Decoupling of Au and As during rapid pyrite crystallization

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A1. List of supplementary figures and tables

Figure DR1. A: Schematic diagram showing the occurrence of breccia orebodies at Daqiao (not to scale). B: Angular slate fragments entrained in calcite-chalcedony veins. C: Pyrite-bearing breccia A was overprinted by chalcedony forming breccia B, which was in turn surrounded by calcite constituting breccia C (borehole 18802). D: Polyhedral angular clasts of breccia A cemented by calcite, chalcedony, and pyrite forming breccia C (sample DQ93). E: Reflected-light photomicrograph showing the overgrowth of cement pyrite on the clasts of disseminated pyrite-bearing breccia A (sample DQ93). F: Reflected-light photomicrograph illustrating the core, mantle, and rim of cement pyrite of breccia C (sample DQ472). Brec–Breccia; Cc–Calcite; Chc–Chalcedony; Py–Pyrite.

Figure DR2. EBSD band contrast maps (A and B) and pole figures (C–H) of the cores, mantles, and rims within cement pyrite of breccia C (sample DQ472) from the Daqiao gold deposit. Note that pyrites within the cores and mantles have generally similar preferred crystallographic orientation, whereas those within the rims are randomly orientated.

Table DR1. LA–MC–ICP–MS *in-situ* sulfur isotope compositions of different zones of cement pyrite from two breccia ores from the Daqiao gold deposit.

A2. Analytical methods

Two C-type breccia ores (DQ93 and DQ472) containing cement pyrite were prepared as polished thick sections (200 μm) and epoxy mounts. The detailed textures were investigated by optical microscopy and a scanning electron microscopy (SEM) on a Hitachi instrument at the Curtin University, Australia, and on an Oxford instrument at the University of Hong Kong. Pyrite aggregates with distinct cores, mantles, and rims from breccia DQ472 (5.5 g/t Au) were selected for subsequent detailed SXRF, EBSD, NanoSIMS, and LA–MC–ICP–MS analyses,

whereas only few pyrite aggregates from breccia DQ93 were selected for LA–MC–ICP–MS sulfur isotope analysis due to the lower Au grade (1.7 g/t Au).

A2.1 SXRF analysis

The SXRF mapping was performed on the X-ray fluorescence microscopy (XFM) beamline equipped with a Maia detector at the Australian Synchrotron. The methodology is consistent with that described by Wu et al. (2020) and is briefly summarized below. The analysis was conducted with a beam energy of 18.5 keV, a step size of 1–2 μm and dwell time of 2–20 ms. The data were processed with the GeoPIXE software using a fundamental parameter model, the Maia detector array efficiency model, and a dynamic analysis matrix method (e.g., Ryan et al., 2005, 2010; Fisher et al., 2015; Wu et al., 2020). The SXRF element maps of the whole analyzed area were firstly created by fitting the full spectra using a yield file based on the mineral assemblage in the samples. A better quantification of element concentrations in selected pyrite regions was produced subsequently by refitting spectra from pyrite with yields calculated for that specific matrix. Particular attention was paid to the recognition of different trace elements within pyrite.

A2.2 EBSD analysis

The EBSD analysis was conducted at Commonwealth Scientific and Industrial Research Organisation (CSIRO) Mineral Resources (Kensington, Australia). Regions of interest identified with SEM were mapped by an EBSD detector (Oxford instrument symmetry) on the Zeiss SEM. Prior to the analysis, the mounts were re-polished with colloidal silica to remove the surface damage induced by mechanical polishing, and then coated with 5 nm carbon layer. Data were collected using a 20-kV accelerating voltage and a 120 μm aperture with probe current of 12 nA. The EBSD map resolution was $1,024 \times 884$ pixels, with a step size down to 0.08 μm . Pattern

quality and phase maps and inverse pole figures were generated with Tango™ and Mambo™ software in Channel 5 (Oxford Instrument Ltd.).

A2.3 NanoSIMS analysis

NanoSIMS analysis was performed on polished epoxy mounts at the Centre for Microscopy, Characterisation and Analysis (CMCA) at the University of Western Australia (UWA), using a CAMECA NanoSIMS 50L optimized as described by Wu et al. (2019). A Cs⁺ ion source with a spot size of approximately 50 nm was employed. Multiple electron multipliers record ion counts from the same sputtered sample volume at seven masses simultaneously.

Each region of interest was pre-sputtered using a beam current of 250 pA, to remove surface contaminants and implant Cs⁺ ions into the sample matrix to achieve a steady state of secondary ion emission. Negative secondary ions of interest (⁷⁵As³²S⁻ and ¹⁹⁷Au⁻) were then sputtered from the sample surface using a beam current of ~2.5 pA. The electron gun was used for charge compensation because the samples were predominantly composed of insulating materials. Analysis areas ranged in size from 15×15 to 40×40 μm², the image sizes were 256×256 to 512×512 pixels, and the dwell times were 40–160 ms per pixel. NanoSIMS images were processed using ImageJ. The ion intensity of each trace element provides a semi-quantitative indication of localized trace element enrichment. Mean ion counts were acquired for the line profile (~6 μm across) and spot (~4 μm in diameter) analyses within the images of ⁷⁵As³²S⁻ and ¹⁹⁷Au⁻.

A2.4 LA–MC–ICP–MS S isotope analysis

Pyrite aggregates with distinct core, mantle, and core zones were selected for the *in-situ* S isotope analysis. The LA–MC–ICP–MS analysis was conducted using a Resonetics-S155 excimer ArF laser ablation system coupled to a Neptune II multicollector ICP–MS, housed at the

State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences (CUG), Wuhan. Detailed analytical conditions and procedures were described by Li et al. (2019). Pyrite was ablated at a spot size of ~30 micrometers with a laser repetition rate of 10 Hz, and the ablation process was set to last for 40 s. Standard-sample bracketing (SSB) was used to determine the $\delta^{34}\text{S}$ values of samples during the analytical sessions. Internal laboratory standards were calibrated with two pyrite standards (WS-1 and WS-2). The 2σ analytical precision is ± 0.2 per mil. After the *in-situ* analyses, all laser pits were imaged by SEM to check the accuracy of laser beam placement, and data from pits containing an obvious mixture of the different pyrite zones were rejected.

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Figure S1

Figure S2