New insights on chimney growth model and native gold enrichment in modern seafloor hydrothermal chimneys

Siyu Hu*
CSIRO-Mineral Resources
ARRC, 26 Dick Perry Ave, Kensington
WA 6151, Australia
Siyu.Hu@csiro.au

Steve Barnes
CSIRO-Mineral Resources
ARRC, 26 Dick Perry Ave, Kensington
WA 6151, Australia
Steve.Barnes@csiro.au

Anais Pagès
CSIRO-Mineral Resources
ARRC, 26 Dick Perry Ave, Kensington
WA 6151, Australia
Anais.Pages@csiro.au

SUMMARY

Seafloor hydrothermal chimneys from back-arc basins are important hosts for metals, e.g. Cu, Zn, Pb, Ag and Au, and bear potential for deep-sea mining. A solid understanding of the distribution of metals requires appreciation of detailed mineralogy and chimney growth histories. This study reports the mineralogy and microstructures of chalcopyrite-lined conduit wall of a multi-conduit hydrothermal chimney from the PACMANUS hydrothermal field (eastern Manus basin, Papua New Guinea). New observations revealed that the conduits are dominated by thick chalcopyrite walls with bi-directional growth (towards and away from the conduit) which are bounded by a thin layer dominated by fine-grained sphalerite. Clustered pyrite grows outwards from the sphalerite substrate. The mineralogy records the early growth stage of chimneys during the initial mixing between hydrothermal fluids and seawater. Late-stage sphalerite and barite then overgrew the conduits at the waning stage. Four types of native gold are observed which has not been reported before. Native gold is interpreted to have precipitated with the sphalerite and barite then overgrew the conduits at the early stage. The mineralogy records the early growth stage of chimneys during the initial mixing between hydrothermal fluids and seawater. Late-stage sphalerite and barite then overgrew the conduits at the waning stage. Four types of native gold are observed which has not been reported before. Native gold is interpreted to have precipitated with the sphalerite and barite then overgrew the conduits at the early stage.

Key words: hydrothermal chimneys, sulphides, growth history, native gold enrichment

INTRODUCTION

Modern hydrothermal sulphide chimneys formed due to the rapid mixing between hot hydrothermal fluids and cold seawater (Haymon, 1983), have been discovered on the seafloor in various geologic settings, including oceanic spreading ridges in a number of oceanic basins (German and Seyfried, 2014). Those from back-arc basins are important hosts for precious metals, such as Au and Ag, as well as other commodities, such as Cu, Zn and Pb (Binns and Scott, 1993; Herzig et al., 1993; Herzig and Hannington, 1995). The hydrothermal fields in Manus Basin, in particular, have attracted interest as potential targets for deep sea mining (Gena, 2013). Previous studies have shown that the mineralogy of chimneys at micron-scale is complex; individual minerals within the same zone present various morphologies and were formed under variable physicochemical conditions (Kristall et al., 2011; Berkenbosch et al., 2012). However, so far there have been relatively few studies investigating the micron to submicron scale mineralogy of sulphide chimneys (e.g. Hu et al., 2019). The characterization of minerals at such small scale is essential to provide detailed information about the microenvironments and a basis for understanding the role of sulphides in controlling the enrichment of precious metals (Kristall et al., 2011).

In this study, we applied a combination of synchrotron-based microbeam x-ray fluorescence mapping (SXFM), scanning electron microscopy (SEM)-electron backscatter diffraction (EBSD) imaging and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses to study a sulphide chimney from the Satanic Mills vent field (Manus basin) and performed the first detailed microstructural investigations of Au-rich chalcopyrite-lined conduits from centimetre to nanometre scale. This study deciphers the mineral association and deposition sequence in the conduits and re-constructs the detailed growth processes of conduits. Four types of native gold are also observed associated with various sulphides; their precipitation mechanisms are assessed.

METHOD AND MATERIALS

The analysed sample is part of a polymetallic chimney fragment, composed of multiple conduits, which has been described in detail by Hu et al. (2019) and in the PACMANUS Memoir (P2+) (Binns et al., 2002). This sample is characterized by multiple sub-parallel chalcopyrite-lined conduits which are surrounded by a chalcopyrite-sphalerite transition zone and further rimmed by a sphalerite-dominated outer zone with variable barite (Figure 1) (Hu et al., 2019). A centimetre-scale sub-sample was taken from a part of the chimney containing multiple chalcopyrite-lined channels. Thin sections are observed with optical microscope and SEM for mineralogy investigation, analysed with EBSD for microstructural study and LA-ICP-MS for trace metal distribution analysis.

Figure 1. Photograph (left) and sketch diagram (right) of the chimney sample showing the distribution of chalcopyrite (Cpy), sphalerite (Sph), barite (Bar) and Fe-Mn oxide surface. The location of sub-sample is indicated in the sketch diagram with the grey rectangle. Modified from Hu et al. (2019).
RESULTS

This sub-sample includes four small conduits through which hydrothermal fluids flowed (Figure 2). Each conduit has its wall lined with coarse-grained chalcopyrite, completely or partly overgrown by late-stage coarse-grained sphalerite (as Sp 1). Chalcopyrite can be separated into two groups (Ccp 1 and Ccp 2), which are characterized by inward-directed growth into the conduit, and outward-directed growth in opposite directions, respectively.

Figure 2. (A) Optical microscopic image of multiple conduits and (B) Corresponding SXFM RGB image showing the distribution of sulfides (chalcopyrite (Ccp), pyrite (Py) and sphalerite (Sp)) and barite (Brt).

Based on the petrographic observations, the chimney conduits are proposed to grow in four stages (Figure 4): 1) the development of an initial sphalerite thin wall, then 2) the accumulation of disseminated euhedral pyrite, followed by 3) the bi-directional overgrowth of chalcopyrite and 4) the late-stage precipitation of sphalerite and barite. Four types of native gold are observed within the conduit walls, three of which are associated with the sphalerite-rich layer in zone 2 (Figure 5). Type 1 gold is associated with tennantite-tetrahedrite solid solution series within chalcopyrite, an association which is likely due to high sulfur activity when hydrothermal fluids mixed with seawater. Type 2 gold occurs at the contacts between early stage sphalerite-chalcopyrite transitions. This enrichment in native gold is attributed to the replacement of Au-rich sphalerite by chalcopyrite. Pyrite is rimmed by type 3 gold, probably resulting from the temperature decreasing during hydrothermal fluid-seawater mixing. Type 4 gold occurs in the cavities which are in the vicinity of dissolution-re-precipitation boundaries of chalcopyrite and is proposed to have re-precipitated from the dissolution of Au-bearing sphalerite.

Comparison to fossil chimney conduits

A similar chimney conduit has been found in the Silurian volcanic-hosted massive sulfide deposit, reported by Maslennikov et al. (2009). It is a well preserved fossil conduit, dominated by chalcopyrite and pyrite. From the inner to outer zone, the conduit includes coarse-grained Ccp 2, drusy chalcopyrite with sphalerite inclusions, and euhedral pyrite cemented by Ccp 1 (Figure 7 in Maslennikov et al. (2009)), which are thought to correspond to zone 1, 2 and 3 in this study, respectively. Native gold was not observed in Maslennikov et al. (2009), and this might be due to the optical observations being conducted at ~ 100 microns scale. However, the LA-ICP-MS data in that study have shown that the sphalerite layer includes high Au content, an association

Table 1. Mineralogical associations in zones and regions.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Mineralogy</th>
<th>Region 1</th>
<th>Region 2</th>
<th>Region 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>Coarse-grained Ccp1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 2</td>
<td>Sp 2, gold-rich, porous</td>
<td>Large Sp 2 patches; least porous</td>
<td>Almost no Sp 2; most porous</td>
<td></td>
</tr>
<tr>
<td>Zone 3</td>
<td>Euhedral Py overgrown by Ccp 2</td>
<td>Thickest</td>
<td>Thinnest</td>
<td></td>
</tr>
<tr>
<td>Zone 4</td>
<td>Disseminated Py overgrown by Ccp 2 and Sp 1</td>
<td>Without Sp 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Degrees of hydrothermal fluid-seawater mixing

Least Moderate Most

Other observations Dissolution and re-precipitation

Conduit 1 is described in detail as it includes all types of observed native gold and exemplifies the critical features of all other conduits. To better illustrate these features, conduit 1 is further divided into region 1, 2, and 3 based on the various distribution of clustered pyrite and late-stage Sp 1. From higher magnification observations, the conduit can be also divided into four distinguishable zones from the inner to the outer part of the conduit. The detailed associations are illustrated in Figure 3 and Table 1.

Figure 3. (A-C) SXFM elemental map of region 1-3, showing the distribution of chalcopyrite (Ccp) in yellow, pyrite (Py) in red and sphalerite (Sp) in blue, in region 1, 2 & 3, respectively. (D-F) SEM-BSE observations of region 1 (D) and 3 (E, F). In region 1, zone 2 includes patches of sphalerite, euhedral pyrite and native gold. In region 3, zone 2 is porous and includes native gold and minor sphalerite.

Degrees of growth into the conduit, and outward-directed growth in opposite directions, respectively.
which was interpreted to result from a fast precipitation of Au with sulfides directly from hydrothermal fluids. Due to the striking similarity in sulfide distributions between the fossil chimney and the studied modern chimney, we propose that the high content of Au associated with sphalerite could be attributed to the occurrence of native Au nanoparticles, and either due to the high sulfur activity of hydrothermal fluids or the temperature decrease during hydrothermal fluid-seawater mixing, or dissolution and re-precipitation. Therefore, the comparison between similar conduits in fossil and modern chimneys provides new insights into the deposition mechanism of gold in sea-floor chimneys.

**CONCLUSIONS**

This study provides a detailed petrographic and microstructural investigation of chalcopyrite-rich conduits of chimneys to decipher the detailed processes of the wall formation and possible mechanisms of native gold enrichment. A thin layer of sphalerite and pyrite is found to form the initial wall deposited during the early mixing between hydrothermal fluids and seawater. Chalcopyrite then grows inwards and outwards from this wall causing the development of the concentric zones. The presence of native gold is attributed to either the high sulphur activity of hydrothermal fluids or the temperature decrease during hydrothermal fluid-seawater mixing. The sub-micron mineralogy provides a better understanding of the micron-scale laser ablation line scanning observations. The comparison between similar conduits in fossil and modern chimneys provides new insights into the deposition mechanism of gold in sea-floor chimneys. This study, therefore, bears important potential for searching for native gold in fossil hydrothermal chimneys and ancient volcanogenic massive sulphide deposits.

![Figure 4. The four stages of formation of chimney conduits. Ccp: chalcopyrite; Py: pyrite; Sp: sphalerite.](image)

**ACKNOWLEDGEMENTS**

The authors would like to acknowledge Drs Michael Verrall, Louise Schoneveld, Joanna Parr, Ray Binns and Zakaria Quadir for data and sample collection. SXFM work was undertaken on the x-ray fluorescence microscopy beamline at the Australian Synchrotron (Proposal 12589), part of Australia’s Nuclear Science and Technology Organization (ANSTO). Drs Chris Ryan and David Paterson are acknowledged for the assistance during data collection. S.H. and S.B. acknowledge the Research-plus postdoctoral fellowship funded by the Commonwealth Science and Industry Research Organization (CSIRO).

**REFERENCES**


Herzig, P.M., and Hannington, M.D., 1995, Polymetallic massive sulfides at the modern seafloor, a review: Ore Geology Reviews, 10, 95-115.

