

Appendix-2

Results

CL textures of quartz

The main advantage of CL imaging is that the textures revealed are typically not observable using conventional SEM detectors (e.g. BSE). CL images of quartz can reveal complex growth patterns allowing for the reconstruction of crystallization history, conditions and associated mineral assemblages.

We obtained CL images of quartz textures from three polished thick sections, selected from the main metallogenic stage (Stage II). Fig. 5j, k shows three distinct generations of quartz. Q1 (first generation) is characterized by dark-grey color that occurs as euhedral-subhedral grains. Q2 (second generation) is defined by euhedral oscillatory growth zones showing variable CL intensity. Q3 (third generation) dark anhedral quartz veins cut the former two generations of quartz. These genetic relationships record the physical and chemical evolution of the hydrothermal system.

Trace elements in quartz

We analyzed selected trace elements in different generations of quartz (Q1-Q3). The elements Li, Na, K, Al, Ti and Ge were analyzed and the results are given in Table 1. Titanium concentrations are generally below the limit of detection, and estimated to vary from approx. 0.35 to 12.3 ppm in three

generations of quartz. Germanium concentrations are $< \sim 6.00$ ppm across all quartz generations (Fig. 7d). Average Li concentrations increase gradually through time, from 2.76 ppm in Q1 to 37.0 ppm in Q2, and then decrease sharply to 0.83 ppm in Q3.

Similarly, K and Na concentrations increase from Q1 (5.68-87.2 ppm and 1.59-24.5 ppm, respectively) to Q2 (1.43-288 ppm and 1.73-125 ppm, respectively), and then decrease sharply (2.29-25.1 ppm and 0.77-15.7 ppm, respectively). Of the trace elements that are identified in quartz from the Wusihe deposit, Al is the most abundant, and concentrations show greater variation than any other element, with 8.46-354 ppm (mean 134 ppm; $n = 8$) in Q1, 171-3049 ppm (mean 1062 ppm; $n = 38$) in Q2, and 3.18-149 ppm (mean 25.4 ppm; $n = 24$) in Q3. Reasonable linear correlations on plots of Li ($R^2=0.7129$), Na ($R^2=0.6550$) and K ($R^2=0.3867$) vs. Al are shown by quartz data (Fig. 7a-c). Al concentrations initially show a general increase from Q1 to Q2), and then become more depleted (Q3) (Fig. 7a-c).

Bulk S isotopes

All data for sulfur isotopic compositions are reported using δ notation relative to Vienna Canyon Diablo Troilite (VCDT). The results of bulk sulfur isotope measurements are summarized in Table 2, and shown on Figs. 8a and 9b. Within individual mineral, the $\delta^{34}\text{S}$ values of sphalerite range from $+5.8\text{‰}$ to $+14.3\text{‰}$ (mean 10.6‰ , $n = 10$). The $\delta^{34}\text{S}$ value of galena range from $+1.8\text{‰}$ to $+12.1\text{‰}$ (mean $+6.9\text{‰}$, $n = 9$). The $\delta^{34}\text{S}$ values of pyrite range from $+8.6\text{‰}$

to +10.9‰ (mean +9.8‰, $n = 5$). There is no distinct correlation between sphalerite colors and $\delta^{34}\text{S}$ values: yellow ($\delta^{34}\text{S} = +9.4\text{--}+14.3\text{‰}$), brown ($\delta^{34}\text{S} = +5.8\text{--}+10.8\text{‰}$), brown-red ($\delta^{34}\text{S} = +8.5\text{--}+14.0\text{‰}$), and red ($\delta^{34}\text{S} = +12.5\text{‰}$). The $\delta^{34}\text{S}$ values do not vary with ore structures: massive ($\delta^{34}\text{S} = +1.8\text{--}+14.0\text{‰}$), brecciated ($\delta^{34}\text{S} = +11.3\text{--}+14.5\text{‰}$), disseminated ($\delta^{34}\text{S} = +2.9\text{--}+10.8\text{‰}$), and veined ($\delta^{34}\text{S} = +3.4\text{--}+5.8\text{‰}$). The variation of fine-grained sulfides ($\delta^{34}\text{S} = +1.8\text{--}+14.3\text{‰}$) is larger than that of the coarse-grained sulfides ($\delta^{34}\text{S} = +7.2\text{--}+14.0\text{‰}$).

In situ S isotopes

Micro-scale S isotopic data are included in Table 3, and shown in Figs. 8b and 9a, c, and their spatial distribution patterns within individual samples are illustrated in Fig. 10a-d. The overall range of in situ $\delta^{34}\text{S}$ values in pyrite and sphalerite grains (-4.3‰ to +26.6‰), which is significantly larger than the range of bulk sulfides (+1.8–+14.3‰; this study). The in situ $\delta^{34}\text{S}$ values of pyrite (-4.3–+26.6‰) have a larger range than that of sphalerite (+0.0–+12.3‰).

Diagenetic pyrite

Sample WSH-07, selected from the ore body of the lower group. Pyrite grains from the siliceous dolostone are characterized by fine-grained (<1mm) euhedral textures (Fig. 10a, i). The $\delta^{34}\text{S}$ values of pyrite vary from +23.4‰ to +24.4‰, with no significant difference among different grain sizes (Fig. 10i).

Lamellar ore (Stage I)

Sample WSH-36, selected from the ore body of the lower group, is

characterized by fine-grained lamellar pyrite. Within wall rocks, pyrite occurs predominantly as a selective replacement phase. Thicker organic-rich layers often contain up to approx. 80% pyrites (Fig. 10b, j).

Measured $\delta^{34}\text{S}$ values vary from +16.5‰ to +26.6‰ in two horizons of different thickness. The $\delta^{34}\text{S}$ values of the two horizons are different, the lower horizon is of +18.0-+26.6‰, and the upper horizon is of +16.5-+19.5‰, showing the $\delta^{34}\text{S}$ values vary widely (up to +8.6‰) within individual layer (Fig. 10j).

Disseminated ore (Stage II)

Sample WSH-23, selected from the upper group of ore bodies, was hosted in strongly silicified dolostone. Pyrite and sphalerite grains are characterized by fine-grained (<1mm) subhedral to anhedral textures (Fig. 10c, k). The disseminated ore minerals, stage-II pyrite and sphalerite share a common boundary, indicating that they formed simultaneously (Fig. 10c).

In sample WSH-23, the $\delta^{34}\text{S}$ values of the pyrite and sphalerite vary from +6.9‰ to +11.8‰ and from +0.1‰ to +8.4‰, respectively. The $\delta^{34}\text{S}$ values of pyrite and sphalerite increase from core to rim (Fig. 10k).

Massive ore (Stage III)

Sample WSH-20, selected from the upper group of ore body, is characterized by fine- to coarse-grained massive galena, sphalerite and pyrite aggregates (Fig. 10d, l).

It has a distinct larger range of sulfur isotopic compositions than those of

the disseminated sulfides (WSH-07 and WSH-23). The $\delta^{34}\text{S}$ values of pyrite vary from -4.3‰ to +3.7‰ and sphalerite from +0.0‰ to +12.3‰. Regardless of the textural form of pyrite or sphalerite mineralization, these results show that the sulfur isotopic composition within a single grain is heterogeneous and can vary by as much as +12.3‰. There is a trend of increasing $\delta^{34}\text{S}$ values from core to rim. The $\delta^{34}\text{S}$ values of pyrite increase from core (-4.3-+0.8‰) to rim (+1.9-+3.7‰), and results for sphalerite show a similar trend from core (+0.0-+0.1‰) to rim (+11.7-+12.3‰) (Fig. 10I).

In situ Pb isotopes

In situ Pb isotopic ratios of galena are presented in Table 4, and shown in Fig. 11a-c. In situ Pb isotope analysis on galena crystals yielded the following ranges: $^{206}\text{Pb}/^{204}\text{Pb} = 18.02\text{-}18.19$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.66\text{-}15.69$ and $^{208}\text{Pb}/^{204}\text{Pb} = 38.14\text{-}38.39$ with μ ($^{238}\text{U}/^{204}\text{Pb}$) values of 9.63-9.67.

The coarse-grained massive galena aggregates appear to fall into separate populations from fine-grained brecciated and banded sulfide ores. The coarse-grained massive sulfide ores have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 18.02-18.09, $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of 15.66-15.67 and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 38.14-38.26, which are slightly lower than those of fine-grained brecciated and banded galena aggregates ($^{206}\text{Pb}/^{204}\text{Pb} = 18.11\text{-}18.19$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.67\text{-}15.69$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.27\text{-}38.39$) (Fig. 11b, c).