CONTRIBUTIONS
Study design: K.L. and J.X.Zhou. Sampling: K.L., J.X.Zhou, and J.W.Z. Analytical methods design: Y.X.F and J.X.Zhao. Data analysis and interpretation: K.L., A.N., and Y.X.F. Drafting manuscript: K.L., J.X.Zhou, I.T.U., and Y.X.F. Revising manuscript: All authors.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

In situ U-Pb Dating of Calcite
from the South China Antimony Metallogenic Belt

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Figure S1. Schematic section of the Dushan Sb ore district, South China. Related to Figure 1c.
Figure S2. LA-ICP-MS U-Pb screening spots (red dots) of Dol-I, Cal-II and Cal-III. Related to Figure 2a.
Figure S3. Tera-Wasserburg plots for LA-MC-ICPMS U-Pb data from AHX-1a. Related to Figure 7 and Table 3.
Figure S4. Tera-Wasserburg plots for LA-MC-ICPMS U-Pb data from ASH-15D. Related to Figure 7 and Table 3.
Table S1. LA-MC-ICPMS in situ U-Pb data for standards NIST-614, ASH15D and AHX-1a. Related to Figure 7 and Table 3.

| Comments   | $^{238}$U/$^{206}$Pb | $^{238}$U/$^{206}$Pb Int2SE | $^{207}$Pb/$^{206}$Pb | $^{207}$Pb/$^{206}$Pb Int2SE |
|------------|----------------------|----------------------------|-----------------------|----------------------------|
| NIST614_1  | 0.6961               | 0.0030                     | 1.4366                | 0.0062                     |
| NIST614_2  | 0.7029               | 0.0038                     | 1.4227                | 0.0077                     |
| NIST614_3  | 0.7098               | 0.0032                     | 1.4088                | 0.0064                     |
| NIST614_4  | 0.7004               | 0.0032                     | 1.4278                | 0.0065                     |
| NIST614_5  | 0.6952               | 0.0033                     | 1.4384                | 0.0068                     |
| NIST614_6  | 0.6963               | 0.0025                     | 1.4362                | 0.0052                     |
| NIST614_7  | 0.6997               | 0.0036                     | 1.4292                | 0.0074                     |
| NIST614_8  | 0.7036               | 0.0032                     | 1.4213                | 0.0065                     |
| NIST614_9  | 0.7070               | 0.0039                     | 1.4144                | 0.0078                     |
| NIST614_10 | 0.7063               | 0.0037                     | 1.4158                | 0.0074                     |
| NIST614_11 | 0.7552               | 0.0037                     | 1.3242                | 0.0065                     |
| NIST614_12 | 0.7064               | 0.0037                     | 1.4156                | 0.0074                     |
| NIST614_13 | 0.7066               | 0.0028                     | 1.4152                | 0.0056                     |
| NIST614_14 | 0.7066               | 0.0030                     | 1.4152                | 0.0060                     |
| NIST614_15 | 0.7062               | 0.0033                     | 1.4160                | 0.0066                     |
| NIST614_16 | 0.7067               | 0.0032                     | 1.4150                | 0.0064                     |
| NIST614_17 | 0.7094               | 0.0034                     | 1.4096                | 0.0068                     |
| NIST614_18 | 0.7110               | 0.0038                     | 1.4065                | 0.0075                     |
| NIST614_19 | 0.7068               | 0.0033                     | 1.4148                | 0.0066                     |
| NIST614_20 | 0.6952               | 0.0033                     | 1.4384                | 0.0068                     |
| NIST614_21 | 0.7098               | 0.0034                     | 1.4088                | 0.0067                     |
| NIST614_22 | 0.7068               | 0.0026                     | 1.4148                | 0.0052                     |
| NIST614_23 | 0.7073               | 0.0032                     | 1.4138                | 0.0064                     |
| NIST614_24 | 0.7089               | 0.0037                     | 1.4106                | 0.0074                     |
| NIST614_25 | 0.7091               | 0.0035                     | 1.4102                | 0.0070                     |
| NIST614_26 | 0.7094               | 0.0039                     | 1.4096                | 0.0077                     |
| NIST614_27 | 0.6759               | 0.0031                     | 1.4795                | 0.0068                     |
| ASH15D_1   | 2212                 | 68.53                      | 0.0590                | 0.0130                     |
| ASH15D_2   | 1623                 | 47.44                      | 0.2590                | 0.0160                     |
| ASH15D_3   | 2058                 | 194.75                     | 0.0760                | 0.0250                     |
| ASH15D_4   | 2283                 | 62.55                      | 0.0780                | 0.0150                     |
| ASH15D_5   | 2037                 | 95.40                      | 0.0840                | 0.0210                     |
| ASH15D_6   | 2257                 | 71.34                      | 0.0600                | 0.0130                     |
| ASH15D_7   | 2232                 | 59.79                      | 0.0640                | 0.0130                     |
| ASH15D_8   | 1869                 | 55.90                      | 0.2020                | 0.0150                     |
| ASH15D_9   | 1389                 | 32.79                      | 0.3550                | 0.0130                     |
| ASH15D_10  | 2242                 | 60.33                      | 0.0455                | 0.0076                     |
| ASH15D_11  | 2257                 | 56.05                      | 0.0906                | 0.0097                     |
| ASH15D_12  | 2188                 | 81.40                      | 0.0750                | 0.0140                     |
| ASH15D_13  | 2188                 | 52.67                      | 0.0681                | 0.0087                     |
| ASH15D_14 | 2879 | 75.40 | 0.0580 | 0.0100 |
| ASH15D_15 | 2994 | 98.61 | 0.0600 | 0.0120 |
| ASH15D_16 | 2155 | 88.25 | 0.0630 | 0.0160 |
| ASH15D_17 | 2183 | 243.1 | 0.0710 | 0.0490 |
| ASH15D_18 | 2237 | 105.1 | 0.0730 | 0.0270 |
| ASH15D_19 | 1953 | 80.11 | 0.1420 | 0.0220 |
| ASH15D_20 | 2273 | 67.15 | 0.0630 | 0.0100 |
| ASH15D_21 | 1953 | 53.41 | 0.1440 | 0.0160 |
| ASH15D_22 | 2304 | 84.95 | 0.0500 | 0.0180 |
| ASH15D_23 | 2128 | 203.7 | 0.0740 | 0.0090 |
| ASH15D_24 | 1923 | 48.08 | 0.1680 | 0.0150 |
| ASH15D_25 | 2370 | 73.00 | 0.0570 | 0.0150 |
| ASH15D_26 | 1912 | 62.15 | 0.1680 | 0.0130 |
| ASH15D_27 | 2179 | 61.70 | 0.0820 | 0.0140 |
| ASH15D_28 | 2132 | 63.65 | 0.0950 | 0.0110 |
| ASH15D_29 | 2101 | 52.96 | 0.1380 | 0.0150 |
| ASH15D_30 | 2124 | 43.74 | 0.1081 | 0.0085 |
| ASH15D_31 | 2257 | 81.53 | 0.0630 | 0.0150 |
| ASH15D_32 | 2110 | 89.02 | 0.1220 | 0.0200 |
| ASH15D_33 | 2090 | 38.87 | 0.1099 | 0.0086 |
| ASH15D_34 | 2183 | 61.97 | 0.0870 | 0.0130 |
| AHX-1a_1  | 31.91 | 0.3767 | 0.0581 | 0.0030 |
| AHX-1a_2  | 30.79 | 0.4834 | 0.0673 | 0.0044 |
| AHX-1a_3  | 31.52 | 0.4569 | 0.0593 | 0.0042 |
| AHX-1a_4  | 30.57 | 0.4393 | 0.0766 | 0.0051 |
| AHX-1a_5  | 31.04 | 0.6165 | 0.0671 | 0.0058 |
| AHX-1a_6  | 31.20 | 0.4576 | 0.0667 | 0.0039 |
| AHX-1a_7  | 31.98 | 0.3784 | 0.0548 | 0.0032 |
| AHX-1a_8  | 30.75 | 0.5012 | 0.0670 | 0.0047 |
| AHX-1a_9  | 31.19 | 0.4086 | 0.0591 | 0.0039 |
| AHX-1a_10 | 30.47 | 0.4828 | 0.0642 | 0.0052 |
| AHX-1a_11 | 30.73 | 0.3305 | 0.0606 | 0.0029 |
| AHX-1a_12 | 31.23 | 0.5072 | 0.0724 | 0.0064 |
| AHX-1a_13 | 30.58 | 0.9352 | 0.0742 | 0.0082 |
| AHX-1a_14 | 31.54 | 0.4177 | 0.0635 | 0.0044 |
| AHX-1a_15 | 31.27 | 0.7138 | 0.0781 | 0.0084 |
| AHX-1a_16 | 31.08 | 0.5894 | 0.0726 | 0.0061 |
| AHX-1a_17 | 31.01 | 0.4807 | 0.0706 | 0.0050 |
| AHX-1a_18 | 31.15 | 0.6211 | 0.0637 | 0.0048 |
| AHX-1a_19 | 31.41 | 0.4143 | 0.0670 | 0.0048 |
| AHX-1a_20 | 31.18 | 0.4959 | 0.0631 | 0.0057 |
| AHX-1a_21 | 30.79 | 0.3981 | 0.0761 | 0.0056 |
| AHX-1a_22 | 31.20 | 0.4283 | 0.0607 | 0.0042 |
| AHX-1a_23 | 31.57 | 0.3288 | 0.0662 | 0.0036 |
|        |       |       |       |       |
|--------|-------|-------|-------|-------|
| AHX-1a_24 | 31.28 | 0.4696 | 0.0600 | 0.0042 |
| AHX-1a_25 | 31.38 | 0.3643 | 0.0596 | 0.0029 |
| AHX-1a_26 | 30.67 | 0.4420 | 0.0775 | 0.0051 |
| AHX-1a_27 | 31.67 | 0.4011 | 0.0579 | 0.0030 |
**Transparent Methods**

Representative ores from the ore body of the Weizhai Sb deposit were cut into finely polished surfaces and secured in epoxy mount. These mounts were then carefully polished with 1000 grade emery paper, and washed with Milli-Q water in an ultrasonic bath for 15 min. After characterization of Cathode luminescence (CL) and back scanning electron (BSE), microdrilling was performed to six selected carbonate veins from these mounts for acid-dissolved carbon (C), oxygen (O) and strontium (Sr) isotopic analyses.

**Carbon and oxygen isotopic analysis**

Bulk carbon and oxygen isotope analysis was undertaken at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China, using a Finnigan MAT-253 mass spectrometer. Calcite reacted with 100% phosphoric acid (H₃PO₄) to produce CO₂. The analytical precision calculated from replicate analyses of unknown samples was ±0.05‰ for δ¹³C and ±0.08 ‰ for δ¹⁸O. The C and O isotopic compositions are reported relative to Vienna Pee Dee Belemnite (V-PDB) (Friedman and O’Neil, 1977). δ¹⁸OSMOW = 1.03086 \times δ¹⁸OPDB + 30.86. The C and O isotopic compositions are expressed vs. SMOW and vs. PDB, respectively.

**Strontium isotopic analysis**

Strontium isotope compositions (⁸⁷Sr/⁸⁶Sr ratios) were obtained in the Radiogenic Isotope Facility (RIF), University of Queensland, Australia. 50 mg of carbonate powder samples were weighed into Teflon beakers and digested
in weak acetic acid to dissolve only the carbonate fraction and avoid leaching
of radiogenic $^{87}$Sr and Rb from the non-carbonate constituents of the samples.

$^{87}$Sr/$^{86}$Sr measurement was conducted on a Nu Plasma I multi-collector
inductively-coupled plasma mass spectrometry (MC-ICPMS) after Sr was
separated following standard cation exchange column procedures and
standard SRM 987 was used for external calibration. The Sr blanks with the
resin are less than 50 pg and at least four orders of magnitude lower than the
sample Sr (> 1000 ng). A SRM 987 standard was run after every five samples
were measured. Long-term repeated measurement of the SRM 987 standard
on this machine yields a mean $^{87}$Sr/$^{86}$Sr value of $0.710250 \pm 0.000032$ (2σ).

**In situ trace element analysis by LA-ICPMS**

In situ trace elements of carbonates were measured using an ASI
RESOlution 193 nm excimer UV ArF laser ablation system with a dual-volume
Laurin Technic ablation cell integrated with a Thermo iCap RQ quadruple mass
spectrometer at the University of Queensland Centre for Geoanalytical Mass
Spectrometry, RIF. The samples were thoroughly cleaned with soap, followed
by MilliQ water with assistance of a sonication, and dried them overnight at
60°C on a hot plate. Samples were then mounted to a sample holder and
placed in the ablation cell. The mass spectrometer was tuned by scanning a
NIST612 glass reference material with a laser parameters of 50 mm spot size,
a 3 mm/s speed, and a 10 Hz repetition rate, to achieve an optimal condition of
high sensitivity and low double charge and oxide rates. Sample ablation was performed with a laser beam of 3J/cm², a spot size of 100 mm, and a repetition rate at 10 Hz. The ablated aerosols were driven into a funnel and were carried to the mass spectrometer by a mixture of ultrapure He and Ar gases with a minor amount of N₂ for boosting transport efficiency and elemental intensity. The sample spots were run in between the reference material Durango apatite, NIST612 and NIST614 which was used as a calibration standard for data reduction undertaken using Iolite 3.6 (Paton et al, 2011). Calcium was assumed to be 40% in the samples, and used as an internal standard for data normalization.

Elemental mapping was performed using the same laser ablation system with similar carry gas settings as described in Ubide et al. (2019). A selected inter-mineral area of calcite and dolomite was mapped using a laser energy of 3J/cm², a repetition rate of 10Hz, 30x30 mm spot size, the overlaps between raster line of 1 μm, and the stage translation speed of 50 μm/s. The background data was collected for 20 s at the beginning of each raster line. The data reduction was performed using Iolite 3.6.

**In situ U-Pb isotopic analysis by LA-MC-ICPMS**

In situ U-Pb isotopic analysis was also undertaken at the RIF, using a Nu Plasma II Multi-Collector ICP-MS interfaced with a RESolution 193nm excimer UV ArF laser ablation system with a dual-volume Laurin Technic ablation cell. Prior to U-Pb dating analysis, the carbonate minerals were screened and
laser-fired by ~5s for each spots while the U/Pb data was acquired using a Thermo ICap RQ ICP-MS. This aims to firstly remove any surficial contamination (first 3s data) and identify a large spread of U/Pb domains (last 2s data). The MC-ICP-MS was equipped with 6 ion counters, in a static mode with an integration time of 0.2s. $^{238}$U was measured on IC5 while $^{208}$Pb, $^{207}$Pb, and $^{206}$Pb isotopes were collected on IC0, IC1, IC2, respectively. Due to high Hg interference from the argon gas on the mass $^{204}$Hg, the data on IC3 ($^{204}$Pb) and IC4 ($^{202}$Pb) were ignored (Shen et al., 2019; Cheng et al., 2020).

The isotopic U and Pb data of samples were acquired from 100um spots with laser energy 3J/cm$^2$ and a repetition rate of 10Hz for 20s for background measurement, 25s for ablation time, and 8s for washout time. NIST614 glass and matrix-matched standards (ASH-15D and AHX-1a) was also run with a ‘standard-sample bracketing’ technique throughout the measurement and used as the external standard for the purposes of monitoring instrumental drift and isotope fractionation, and laser induced elemental fractionation. Data reduction was performed using Iolite 3.6 (Paton et al., 2010). U and Pb concentrations were semi-quantitatively calculated, using NIST614 as the calibration standard. The approximate U or Pb concentration for each spot analysis was calculated by the total counts of U or Pb isotopes.

For mass-bias correction of the measured $^{238}$U/$^{206}$Pb, we used the 3.001±0.012 Ma (2σ) calcite speleothem ASH-15D standard dated by thermal ionization mass spectrometry (TIMS) (Mason et al., 2013; Vaks et al., 2013;
Nuriel et al., 2017) and the 209.8±1.3 Ma (weighted mean age; n=21, MSWD=2.7) standard AHX-1a dated by LA-MC-ICPMS (Cheng et al., 2020). The corrected U-Pb isotopic data of the calcite standard AHX-1a was plotted on the Tera-Wasserburg diagram ($^{238}$U/$^{206}$Pb vs. $^{207}$Pb/$^{206}$Pb) using the Isoplot v4.15 software (Ludwig, 2011) to obtain the measured age. The offset factor between the measured age and the true age of this calcite standard was used to normalize the $^{238}$U/$^{206}$Pb ratios of the samples (Detailed correction procedure see Roberts et al. (2017)). After normalization process, the U-Pb isotopic data of the samples was plotted on the Tera-Wasserburg diagrams. The common Pb isotopic composition is determined by the y-intercept delineating the $^{207}$Pb/$^{206}$Pb ratio.

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