Acta Oceanol. Sin., 2019, Vol. 38, No. 9, P. 59–70 https://doi.org/10.1007/s13131-019-1475-z http://www.hyxb.org.cn E-mail: hyxbe@263.net

Origin of Cu in the PACMANUS hydrothermal field from the eastern Manus back-arc basin: evidence from mass balance modeling

Yao Ma^{1, 2}*, Xiaoyuan Wang^{1, 2}, Shuai Chen^{1, 2}, Xuebo Yin¹, Bowen Zhu^{1, 3}, Kun Guo^{1, 2, 4}, Zhigang Zeng^{1, 2, 3}

¹Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

² Laboratory for Marine Mineral Resources, Pilot National Laboratory for Marine Science and Technology (Qingdao), Qingdao 266071, China

³University of Chinese Academy of Sciences, Beijing 100049, China

⁴Ocean Science Isotope and Geochronology Center, Pilot National Laboratory for Marine Science and Technology (Qingdao), Qingdao 266071, China

Received 11 September 2018; accepted 31 October 2018

© Chinese Society for Oceanography and Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

Hydrothermal precipitates associated with active vents in the eastern Manus Basin, an actively opening back-arc basin in the Bismarck Sea, Papua New Guinea, are among the most Cu-rich on the modern seafloor. The volcanic rocks associated with this mineralization may be insufficiently enriched in Cu to account for the Cu content of the sulfides by simple leaching. The PACMANUS hydrothermal field lies in the eastern portion of the eastern Manus Basin. Mass balance modeling of the PACMANUS hydrothermal system indicates that simple leaching of a stationary reaction zone (0.144 km³) by hydrothermal fluids cannot yield the Cu found in associated sulfide deposits because unacceptably high leaching, transportation and precipitation efficiencies are required to derive the Cu in sulfides by leaching processes. With 100% leaching, transport and precipitating efficiency, 0.166 km3 of volcanic rocks would need to be leached to account for the Cu budget of hydrothermal sulfide deposits. The key requirement for forming metal-rich magmatic fluids is a large amount of metals available to enter the exsolved vapor phase. Magmas generated in the eastern Manus Basin inherently have high fO_2 because of metasomatism of the mantle source by oxidized materials from the subducted slab, leading to copper enrichment in the magma chamber. Moreover, the presence of Cu in gas-rich melt inclusi on bubbles in Pual Ridge andesite is evidence that degassing and partitioning of Cu into the magmatic volatile phase has occurred in the eastern Manus Basin. Numerical mass balance modeling indicates that approximately 0.236 Mt Cu was potentially transferred to the hydrothermal system per cubic kilometer magma. Magmatic degassing seems to play a more significant role than leaching.

Key words: back-arc basin, mass balance model, PACMANUS hydrothermal field, source of Cu

Citation: Ma Yao, Wang Xiaoyuan, Chen Shuai, Yin Xuebo, Zhu Bowen, Guo Kun, Zeng Zhigang. 2019. Origin of Cu in the PACMANUS hydrothermal field from the eastern Manus back-arc basin: evidence from mass balance modeling. Acta Oceanologica Sinica, 38(9): 59–70, doi: 10.1007/s13131-019-1475-z

1 Introduction

The source of ore metals in seafloor hydrothermal systems is important for understanding the genesis of modern seafloor hydrothermal sulfide deposits and their relation to similar types of volcanogenic (or volcanic-hosted) massive sulfides in the ancient geologic record. Previous studies have examined enrichment in Au (Moss et al., 2001), Pb (Beaudoin and Scott, 2009) and other metals (Yang and Scott, 1996, 2002; Landtwing et al., 2010;

Foundation item: The National Natural Science Foundation of China under contract Nos 41706052, 41476044 and 41325021; the National Program on Global Change and Air-Sea Interaction under contract No. GASI-GEOGE-02; the National Basic Research Program (973 Program) of China under contract No. 2013CB429700; the International Partnership Program of Chinese Academy of Sciences under contract No. 133137KYSB20170003; the Strategic Priority Research Program of the Chinese Academy of Sciences under contract No. XDA11030302; the Special Fund for the Taishan Scholar Program of Shandong Province under contract No. ts201511061; the National Special Fund for the 13th Five Year Plan of COMRA under contract No. DY135-G2-1-02; the AoShan Talents Program supported by Qingdao National Laboratory for Marine Science and Technology under contract No. 2015ASTP-0S17; the Innovative Talent Promotion Program under contract No. 2012RA2191; the Science and Technology Development Program of Shandong Province under contract No. 2013GRC31502; the Scientific and Technological Innovation Project financially supported by Qingdao National Laboratory for Marine Science and Technological Innovation Project financially supported by Qingdao National Laboratory for Marine Science and Technological Innovation Project financially supported by Qingdao National Laboratory for Marine Science and Technological Innovation Project financially supported by Qingdao National Laboratory for Marine Science and Technology under contract No. 2015ASKJ03; the National High Level Talent Special Support Program, CAS/SAFEA International Partnership Program for Creative Research Teams, and Qingdao Collaborative Innovation Center of Marine Science and Technology.

*Corresponding author, E-mail: mayao@qdio.ac.cn

Li et al., 2016) in hydrothermal fields, through inclusions, microanalysis in situ and numerical modeling. Two end-member models are used to explain the source of the ore metals in volcanogenic massive sulfide deposits: (1) metals are derived through leaching of rock by seawater, with an underlying heat source sustaining subseafloor hydrothermal convection (Hannington et al., 1995); and (2) metals are derived directly from a magmatic fluid through degassing of metal-enriched volatiles into the hydrothermal system (Stanton, 1991; Li et al., 2016). Since the early 1960s, several studies of hydrothermally formed minerals have emphasized the importance of rock/water reaction in seafloor hydrothermal systems (Taylor, 1997). These studies imply substantial leaching of ore metals from volcanic rocks by circulating seawater. However, a leaching model may explain the genesis of some sulfide-rich mineralizations but fails to explain the metal budget of large ore deposits (Yang and Scott, 2006), suggesting other sources of metals besides hydrothermally altered volcanic rocks.

It has been recognized that magmatic fluid exsolved from the arc-like submarine magmas of immature back-arc basins can directly contribute metals such as Cu and Au to seafloor hydrothermal systems (Li et al., 2016). Much previous research on seafloor hydrothermal processes has emphasized magmatic degassing as an efficient process for transferring metals to a hydrothermal system (Symonds et al., 1992; Rubin, 1997; Fouquet et al., 1998; Hekinian et al., 2000; Yang and Scott, 2005; Beaudoin and Scott, 2009; de Ronde et al., 2011, 2014; Gruen et al., 2014; Li et al., 2016). The pre-enrichment of metals in magma before largescale pre-eruptive degassing is a crucial step in the generation of an ore-bearing magmatic-hydrothermal system (Jenner et al., 2010; Richards, 2011; Li et al., 2016). In the eastern Manus magmas, it has been determined that Cu initially behaves incompatibly due to high fO_2 (oxygen fugacity) caused by subducted sediment inputs to melts, and the Cu content increases to almost five times the initial amount, potentially resulting in Cu-rich magmatic fluids (Li et al., 2016). As attested by the observation of high-temperature fumarolic processes (Symonds et al., 1987, 1992), ore metals are transported as stable chloride and sulfide complexes in volatile phases under conditions of high temperatures and vapor pressures (Stanton, 1994). Studies of melt inclusions have suggested that Cu could be transported via CO₂ and Srich volatile phases in magmas (Lowenstern et al., 1991; Lowenstern, 1993, 1995; Yang and Scott, 1996; Zajacz and Halter, 2009). Sublimates on vesicle walls occurring in the glass matrix of volcanic rocks contain a variety of metal species in lavas of diverse chemical compositions (Yang and Scott, 2002). For instance, Ni, Cu, Zn and Fe sulfide/chloride sublimates are typically associated with vesicles in rocks of basaltic and basaltic andesite compositions, whereas Cu, Zn and Fe-bearing sublimates are found in vesicles contained in andesite. Sublimates in rocks of dacitic composition are predominantly Cu- and Fe-bearing, with Fe sulfides and chlorides present only in sublimates associated with rhyodacite and Fe and Zn sublimates in rhyolite (Yang and Scott, 2002). These associations suggest that Cu and other ore metals may be transported during syn- and post-eruptive degassing processes. Moreover, Cu enrichment has been observed in vapordominated inclusions of hydrothermally altered rocks associated with gold and other metal deposits (Heinrich et al., 1992; Yang and Scott, 1996; Zajacz and Halter, 2009). For example, the contents of Cu in inclusions hosted in continental and oceanic volcanic rocks are >0.48 wt% (Zajacz and Halter, 2009) and 7.2 wt% (Yang and Scott, 1996), respectively. Thus, the enhanced Cu in sulfide deposits is attributed with strong possibility to the direct

contribution of ore metals exsolved from magmatic fluid through magma degassing.

In this paper, we try to distinguish the ore metal contribution between the two processes by examining currently active sulfide deposits in the Manus Basin of the Bismarck Sea off the east coast of Papua New Guinea and to understand the formation mechanism and mass supply of hydrothermal activity, through evaluating both subseafloor water-rock reaction (leaching) and magmatic fluid (magmatic degassing) as possible sources of Cu. Moss et al. (2001) and Beaudoin and Scott (2009) demonstrated that leaching of basaltic oceanic crust associated with black smoker hydrothermal activity cannot adequately explain the concentrations of Au and Pb presented in the PACMANUS hydrothermal precipitates. The contributions of Moss et al. (2001) and Beaudoin and Scott (2009) and other previous works provide valuable references for this study.

2 Geologic background

The Manus back-arc extensional basin is located in the eastern part of the Bismarck Sea (Thal et al., 2014), surrounded by Manus Island, New Ireland, New Britain Island and Papua New Guinea and bounded by the active New Britain Trench to the south and the inactive Manus Trench to the north (Fig. 1a; Beaudoin and Scott, 2009; Thal et al., 2014). The Manus Basin was formed by the northward oblique subduction of the Solomon Sea Plate into the New Britain Trench (Taylor, 1979; Martinez and Taylor, 1996, 2003; Lee and Ruellan, 2006; Thal et al., 2014). Crustal extension of the Manus Basin is achieved along several oceanic crustal segments: the Manus spreading center (MSC), the Manus extensional transform zone (METZ), the Southern Rifts (SR) and the Southeast Ridges (SER) (Taylor, 1979; Scott and Binns, 1992; Martinez and Taylor, 1996; Beaudoin and Scott, 2009); the seafloor spreading rate is approximately 10 cm/a (Beaudoin and Scott, 2009; Beier et al., 2015).

The eastern Manus Basin is a pull-apart rift associated with a suite of volcanic rocks ranging in composition from basalt to rhyolite (Yang and Scott, 2002; Beaudoin and Scott, 2009; Yeats et al., 2014). The ridges spread en echelon on tectonically stretched arc crust between the Djaul and Weitin transform faults (Thal et al., 2014; Beier et al., 2015). There are three main hydrothermal fields located within the eastern Manus Basin and associated with hydrothermal sulfide deposits: PACMANUS, Desmos and the Susu Knolls (Fig. 1b; Binns and Scott, 1993, Scott and Binns, 1995; Auzende and Urabe, 1996a, 1996b; Gemmell et al., 1996; Binns et al., 1997; Yang and Scott, 2005). Hydrothermal activity is widespread throughout the Manus Basin and is commonly associated with volcanic ridges. For example, Nautilus Minerals has identified 19 sites of hydrothermal activity in the Manus Basin (Yeats et al., 2014 and references therein), including four sites (known as Solwara 4, 6, 7 and 8) in the PACMANUS hydrothermal field.

The PACMANUS hydrothermal field is located on the crest of Pual Ridge, which is built along a 20 km-long × 1 to 1.5 km-wide elongated volcanic center, towering 500 to 600 m above the surrounding seafloor (Fig. 1b; Binns and Scott, 1993; Bartetzko et al., 2003; Paulick et al., 2004; Thal et al., 2014). The entire Pual Ridge may have been generated by successive eruptions emanating from a single, underlying shallow magma chamber initially producing mafic lavas, followed by andesite, and terminating with felsic lavas (dacite, rhyodacite and minor rhyolite) (Binns and Scott, 1993; Moss et al., 1997, 2001; Yang and Scott, 2002, 2005). Compared to other lavas exposed in the eastern Manus Basin, the Pual Ridge volcanics are more vesicular, aphyric and seldom porphyritic (Binns et al., 2007), and these rocks carry the trace ele-

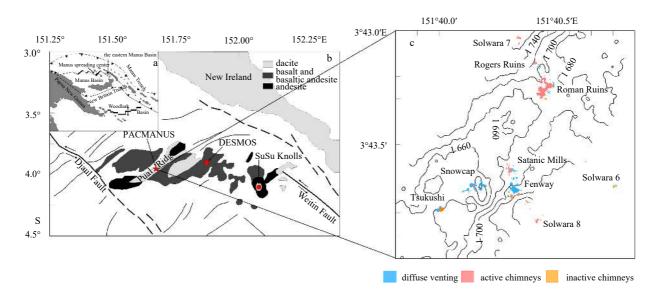


Fig. 1. Tectonic framework of the Manus basin. a. Main tectoinc elements of the Manus basin region (modified from Binns et al. (2007)); b. location of the PACMANUS hydrothermal field, volcanic rock types, and tectonic framework of the eastern Manus Basin (modified from Binns et al. (2007)); c. distribution and localization of hydrothermal venting sites in the PACMANUS field situated on the crest of the Pual Ridge (modified from Thal et al. (2014)).

ment and isotopic geochemical signatures characteristic of subduction-related volcanic rocks (Park et al., 2010). Hydrothermally altered sulfide-rich rocks have been discovered in the main zone of the Pual Ridge (Yang and Scott, 2005) associated with 1 m to 3 m-high (up to 20 m) chimneys particularly rich in chalcopyrite, sphalerite, gold and silver (Parr et al., 2003; Moss et al., 2001; Binns et al., 2007). From south to north in the PACMANUS hydrothermal field, nine main hydrothermal vents are identified: Tsukushi (Solwara 4f), Snowcap (Solwara 4d), Solwara 8, Fenway (Solwara 4e), Solwara 6, Satanic Mills (Solwara 4c), Roman Ruins (Solwara 4b), Rogers Ruins (Solwara 4a) and Solwara 7 (Fig. 1c; Thal et al., 2014).

3 Methods and parameters

3.1 Model specifications

To evaluate and compare the contributions of magma degassing (magmatic fluid) and hydrothermal leaching (water-rock reaction) to the Cu budget of an active hydrothermal system, a mass balance model (Beaudoin and Scott, 2009) and a leaching model (Moss et al., 2001) are used, based on the scenario that all Cu in the PACMANUS field is derived from either direct magmatic input or water-rock reaction. Such calculations rely on many assumptions and approximations, some of which are poorly constrained. However, if the calculated volume of rock and the tonnage of massive sulfides are not unreasonably large, then the mass balance model should be feasible. The mass balance model can be simply described by the following Eq. (1), in which the total mass of Cu in hydrothermal sulfide precipitates is the sum of copper leached from the basement rock and copper transferred during magma degassing:

$$M_{\text{total}} = M_{\text{leaching}} + M_{\text{degassing}},\tag{1}$$

where M_{total} represents the total budget of Cu and M_{leaching} and $M_{\text{degassing}}$ represent the leaching source (derived from seawater-rock reaction) and magmatic input, respectively.

3.2 Volume of high-temperature reaction zone

For modeling purposes, a minimum bulk tonnage is also needed. In addition, the first basic input required for the mass balance model is a realistic approximation of the volume of a static high-temperature reaction zone. Cathles (1993) developed a model to calculate the volume of a high-temperature reaction zone combining field observations and thermodynamic data of ridge axis hydrothermal systems. Moss et al. (2001) applied the method presented by Cathles (1993) with specific data for the PACMANUS hydrothermal field and determined the volume of the static high-temperature reaction zone to be 0.144 km³ with a thickness of 6 m calculated through Eq. (2) and Eq. (3). More details of the geometric model for the PACMANUS high-temperature reaction zone follow in the next section for better understanding of the mass balance calculation.

The width of the reaction zone is given by (Cathles, 1993; Moss et al., 2001):

$$\Delta r_{\rm fz} = Q / \left(P q_{\rm fz} \right), \tag{2}$$

where *Q* is the discharge rate of the vent fluid in g/s (grams per second), *P* is the perimeter of the flow zone in cm (centimeters) and q_{fz} is the fluid mass flux upward through the flow zone in g/(cm²·s); this flux is given by (Cathles, 1993; Moss et al., 2001):

$$q_{\rm fz} = k_{\rm fz} \Delta \rho g / \nu, \tag{3}$$

where k_{fz} is the permeability of the flow zone in cm², $\Delta \rho$ is the difference in fluid density inside and outside the 350°C flow zone, *g* is the gravitational acceleration and ν is the fluid viscosity (see the parameters listed in Table 1).

It has been proposed that the high-temperature reaction zone is a thin but relatively permeable layer parallel to the margin of the magma chamber but separated from it by an impermeable thermal boundary zone of heated country rock (Moss et al., 2001). The extent of the contact area has been suggested to depend on the periodicity of vents. However, distances between vent fields in PACMANUS are on the scale of tens of kilometers

Table 1. Values used in the calculation of the width of the hydrothermal seafloor reaction zone in the PACMANUS area (seeEq. (2) in the text and Moss et al. (2001))

Parameter	Value	Source				
$Q/g \cdot s^{-1}$	9.2×10^4	Moss et al. (2001)				
P/cm	10^{6}	Moss et al. (2001)				
$k_{ m fz}/ m cm^2$	10 ⁻¹⁰	Becker et al. (1994)				
$\Delta \rho/g \cdot cm^{-3}$	0.3	Cathles (1993)				
g/cm·s ⁻²	10 ³	Cathles (1993)				
$\nu/{ m cm}\cdot{ m s}^{-2}$	2×10 ⁻³	Cathles (1993)				

(Lowell et al., 1995). Furthermore, the distances between vent fields in the Pacific, including the PACMANUS field, are generally on the scale of tens of kilometers. Thus, the contact area between the hydrothermal flow zone and the magma chamber is likely to be a large area beneath the Pual Ridge (Moss et al., 2001). The depth of the magma chamber underlying the Pual Ridge is uncertain but is considered relatively shallow (Beier et al., 2015). Reflection seismic surveys conducted in the East Pacific Rise and Lau Basin have shown the tops of magma chambers to be < 3.5 km beneath the seafloor (Moss et al., 2001). To make the mass balance calculation more convincing, the volume of the static reaction zone, as well as the extent of the contact area, should be maximum within a reasonable range. Based on field observations and reasonable speculation, Moss et al. (2001) considered that the most applicable intrusive geometry was dikelike with the long axis parallel to Pual Ridge and thus estimated the depth of the top of the magma chamber beneath the PAC-MANUS hydrothermal field at approximately 3 km below the seafloor and the width at 1 km. Using a similar length-to-width ratio for the active vent sites at PACMANUS, which form a 1 200 mlong × 300 m-wide ellipse (4:1), the length of the magma chamber is estimated at 4 km (Moss et al., 2001; Beaudoin and Scott, 2009). Therefore, within a reasonable range, the maximum contact area on either side of the magma chamber is approximately 12 km^2 (3 km × 4 km) with a width of 6 m, which gives a total volume of 0.144 km3 for the high-temperature reaction zone (Moss et al., 2001).

3.3 Budget of seafloor massive sulfides

In the mass balance model, the total budget of seafloor sulfides is a key parameter that has a crucial effect on the conclusion. However, in previous studies, the estimation of sulfides was quite variable. For example, a total budget of hydrothermally produced sulfides in the PACMANUS hydrothermal field was estimated at 42 613 t by Moss et al. (2001); contrarily, another total budget of 1 841 893 t was calculated by Beaudoin and Scott (2009). In the mass balance calculation, a measured resource is more logical than an inferred resource or indicated resource. Nevertheless, although the PACMANUS hydrothermal field has been well surveyed in recent decades, especially by Nautilus Minerals, Inc., much data including the measured resource is proprietary due to commercial confidentiality. Due to the lack of the measured resource, a minimum of inferred resources within a reasonable range is regarded as a substitute with the errors taken into account. Based on the previous studies, the differences in assessments largely depend on the various volumes of the massive sulfide, which are influenced by the thickness and distribution extent. Furthermore, a seafloor hydrothermal area is always zoned and is generally composed of a chalcopyrite-pyritetennantite inner zone and a barite-dominated outer zone, which is an ineligible factor.

A systematic analysis is presented, using a geographical information systems (GIS) database of autonomous underwater vehicle (AUV)-based microbathymetry combined with remotely operated vehicle (ROV) video recordings, rock analyses and temperature measurements of individual hydrothermal discharge sites for the hydrothermal fields of the PACMANUS hydrothermal area in the eastern Manus Basin (Thal et al., 2014). The total area of hydrothermal activity involving sulfides is estimated at 20 279 m² based on high-resolution microbathymetry maps with meter-scale precision obtained by AUV ABE and 20 ROV dive video observations (Thal et al., 2014). According to Thal et al. (2014), the overall size of the vent fields is considerably smaller than the original estimates (Binns and Scott, 1993), due to accurate navigation and a quantitative GIS-based analysis. According to Hannington et al. (2010), the active hydrothermal vents and associated sulfide mounds occur over an area of approximately 45 000 m². The 2010 technical report by Nautilus Minerals, Inc., (Jankowski et al., 2011) presents a more precise measurement of the hydrothermal area. With further demarcation, Rogers Ruins (known as Solwara 4a) is an area of approximately 100 m by 80 m; Roman Ruins (known as Solwara 4b), 250 m by 150 m; Snowcap (known as Solwara 4d), 150 m by 200 m; Solwara 6, 50 m by 50 m; and Solwara 7 200 m by 20-50 m (Jankowski et al., 2011). Satanic Mills (known as Solwara 4c), Fenway (known as Solwara 4e) and Solwara 8 are adjacent and contain both active and inactive chimneys, with a strike distance of 580 m and a width varying from 50 to 150 m (Jankowski et al., 2011). The Tsukushi (known as Solwara 4f) vent site is a very young and developing seafloor massive sulfide deposit and not involved in the following estimation. Therefore, based on the systematic investigation by Nautilus Minerals, Inc., the area of PACMANUS is approximate 111 000 m²~ 155 000 m² (Jankowski et al., 2011). Considering that a seafloor hydrothermal area is always zoned, the extent of the area covered with sulfides is estimate at 22 200-31 000 m² assuming a rate of 20%. Since the discovery of PACMANUS in 1991, it has often been described as one of the largest marine hydrothermally active areas with metal-rich precipitates (e.g., Petersen et al., 2003). Thus, it is feasible rather than overestimated that the total hydrothermal activity area covered with sulfides is 20 279 m² (with a rate of approximately 13% to 18%).

In 2000, the Ocean Drilling Program (ODP) Leg 193 drilling expedition provided subsurface information on the volcanic facies present at three of the PACMANUS hydrothermal vent fields. The PACMANUS ODP drilling program resulted in holes penetrating between 100 and 380 m deep into the crust of the Snowcap and Roman Ruins areas and 20 mbsf at Satanic Mills (Binns et al., 2007). Further drilling (Condrill SO-166) was undertaken in 2002, which consisted of ten holes (Jankowski et al., 2011). Three drill holes intersected massive chalcopyrite mineralization, and six returned samples of sphalerite-bearing debris (chimney fragments) confirming the existence of a sulfide mound below the hydrothermal vents or chimneys (Jankowski et al., 2011). Drilling at the Roman Ruins site recovered 9 m of spectacular massive sulfides (Petersen et al., 2003). Another four holes for 18.43 m were drilled in PACMANUS (Solwara 4 and 8) by Nautilus Minerals, Inc., and the returned samples consist of massive and semi-massive sulfides with highest assay grades of 25.2% Cu (Jankowski et al., 2011). Based on the data from the ODP drill sites 1188 (Snowcap) and 1189 (Roman Ruins, Binns et al., 2007) and the Condrill SO-166 drill holes (Herzig et al., 2003), an approximately 5 m-thick zone of massive sulfide above weakly to intensely altered dacite is revealed (Herzig et al., 2003; Beaudoin and Scott, 2009). Furthermore, samples from the ODP 1189 drill hole in Roman Ruins suggest that the hole intersected altered dacite breccia and sulfidesilica-anhydrite stockwork mineralization deeper than 200 mbsf (meters below sea floor). East of PACMANUS, the Solwara 1 sulfide deposit, also known as Suzette in SuSu Knolls hydrothermal field, is a stratabound zone of massive and semi-massive sulfide mineralization that occurs on a submarine volcanic mound, which extends approximately 150 m to 200 m above the surrounding seafloor. In Solwara 1, many drill holes indicate that the thickness of sulfide deposits ranges from 4.7 m to 18.9 m (Lipton, 2008). For these reasons, 5 m is a reasonable average thickness for massive sulfide piles in PACMANUS, which is used in the budget estimation of mass balance model in this study.

Because the density of the PACMANUS sulfides has not been measured, we use a measured mean dry bulk massive sulfide density of 3.36 g/cm³ as determined for the nearby SuSu site (Lipton, 2008). According to Lipton (2008), measurements of dry bulk density were determined on over 300 drill core samples using two water displacement methods and assigned to each logged lithology prior to block grade estimation by ordinary kriging. Therefore, according to previous research and reasonable estimation, the total volume and budget of massive sulfides on the seafloor surface are approximately 101 395 m³ and 340 687.2 t, respectively. In addition, we stress that the figures cited represent a minimum estimate, since the parameters involved in the estimation apply as minimum values within the reasonable range and the extent of the PACMANUS hydrothermal system is not fully established. If it is implemented, there may be a greater amount of massive sulfide, which would emphasize the discrepancy between the deposited and available Cu under the mass balance model.

3.4 Budgets of active and inactive chimneys

The chimneys are formed dominantly of sulfide and sulfate minerals including chalcopyrite, sphalerite, pyrite, barite and anhydrite. Thus, it is necessary to estimate a bulk tonnage of the sulfide-rich chimneys, which are an important reservoir of copper. In the following section, we introduce the estimation of the budgets of active and inactive chimneys of Tsukushi (Solwara 4f), Snowcap (Solwara 4d), Solwara 8, Fenway (Solwara 4e), Solwara 6, Satanic Mills (Solwara 4c), Roman Ruins (Solwara 4b), Rogers Ruins (Solwara 4a) and Solwara 7 site in the PACMANUS hydrothermal field.

In western Tsukushi (known as Solwara 4f), the area of the hydrothermal field exhibiting active and diffuse discharge is approximately 1 792 m² (32 m×56 m), whereas on the eastern side, it amounts to 1 225 m² (35 m×35 m) with two 13 m-high and < 10 mdiameter clusters of inactive sulfide-enriched chimneys (Thal et al., 2014). These clusters display an approximate area of 2 041 m³ $(2 \times 13 \text{ m} \times \pi \times (10 \text{ m} / 2)^2 = 2.041 \text{ m}^3)$. Because the diameters of chimney clusters are less than 10 m and channels are present, we assess that the total volume of the Tsukushi chimneys is probably a quarter of this value, approximately 510 m³. In the Snowcap (known as Solwara 4d) venting field, four main chimney clusters are identified (Thal et al., 2014). One of the chimney clusters is inactive and consists of a few minor chimneys (< 1 m in height) (Thal et al., 2014). On the central west Snowcap ridge, a second chimney cluster comprises numerous solitary chimneys that are usually 3 to 4 m high (Thal et al., 2014). The other two clusters comprise several solitary chimneys or chimney complexes with 6 to 7 m-high adjacent branching chimneys situated in the trough bounded by the west Snowcap and Snowcap domes (Thal et al., 2014). Based on assumptions and calculations, the total volume of the chimneys is estimated at approximately 204 m³.

The Fenway (known as Solwara 4e) hydrothermal site is located east of the Snowcap vent and south of the Satanic Mills hydrothermal field and consists of four chimney clusters and a twotiered mound with a principal black smoker chimney complex (Thal et al., 2014). The main chimney mound site is composed of anhydrite-sulfide sand mixed with chimney fragments and massive anhydrite-sulfide blocks (Jankowski et al., 2011; Thal et al., 2014). The other four clusters comprise branching chimneys of various heights (< 1 m, < 2 m, < 5 m, < 8 m, respectively; Thal et al., 2014), resulting in a total volume of the Fenway chimneys of approximately 150 m³. The Satanic Mills (known as Solwara 4c) site is located to the northeast of the Snowcap dome and composed of countless active solitary chimneys (< 10 m high and < 20 cm in diameter) or small clusters (Thal et al., 2014). The total volume of chimneys is evaluated as at least 50 m³. The northern PAC-MANUS vent area includes three main venting fields: the Roman Ruins (known as Solwara 4b), the smaller Rogers Ruins (known as Solwara 4a) and Solwara 7. The Roman Ruins is the largest hydrothermal site and composed of several 0.5 to 7 m-high columnar, solitary or complex branching active chimneys and of a compact wall of coalesced chimneys discharging black smoker fluids (Thal et al., 2014). The Rogers Ruins hydrothermal site is located on the northern Pual Ridge, separated from the Roman Ruins vent field by a small volcanic knoll, and consists of numerous large (< 20 m) inactive sulfide chimneys, with a few chimneys that are actively venting hydrothermal fluid (Jankowski et al., 2011). The Solwara 7 field lies on the northernmost segment of the PACMANUS hydrothermal field exposing sulfide talus and several active chimneys (Thal et al., 2014). These chimneys occur in clusters of dozens and are surrounded by large mounds of collapsed chimney rubble forming piles at least two or three m high in some places (Jankowski et al., 2011). Since there is little information on other chimneys found in the northern PACMANUS site and the Roman Ruins is the largest hydrothermal site in the area, we would assume that the chimney volume of the north PACMANUS area is 510 m³, similar to that of the Tsukushi field. Solwara 6 next to Roman Ruins consists of standing and collapsed chimneys (Jankowski et al., 2011).

Solwara 8 consists of both active and inactive chimneys, adjacent to Satanic Mills, Fenway and Solwara 8. Due to the lack of reference data, chimneys from Solwara 6 and Solwara 8 are not involved in the estimation. Furthermore, chimneys collected from Roman Ruins and Satanic Mills are composed predominantly of chalcopyrite and sphalerite, with subsidiary pyrite, bornite, tennantite, etc. (Scott and Binns, 1995), indicating an enrichment in copper. In total, we estimate the volume of active and inactive chimneys within the PACMANUS hydrothermal field to be approximately 1 424 m³. Therefore, the total budgets of both active and inactive chimneys resting on the seafloor are approximately 3 132.8 t (using an average dry bulk density of 2.2 g/cm³ of 86 measurements; Lipton, 2008). We also stress that the figure cited represents a minimum estimation.

3.5 Cu in massive sulfides and chimneys from the PACMANUS hydrothermal field

In the previous sections, we have separately evaluated the overall budgets of sulfides and chimneys that are enriched in Cu. The approximate budget of copper could be calculated if the concentrations of massive sulfides and sulfide-enriched chimneys were known. In eastern Manus Basin, the concentrations of Cu in sulfides and chimneys vary across a wide range. For instance, the average composition of 34 chimney samples from Suzette is 12.8 wt% Cu, 2.9 wt% Zn, 18 wt% Fe, and 21.9 wt% Ba (Yeats et al.,

2014). According to Yeats et al. (2014), the average Cu concentrations of sulfidic chimneys from Roger Ruins and Roman Ruins are 7.3 wt% (n=8) and 9.0 wt% (n=9), respectively. A total of 85 chimney fragments cut from one large grab of chimney samples from Satanic Mills indicates the chimney contains 8.79 wt% Cu (Jankowski et al., 2011). The highest concentration of Cu is 30.3 wt% in a chimney sample from the PACMANUS hydrothermal field (Binns and Scott, 1993). In the 2010 technical report by Nautilus Minerals (Jankowski et al., 2011), average concentrations of chimneys from Solwara 4, Solwara 6, Solwara 7 and Solwara 8 are collected, with values of 12.3 wt% (n=43), 11.7 wt% (n=7), 3.7 wt% (n=11), and 5.6 wt% (n=13), respectively, resulting in an average content of 9.79 wt% Cu for the chimney samples from the PAC-MANUS hydrothermal field. Petersen et al. (2003) presented the chemical compositions of massive and semi-massive sulfide cores of Condrill holes, ranging from 2.4 wt% to 26.9 wt% Cu. Dredge massive sulfides of Satanic Mills indicated significant polymetallic sulfide mineralization with average grade samples of 13% Cu, 20.8% Zn, 164 g/t Ag and 14.4 g/t Au from 48 massive sulfides (Binns, 2004). During the RV Melville cruise in 2006, three and sixteen grab massive sulfides were recovered from Snowcap and Fenway, containing average grades of 17.1 wt% Cu and 9.6 wt% Cu (Jankowski et al., 2011), respectively. A systematic chemical analysis performed by Hannington et al. (2010) suggested average Cu concentrations of seafloor massive sulfides from different vents of the PACMANUS hydrothermal field of 7.3 wt% (n=257, Solwara 4), 14.0 wt% (n=14, Solwara 6), 4.3 wt% (n=27, Solwara 7) and 9.0 wt% (n=43, Solwara 8), leading to a total average concentration in seafloor massive sulfides of 7.55 wt% Cu. However, the average grades stated reflect only the average of the samples selected rather than the average value of the seafloor massive sulfide deposit of PACMANUS. Because the average grade of Cu from the PACMANUS sulfide deposit is indeterminate, we regard the mean concentrations of Cu as the average grades in the mass balance calculation, 9.79 wt% (Jankowski et al., 2011) for the chimneys and 7.55 wt% (Hannington et al., 2010) for the massive sulfides. As a consequence, the total budget of Cu in massive sulfides and chimneys from the PACMANUS hydrothermal field is 26 028.6 t. Moreover, chalcopyrite is intergrown with black sphalerite in the surface layer of the PAC-MANUS hydrothermal area (Petersen et al., 2003), implying an enrichment in Cu in the massive sulfides, chimneys and polymetallic deposits. Thus, there may in fact be a greater amount of massive sulfides, requiring a larger Cu source.

4 Results

4.1 Cu leached from the volcanic component

For accurate calculations in the mass balance model, the average Cu content in the basement rocks is of great significance. Although drill data indicate rock core samples are primary composed of andesite and dacite, the composition of basement rocks is still unclear, since we cannot rule out other type of rocks. In eastern Manus Basin, the concentrations of Cu in volcanic rocks vary over a wide range. Published data from previous studies indicate Cu concentrations range from 8×10^{-6} to 406×10^{-6} (average concentration=71.4×10⁻⁶, *n*=140; including basalt, andesite and dacite) (Fig. 2; Binns and Scott, 1993; Kamenetsky et al., 2001; Moss et al., 2001; Sinton et al., 2003; Beaudoin et al., 2007; Park et al., 2010). The average Cu content of the eastern Manus Basin volcanic rocks is similar to that of volcanic rocks from the midocean ridge (average concentration=74×10⁻⁶, *n*=357; Gale et al., 2013). On account of the slight difference in the Cu contents of

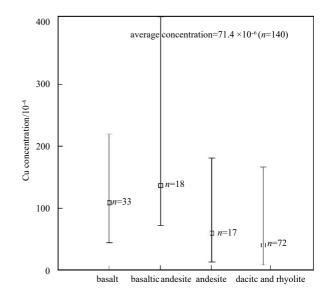


Fig. 2. Distribution of Cu concentrations in various volcanic rocks from the eastern Manus Basin (Binns and Scott, 1993; Kamenetsky et al., 2001; Moss et al., 2001; Sinton et al., 2003; Beaudoin et al., 2007; Park et al., 2010).

different rocks, the mean value of 71.4×10⁻⁶ for the Cu content of eastern Manus Basin rocks was used in the mass balance calculation. Assuming solid rock in PACMANUS with a constant density of 2.2 g/cm³ (Lipton, 2008), the high-temperature static reaction zone (0.144 km³) contains a total Cu tonnage of 22 619.5 t. An enriched source of Cu may be expected to have a significant effect on the copper content of the resulting sulfide deposits, if the Cu is efficiently transported and precipitated. The results essentially represent a maximum estimate of the copper content through leaching from volcanic rocks in the high-temperature reaction zone. Assuming a 100% leaching and precipitation efficiency, a volume of 0.166 km3 of volcanic rock would account for the total Cu content in sulfides and chimneys in PACMANUS. Table 2 provides the total volume of leached volcanic rocks (in km3) required to provide the total Cu content of sulfides in the PAC-MANUS hydrothermal field at various efficiencies of leaching, transport and precipitation. The numbers of high-temperature reaction zone volumes required to be leached in order to account for the Cu observed in the PACMANUS seafloor sulfides are listed in Table 3.

5 Discussion

5.1 Cu budget of the PACMANUS hydrothermal field

An effective way to assess the potential metal sources of hydrothermal deposits is by comparing their contents of massive sulfides and associated volcanic rocks. The previous sections have separately evaluated the overall availability of copper from both the leaching of the volcanic pile and the total budget of the hydrothermal deposit. Based on the mass balance modeling, at least 0.166 km³ of volcanic pile needs to be leached to account for the Cu in the PACMANUS hydrothermal system, assuming a 100% efficiency in hydrothermal leaching, transport and precipitation. However, it is clear from previous studies that efficiencies for leaching (e.g., Seewald and Seyfried, 1990) and precipitation (e.g., Scott, 1997) are much less than 100% in seafloor hydrothermal systems. For instance, according to Mühe et al. (1997), 50% to 60% of Pb is leached from seafloor basalts that have un-

I l- : /07	Transport and precipitation efficiency/%									
Leaching efficiency/%	10	20	30	40	50	60	70	80	90	100
10	16.57	8.29	5.52	4.14	3.31	2.76	2.37	2.07	1.84	1.66
20	8.29	4.14	2.76	2.07	1.66	1.38	1.18	1.04	0.921	0.829
30	5.52	2.76	1.84	1.38	1.10	0.921	0.789	0.690	0.614	0.552
40	4.14	2.07	1.38	1.04	0.829	0.690	0.592	0.518	0.460	0.414
50	3.31	1.66	1.10	0.829	0.663	0.552	0.473	0.414	0.368	0.33
60	2.76	1.38	0.921	0.690	0.552	0.460	0.395	0.345	0.307	0.27
70	2.37	1.18	0.789	0.592	0.473	0.395	0.338	0.296	0.263	0.23
80	2.07	1.04	0.690	0.518	0.414	0.345	0.296	0.259	0.230	0.207
90	1.84	0.921	0.614	0.460	0.368	0.307	0.263	0.230	0.205	0.18
100	1.66	0.829	0.552	0.414	0.331	0.276	0.237	0.207	0.184	0.16

Table 2. Total volume of hydrothermally leached volcanic rocks (km³) required to explain the Cu concentration in sulfides from the PACMANUS hydrothermal field using different rates of efficiency in leaching, transport and precipitation

Table 3. The number of high-temperature reaction zone volume of volcanic rocks (km³) required to be leached in order to account for the Cu observed in the PACMANUS seafloor sulfides

T 1		Transport and precipitation efficiency/%								
Leaching efficiency/%	10	10 20 30 40 50 60					70	80	90	100
10	115.1	57.5	38.4	28.8	23.0	19.2	16.4	14.4	12.8	11.5
20	57.5	28.8	19.2	14.4	11.5	9.6	8.2	7.2	6.4	5.8
30	38.4	19.2	12.8	9.6	7.7	6.4	5.5	4.8	4.3	3.8
40	28.8	14.4	9.6	7.2	5.8	4.8	4.1	3.6	3.2	2.9
50	23.0	11.5	7.7	5.8	4.6	3.8	3.3	2.9	2.6	2.3
60	19.2	9.6	6.4	4.8	3.8	3.2	2.7	2.4	2.1	1.9
70	16.4	8.2	5.5	4.1	3.3	2.7	2.3	2.1	1.8	1.6
80	14.4	7.2	4.8	3.6	2.9	2.4	2.1	1.8	1.6	1.4
90	12.8	6.4	4.3	3.2	2.6	2.1	1.8	1.6	1.4	1.3
100	11.5	5.8	3.8	2.9	2.3	1.9	1.6	1.4	1.3	1.2

dergone hydrothermal alteration. Using the same leaching efficiency for copper and a 100% transport and precipitation efficiency, the volume of volcanic rock required to account for all the Cu in the PACMANUS system is between 0.276 and 0.311 km³. Applying a more realistic 10% to 20% precipitation efficiency, 9.6 to 23 volumes of the volcanic rocks available in the static reaction zone (0.144 km³) would be required to leach. Actually, 50% to 60% leaching efficiency is considerably high and unlikely to be achieved in a hydrothermal system; experiments on the interaction of basaltic rocks with seawater at a temperature of 400°C and reaction times up to near 1 000 h indicate a maximum leaching efficiency of 2% for Cu (Seewald and Seyfried, 1990). This rate would correspond to a maximum transfer of 452.4 t Cu into the seafloor sulfides, which is much less than the mass balance estimate of 26 028.6 t. Applying a 2% leaching efficiency, 8.29 km3 of volcanic rock would need to be leached to account for the Cu content in the PACMANUS hydrothermal system.

In the leaching hypothesis, all the Cu is assumed to be leached from subseafloor rocks, but the volume of rock available for leaching in the PACMANUS high temperature reaction zone is estimated to be 0.144 km³, which is smaller than the required minimum volume (0.166 km³) calculated by mass balance with 100% leaching and precipitation efficiencies. The volume of rock available for leaching in a reaction zone of dimensions comparable to those considered here appears insufficient to supply the Cu in the PACMANUS hydrothermal precipitates. The efficiency of precipitation at the seafloor is expected to be low due to the loss of much of the transported metal to the hydrothermal plume (Moss et al., 2001). Polymetallic sediment is not involved in the estimate of the total Cu budget in the PACMANUS hydrothermal precipitates. If polymetallic sediments are taken into account, the results would suggest a greater amount of hydrothermal Cu or lower precipitation efficiencies. Therefore, it is clear from our modeling, in combination with real geologic cases, that leaching as the only source of metals cannot account for all the copper found in seafloor massive sulfide deposits, especially larger and/or metal-rich systems, implying other sources of copper for the PACMANUS hydrothermal precipitates.

5.2 Evidence for magmatic contribution to PACMANUS hydrothermal system

5.2.1 Enrichment of Cu in magma

The pre-enrichment of metals in magma before large-scale pre-eruptive degassing is a crucial step in the generation of an ore-bearing magmatic-hydrothermal system (e.g., Jenner et al., 2010; Richards, 2011). Li et al. (2016) have investigated how the controlling factors (fO2-H2O-P) affect Cu behavior and what conditions are favorable for Cu enrichment during magma evolution. Previous studies have suggested that the abundance of chalcophile elements, such as Cu and Au, in magma depends mainly on the sulfur content and speciation (Jugo et al., 2010; Li et al., 2016). Cu partitions strongly into magmatic sulfides, up to several orders of magnitude higher than the partitioning into silicate or oxide minerals (D_{Cu} = 1 334 ± 201; Patten et al., 2013). Cu behaves incompatibly when sulfate is the dominant sulfur species but becomes strongly compatible with the onset of sulfide saturation (Sun et al., 2015). Hence, the behavior of Cu during magma differentiation is determined mainly by changes in sulfur speciation (Li et al., 2016). High fO_2 is the principal factor that favors

Cu enrichment in evolved magma because such conditions avoid the sulfide saturation that accompanies Cu removal from the melt (Li et al., 2016). In the eastern Manus Basin, Cu behaves incompatibly and does not increase immediately but remains constant during the early stages of magma differentiation. This result occurs because high fO_2 conditions could lead to earlier magnetite saturation, which subsequently controls sulfide saturation due to the formation of S^{2–} through the reaction 12FeO + SO₄^{2–} = 4Fe₃O₄ + S^{2–} (Sun et al., 2015).

It is widely accepted that hydrous magmas generated at subduction zones inherently have higher fO_2 than MORB because of the metasomatism of the mantle source by oxidized materials from the subducted slab (Evans et al., 2012; Kelley and Cottrell, 2012; Chen et al., 2018; Guo et al., 2018; Li et al., 2019). Consequently, the magmas of eastern Manus have high oxygen fugacity because of subduction inputs of sediment melt into their mantle sources. Thus, in the eastern Manus magmas, Cu initially behaves incompatibly, and its content increases to almost five times the initial amount, potentially resulting in Cu-rich magmatic fluids (Li et al., 2016). In fact, magmas with high fO_2 are always linked to the formation of Cu-Au-rich sulfide deposits. For example, Cu-Au-rich sulfide deposits are associated with the eastern Manus Basin (Binns and Scott, 1993).

5.2.2 Possibility of transfer of magmatic Cu in the hydrothermal system

Previous studies have suggested a magmatic contribution to the metal budget of hydrothermal systems (Yang and Scott, 1996, 2002, 2005; Moss et al., 2001; Beaudoin and Scott, 2009). The evidence of extensive acid sulfate alteration in ODP drill cores at the PACMANUS site suggests the involvement of magmatic fluids (Binns et al., 2007). Whereas volcanic rocks contain trace amount of metals (Zn, Cd, Au, Cu, Br, As, Sb, Hg, Se and Ir), such metals may be highly enriched in aerosols formed by vapor condensation. These aerosols consist of sulfate, Cl-rich droplets and particles of various sizes including (Na, K)Cl and vapor sublimates discharged from subaerial volcanoes and high-temperature fumaroles (Ammonn et al., 1993; Yang and Scott, 2006). Hightemperature experiments on supercritical fluids degassed from a magma demonstrate their capacity to transport metals (Fleet and Wu, 1993; Ballhaus et al., 1994). These experiments have been confirmed by observing high-temperature fumarolic processes relevant to volcanic eruptions, which show base and precious metals transported as simple chlorides in the volatile phase under high-temperature magmatic conditions (Symonds et al., 1987, 1992; Yang and Scott, 2006). The metal complexes are principally high-vapor pressure chlorides and sulfides stable at elevated temperatures (Stanton, 1994; Yang and Scott, 2006). Douville et al. (1999) reported exceptionally high Cl, SO₄, H₂S, and F contents within the hydrothermal fluids emanating from the PACMANUS vents and adding magmatic volatiles to the hydrothermal system. Ishibashi et al. (1996) also inferred significant magmatic input to the gas composition of vent fluids. The magmatic fluids are generated from volatile-rich felsic magmas at a convergent plate margin setting. These fluids could be involved in the formation of "giant" volcanogenic massive sulfide deposits bearing some similarity to porphyry-type deposits (Yang and Scott, 2006).

Wall sublimates found in vesicles incorporated in the matrix glass of volcanic rocks from PACMANUS have been analyzed, revealing an enrichment and systematic change in metal species relative to that of the volcanic rocks (Yang and Scott, 2002). The sublimates are commonly formed by Ni, Cu, Zn and Fe sulfides and chlorides in basalt and basaltic andesite, with Cu-, Zn- and Fe-bearing sublimates in andesite (Yang and Scott, 2002). Cu and Fe are the major ore metals found in the dacite sublimates, whereas Fe and Zn are present in rhyodacite and rhyolite sublimates (Yang and Scott, 2002). Isotope data on Kuroko-type deposits reveal all the Cu and some Pb, Zn and Ba were derived from a fluid of magmatic origin (Yang and Scott, 2005). The presence of Cu in gas-rich melt inclusion bubbles in the Pual Ridge andesites indicates a portion of the Cu degassed into the magmatic volatile phase (Moss et al., 2001). Evidence is also obtained from different regions for other magma compositions. Heinrich et al. (1992) reported Cu enrichment in a sulfur-rich vapor phase associated with the formation of the Mole Granite, Australia. Melt inclusions in a quartz phenocryst from a peralkaline rhyolite from Pantelleria, Italy, indicated a preferential partition of Cu into a CO₂-rich, Cl-bearing volatile phase (Lowenstern et al., 1991). This work suggested that Cu could be derived from a small droplet of immiscible hydrosaline liquid trapped along with a CO_2 -bearing vapor bubble in the melt inclusions. Moreover, the presence of Cu in gas-rich melt inclusion bubbles in Pual Ridge andesite is evidence that degassing and partitioning of Cu into the magmatic volatile phase has also occurred in the eastern Manus Basin (Moss et al., 2001).

5.2.3 Mass flux of Cu potentially degassed from a PACMANUS magmatic source

Initially, we can use the duration and discharge flux of magmatic degassing to estimate the magmatic contribution to the hydrothermal system. Yang and Scott (2005) estimated a minimum period of 5 to 48 a for magmatic degassing through a 10⁻¹⁰ cm/s phenocryst (0.2 to 3.0 mm in size) growth rate during crystallization and magmatic fractionation (olivine, pyroxene and plagioclase; Resmini and Marsh, 1995). The vesiculation process could span at least the above period in the magma chamber. A Cu magmatic vapor mass transfer rate of 1.4×10^{10} g/a from a typical MOR volcanic rock to seawater (Rubin, 1997), produces at least 70 000 t to 672 000 t of magmatic Cu to the hydrothermal system during the vesiculation event. Fast-spreading ridges such as the East Pacific Rise and the Trans-Atlantic Geotraverse (TAG) hydrothermal field of the slow-spreading Mid-Atlantic Ridge have periods of hydrothermal activity lasting 1 000 a (Lalou et al., 1985) and 100 000 a (Lalou et al., 1993), respectively. These values are adopted as the minimum and maximum timescales (Beaudoin and Scott, 2009). Moreover, each vesiculation event may generate a substantial amount of volatile bubbles in the melt with more than one vesiculation event taking place in a crystallizing magma chamber (Hurwitz and Navon, 1994; Yang and Scott, 2005) during a 1 000 a to 100 000 a period. Thus, Cu is more likely to come from magmatic degassing and transfer to the hydrothermal system than from hydrothermal leaching of the surrounding volcanic rocks.

Yang and Scott (1996, 2002, 2005) and Beaudoin and Scott (2009) suggested 35.1 Mt to 48.6 Mt of magmatic fluid could be degassed from a 1 km³ magma body lying beneath the PAC-MANUS hydrothermal field. Assuming the hydrothermal fluids to contain 7.2 wt% Cu (Yang and Scott, 1996), then 2.5 to 3.5 Mt of Cu would be contributed to the hydrothermal system. Therefore, to afford the 25 219.4 t Cu in seafloor sulfides of the PACMANUS field, only 0.72% to 1.0% of magmatic fluid would be needed. Our findings corroborate those of Yang and Scott (2006) and suggest that a small amount (1 wt%) of metal-rich magmatic fluid could contribute over 85% of the total tonnage of metals forming an ore body.

Yang and Scott (1996), relying on melt inclusion data, calculated the amount of magmatic degassing associated with the activity of the PACMANUS field and suggested that melt inclusions containing gas bubbles represented from 0 to 58% degassing of a magma chamber and up to 72% degassing in basaltic andesite (Yang and Scott, 2005). Beaudoin and Scott (2009) determined the H₂O content of melt inclusions by secondary ion mass spectrometry (SIMS) analyses (Yang and Scott, 1996, 2002) to obtain a minimum value of 2.5 wt% and a whole-rock value (i.e., postdegassing) of 0.8 wt%. The 1.7 wt% difference would represent a degassed volume of 68% H₂O. Since not all molecular water present in bubbles is detected by SIMS analysis (Deloule et al., 1995), the original water loss due to degassing might be much higher. The conclusions of Yang and Scott (2005) and Beaudoin and Scott (2009) imply an appropriate value of 60% loss due to degassing. An average Cu content of 71.4×10⁻⁶ (Binns and Scott,

1993; Kamenetsky et al., 2001; Moss et al., 2001; Sinton et al., 2003; Beaudoin et al., 2007; Park et al., 2010) and a density of 2.2 g/cm³ for magma beneath the PACMANUS hydrothermal field, combined with ~ 60% volatile loss, results in 0.236 Mt of Cu potentially transferred to the hydrothermal system per km³ magma.

We conclude that only a small amount (less than 1 wt%) of metal-rich magmatic fluid released through magmatic degassing would supply most base and precious metals forming an orebody if a magma chamber is larger than 10 km³. Magmatic degassing seems to play a more significant role than leaching (Fig. 3). The fate of the remaining Cu not transferred into the hydrothermal sulfide is not well known. Perhaps this Cu resides in Fe-Mn concretions, a Co-rich crust, or hydrothermal metallic sediments or is simply diffused into the seawater through the activity of the hydrothermal plume.

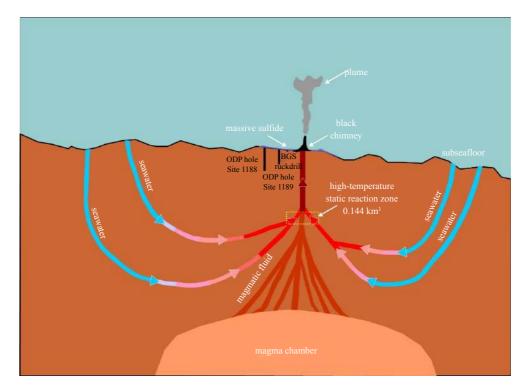


Fig. 3. A schematic of the Cu source for the PACMANUS hydrothermal system.

6 Conclusions

An estimated total budget of approximately 343 820 t of sulfides and sulfide-enriched chimneys on the seafloor of the PAC-MANUS hydrothermal field would contain 26 028.6 t of Cu. Numerical mass balance modeling indicates that a hydrothermal leaching model is inadequate to provide the Cu content of sulfides associated with the PACMANUS hydrothermal field. For instance, the total tonnage of Cu in the high-temperature static reaction zone (0.144 km³; Moss et al., 2001) is 22 619.5 t, which is insufficient to yield the amount of Cu in sulfides with 100% efficiency in leaching, transportation and precipitation. A mass balance model assuming 100% efficiency in leaching and precipitation necessitates hydrothermal leaching of 0.166 km3 of volcanic rocks to explain the Cu concentrations in the PACMANUS sulfides. The volume of volcanic rocks is increased to 8.29 km3 for more realistic leaching efficiency rates. The enrichment of magma in Cu, the possible transfer of magmatic Cu into the hydrothermal system, and the mass flux of Cu potentially degassed from a magmatic source in the eastern Manus Basin indicate that magmatic fluid through degassing contributes to the PAC-MANUS hydrothermal system and plays an important role in the hydrothermal Cu source.

Acknowledgements

We are very appreciative towards the anonymous reviewers for their valuable comments on the manuscript revision. We also thank Cushley David for language editing and Zhang Kaidi and Zhang Jie from the Institute of Oceanology, Chinese Academy of Sciences, for valuable advice during the revision.

References

- Ammonn M, Hauert R, Burtscher H, et al. 1993. Photoelectric charging of ultrafine volcanic aerosols: detection of Cu(I) as a tracer of chlorides in magmatic gases. Journal of Geophysical Research, 98(B1): 551–556, doi: 10.1029/92JB01870
- Auzende J M, Urabe T. 1996a. Cruise explores hydrothermal vents of

the Manus Basin. Eos, Transactions American Geophysical Union, 77: 244, doi: 10.1029/96EO00174

- Auzende J M, Urabe T. 1996b. Submersible observation of tectonic, magmatic and hydrothermal activity in the Manus Basin (Papua New Guinea). Eos, Transactions American Geophysical Union, 77: 115
- Ballhaus C, Ryan C G, Mernagh T P, et al. 1994. The partitioning of Fe, Ni, Cu, Pt, and Au between sulfide, metal, and fluid phases: a pilot study. Geochimica et Cosmochimica Acta, 58(2): 811–826, doi: 10.1016/0016-7037(94)90507-X
- Bartetzko A, Paulick H, Iturrino G, et al. 2003. Facies reconstruction of a hydrothermally altered dacite extrusive sequence: evidence from geophysical downhole logging data (ODP Leg 193). Geochemistry, Geophysics, Geosystems, 4(10): 1087
- Beaudoin Y, Scott S D. 2009. Pb in the PACMANUS sea-floor hydrothermal system, eastern Manus Basin: numerical modeling of a magmatic versus leached origin. Economic Geology, 104(5): 749-758, doi: 10.2113/gsecongeo.104.5.749
- Beaudoin Y, Scott S D, Gorton M P, et al. 2007. Effects of hydrothermal alteration on Pb in the active PACMANUS hydrothermal field, ODP Leg 193, Manus Basin, Papua New Guinea: a LA-ICP-MS study. Geochimica et Cosmochimica Acta, 71(17): 4256-4278, doi: 10.1016/j.gca.2007.06.034
- Becker K, Morin R H, Davis E E. 1994. Permeabilities in the Middle Valley hydrothermal system measured with packer and flowmeter experiments. In: Davis E E, Mottl M J, Fisher A T, et al., eds. Proceedings of the Ocean Drilling Program, Scientific Results, 139: 613-625
- Beier C, Bach W, Turner S, et al. 2015. Origin of silicic magmas at spreading centres: an example from the South East Rift, Manus Basin. Journal of Petrology, 56(2): 255–272, doi: 10.1093/petrology/egu077
- Binns R A. 2004. Eastern Manus basin, Papua New Guinea: guides for volcanogenic massive sulphide exploration from a modern seafloor analogue. CSIRO Explores, 2: 59–80
- Binns R A, Barriga F J A S, Miller D J. 2007. Leg 193 synthesis: Anatomy of an active felsic-hosted hydrothermal system, eastern Manus Basin, Papua New Guinea. In: Barriga F J A S, Binns R A, Miller D J, et al., eds. Proceedings of the Ocean Drilling Program, Scientific Results. College Station: TX (Ocean Drilling Program), 193: 1–71
- Binns R A, Scott S D. 1993. Actively forming polymetallic sulfide deposits associated with felsic volcanic rocks in the eastern Manus back-arc basin, Papua New Guinea. Economic Geology, 88(8): 2226–2236, doi: 10.2113/gsecongeo.88.8.2226
- Binns R A, Scott S D, Gemmell J B, et al. 1997. The Susu Knolls hydrothermal field, eastern Manus Basin, Papua New Guinea. Eos, Transactions American Geophysical Union, 78: 772
- Cathles L M. 1993. A capless 350°C flow zone model to explain megaplumes, salinity variations, and high-temperature veins in ridge axis hydrothermal systems. Economic Geology, 88(8): 1977–1988, doi: 10.2113/gsecongeo.88.8.1977
- Chen Zuxing, Zeng Zhigang, Wang Xiaoyuan, et al. 2018. U-Th/He dating and chemical compositions of apatite in the dacite from the southwestern Okinawa Trough: Implications for petrogenesis. Journal of Asian Earth Sciences, 161: 1–13, doi: 10.1016/j. jseaes.2018.04.032
- Deloule É, Paillat O, Pichavant M, et al. 1995. Ion microprobe determination of water in silicate glasses: methods and applications. Chemical Geology, 125(1-2): 19–28, doi: 10.1016/0009-2541(95)00070-3
- de Ronde C E J, Massoth G J, Butterfield D A, et al. 2011. Submarine hydrothermal activity and gold-rich mineralization at Brothers Volcano, Kermadec Arc, New Zealand. Mineralium Deposita, 46(5-6): 541-584, doi: 10.1007/s00126-011-0345-8
- de Ronde C E J, Walker S L, Ditchburn R G, et al. 2014. The anatomy of a buried submarine hydrothermal system, Clark volcano, Kermadec arc, New Zealand. Economic Geology, 109(8): 2261–2292, doi: 10.2113/econgeo.109.8.2261
- Douville E, Bienvenu P, Charlou J L, et al. 1999. Yttrium and rare earth elements in fluids from various deep-sea hydrothermal

systems. Geochimica et Cosmochimica Acta, 63(5): 627-643, doi: 10.1016/S0016-7037(99)00024-1

- Evans K A, Elburg M A, Kamenetsky V S. 2012. Oxidation state of subarc mantle. Geology, 40(9): 783–786, doi: 10.1130/G33037.1
- Fleet M E, Wu T W. 1993. Volatile transport of platinum-group elements in sulfide-chloride assemblages at 1000°C. Geochimica et Cosmochimica Acta, 57(15): 3519–3531, doi: 10.1016/0016-7037(93)90136-K
- Fouquet Y, Eissen JP, Ondréas H, et al. 1998. Extensive volcaniclastic deposits at the Mid-Atlantic Ridge axis: results of deep-water basaltic explosive volcanic activity?. Terra Nova, 10(5): 280–286, doi: 10.1046/j.1365-3121.1998.00204.x
- Gale A, Dalton C A, Langmuir C H, et al. 2013. The mean composition of ocean ridge basalts. Geochemistry, Geophysics, Geosystems, 14(3): 489–518, doi: 10.1029/2012GC004334
- Gemmell J B, Binns R A, Parr J M. 1996. Comparison of sulfur isotope values between modern back-arc and mid-ocean ridge seafloor hydrothermal systems. Eos, Transactions American Geophysical Union, 77: 117
- Gruen G, Weis P, Driesner T, et al. 2014. Hydrodynamic modeling of magmatic-hydrothermal activity at submarine arc volcanoes, with implications for ore formation. Earth and Planetary Science Letters, 404: 307–318, doi: 10.1016/j.epsl.2014.07.041
- Guo Kun, Zhai Shikui, Wang Xiaoyuan, et al. 2018. The dynamics of the southern Okinawa Trough magmatic system: New insights from the microanalysis of the An contents, trace element concentrations and Sr isotopic compositions of plagioclase hosted in basalts and silicic rocks. Chemical Geology, 497: 146–161, doi: 10.1016/j.chemgeo.2018.09.002
- Hannington M D, Jonasson I R, Herzig P M, et al. 1995. Physical and chemical processes of seafloor mineralization at mid-ocean ridges. In: Humphris S, Zierenberg R, Mullineaux L, et al., eds. Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions. Washington DC: AGU, 115–157
- Hannington M, Jamieson J, Monecke T, et al. 2010. Modern sea-floor massive sulfides and base metal resources: toward an estimate of global sea-floor massive sulfide potential. Society of Economic Geologists Special Publication, 15: 317–338
- Heinrich C A, Ryan C G, Mernagh T P, et al. 1992. Segregation of ore metals between magmatic brine and vapor: a fluid inclusion study using PIXE microanalysis. Economic Geology, 87(6): 1566–1583, doi: 10.2113/gsecongeo.87.6.1566
- Hekinian R, Pineau F, Shilobreeva S, et al. 2000. Deep sea explosive activity on the Mid-Altantic Ridge near 34°15′ N: Magma composition, vesicularity and volatile content. Journal of Volcanology and Geothermal Research, 98(1–4): 49–77, doi: 10.1016/S0377-0273(99)00190-0
- Herzig P M, Petersen S, Kuhn T, et al. 2003. Shallow drilling of seafloor hydrothermal systems using R/V Sonne and the BGS rockdrill, Conical Seamount (New Ireland fore-arc) and Pacmanus (eastern Manus Basin), Papua New Guinea. InterRidge News, 12: 22–26
- Hurwitz S, Navon O. 1994. Bubble nucleation in rhyolitic melts: Experiments at high pressure, temperature, and water content. Earth and Planetary Science Letters, 122(3-4): 267–285, doi: 10.1016/0012-821X(94)90001-9
- Ishibashi J, Wakita H, Okamura K, et al. 1996. Chemical characteristics of hydrothermal fluids from the Manus back-arc basin, Papua New Guinea. Eos, Transactions American Geophysical Union, 77: 116
- Jankowski P, Lipton I, Blackburn J. 2011. Nautilus Minerals Incorporated NI43-101 Technical Report 2010 PNG, Tonga, Fiji, Solomon Islands, New Zealand, Vanuatu and the ISA. Australia: SRK Consulting Pty Ltd., 1–201
- Jenner F E, O'Neill H S C, Arculus R J, et al. 2010. The magnetite crisis in the evolution of arc-related magmas and the initial concentration of Au, Ag and Cu. Journal of Petrology, 51(12): 2445-2464, doi: 10.1093/petrology/egq063
- Jugo P J, Wilke M, Botcharnikov R E. 2010. Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: implications for S speciation and S content as function of oxygen fugacity.

68

Geochimica et Cosmochimica Acta, 74(20): 5926–5938, doi: 10.1016/j.gca.2010.07.022

- Kamenetsky V S, Binns R A, Gemmell J B, et al. 2001. Parental basaltic melts and fluids in eastern Manus backarc basin: Implications for hydrothermal mineralisation. Earth and Planetary Science Letters, 184(3-4): 685-702, doi: 10.1016/S0012-821X(00)00352-6
- Kelley K A, Cottrell E. 2012. The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma. Earth and Planetary Science Letters, 329–330: 109–121, doi: 10.1016/j. epsl.2012.02.010
- Lalou C, Brichet E, Hekinian R. 1985. Age dating of sulfide deposits from axial and off axial structures on the East Pacific Rise near 12°50' N. Earth and Planetary Science Letters, 75(1): 59–71, doi: 10.1016/0012-821X(85)90050-0
- Lalou C, Reyss J L, Brichet E, et al. 1993. New age data for Mid-Atlantic ridge hydrothermal sites: TAG and Snakepit chronology revisited. Journal of Geophysical Research, 98(B6): 9705–9713, doi: 10.1029/92JB01898
- Landtwing M R, Furrer C, Redmond P B, et al. 2010. The Bingham canyon porphyry Cu-Mo-Au deposit. III. Zoned copper-gold ore deposition by magmatic vapor expansion. Economic Geology, 105(1): 91–118, doi: 10.2113/gsecongeo.105.1.91
- Lee S M, Ruellan E. 2006. Tectonic and magmatic evolution of the Bismarck Sea, Papua New Guinea: review and new synthesis. In: Christie D M, Fisher C R, Lee S M, et al., eds. Back-Arc Spreading Systems: Geological, Biological, Chemical, and Physical Interactions. Washington DC: American Geophysical Union, 166: 263–286
- Li Zhenggang, Chu Fengyou, Dong Yanhui, et al. 2016. Origin of selective enrichment of Cu and Au in sulfide deposits formed at immature back-arc ridges: Examples from the Lau and Manus basins. Ore Geology Reviews, 74: 52–62, doi: 10.1016/j.oregeorev.2015.11.010
- Li Xiaohui, Zeng Zhigang, Yang Huixin, et al. 2019. Geochemistry of silicate melt inclusions in middle and southern Okinawa Trough rocks: Implications for petrogenesis and variable subducted sediment component injection. Geological Journal, 54(3): 1160-1189, doi: 10.1002/gj.v54.3
- Lipton I. 2008. Mineral resource estimate, Solwara 1 project, Bismarck Sea, Papua New Guinea. Technical Report NI43-101. Toronto: Nautilus Minerals Inc.
- Lowell R R, Rona P A, von Herzen R P. 1995. Seafloor hydrothermal systems. Journal of Geophysical Research, 100(B1): 327–352, doi: 10.1029/94JB02222
- Lowenstern J B. 1993. Evidence for a copper-bearing fluid in magma erupted at the Valley of ten thousand smokes, Alaska. Contributions to Mineralogy and Petrology, 114(3): 409–421, doi: 10.1007/BF01046542
- Lowenstern J B. 1995. Application of silicate-melt inclusions to the study of magmatic volatiles. In: Thompson J F H, ed. Magmas, Fluids, and Ore Deposits. Canada: Mineralogical Society of Canada, 71-99
- Lowenstern J B, Mahood G A, Rivers M L, et al. 1991. Evidence for extreme partitioning of copper into a magmatic vapor phase. Science, 252(5011): 1405–1409, doi: 10.1126/science.252.5011.1405
- Martinez F, Taylor B. 1996. Backarc spreading, rifting, and microplate rotation, between transform faults in the Manus Basin. Marine Geophysical Researches, 18(2-4): 203-224, doi: 10.1007/BF00286078
- Martinez F, Taylor B. 2003. Controls on back-arc crustal accretion: insights from the Lau, Manus and Mariana basins. In: Larter R D, Leat P T, eds. Intra-Oceanic Subduction Systems: Tectonic and Magmatic Processes. Geological Society, London, Special Publications, 219: 19–54
- Moss R, Scott S D, Binns R A. 1997. Concentrations of gold and other ore metals in volcanics hosting the Pacmanus seafloor sulfide deposit. JAMSTEC Journal of Deep Sea Research, 13: 257–267
- Moss R, Scott S D, Binns R A. 2001. Gold content of eastern Manus Basin volcanic rocks: implications for enrichment in associated hydrothermal precipitates. Economic Geology, 96(1): 91–107

- Mühe R, Peücker-Ehrenbrink B, Devey C W, et al. 1997. On the redistribution of Pb in the oceanic crust during hydrothermal alteration. Chemical Geology, 137(1-2): 67–77, doi: 10.1016/S0009-2541(96)00151-9
- Park S H, Lee S M, Kamenov G D, et al. 2010. Tracing the origin of subduction components beneath the South East Rift in the Manus Basin, Papua New Guinea. Chemical Geology, 269(3–4): 339–349, doi: 10.1016/j.chemgeo.2009.10.008
- Parr J, Yeats C, Binns R. 2003. Petrology, trace element geochemistry and isotope geochemistry of sulfides and oxides from the PAC-MANUS hydrothermal field, eastern Manus Basin, Papua New Guinea. In: Yeats C, ed. Seabed Hydrothermal Systems of the Western Pacific: Current Research and New Directions. CSIRO Exploration and Mining Report 1112, 58-64
- Patten C, Barnes S J, Mathez E A, et al. 2013. Partition coefficients of chalcophile elements between sulfide and silicate melts and the early crystallization history of sulfide liquid: LA-ICP-MS analysis of MORB sulfide droplets. Chemical Geology, 358: 170–188, doi: 10.1016/j.chemgeo.2013.08.040
- Paulick H, Vanko D A, Yeats C J. 2004. Drill core-based facies reconstruction of a deep-marine felsic volcano hosting an active hydrothermal system (Pual Ridge, Papau New Guinea, ODP Leg 193). Journal of Volcanology and Geothermal Research, 130(1–2): 31–50, doi: 10.1016/S0377-0273(03)00275-0
- Petersen S, Herzig P M, Hannington M D, et al. 2003. Gold-rich massive sulfides from the interior of the felsic-hosted PAC-MANUS massive sulfide deposit, eastern Manus Basin (PNG).
 In: Eliopoulos D G, et al., eds. Mineral Exploration and Sustainable Development. Rotterdam: Millpress, 171–174
- Resmini R G, Marsh B D. 1995. Steady-state volcanism, paleoeffusion rates, and magma system volume inferred from plagioclase crystal size distributions in mafic lavas: Dome Mountain, Nevada. Journal of Volcanology and Geothermal Research, 68(4): 273–296, doi: 10.1016/0377-0273(95)00003-5
- Richards J P. 2011. Magmatic to hydrothermal metal fluxes in convergent and collided margins. Ore Geology Reviews, 40(1): 1–26, doi: 10.1016/j.oregeorev.2011.05.006
- Rubin K. 1997. Degassing of metals and metalloids from erupting seamount and mid-ocean ridge volcanoes: observations and predictions. Geochimica et Cosmochimica Acta, 61(17): 3525–3542, doi: 10.1016/S0016-7037(97)00179-8
- Scott S D. 1997. Submarine hydrothermal systems and deposits. In: Barnes H L, ed. Geochemistry of Hydrothermal Ore Deposits. New York: Wiley
- Scott S D, Binns R A. 1992. The PACMANUS deposit; actively forming submarine polymetallic sulfides in felsic volcanic rocks of Manus Basin, Papua New Guinea. International Geological Congress, 29: 754
- Scott S D, Binns R A. 1995. Hydrothermal processes and contrasting styles of mineralization in the western Woodlark and eastern Manus Basins of the western Pacific. Geological Society, London, Special Publication, 87(1): 191–205, doi: 10.1144/GSL.SP.1995. 087.01.16
- Seewald J S, Seyfried W E Jr. 1990. The effect of temperature on metal mobility in subseafloor hydrothermal systems: constraints from basalt alteration experiments. Earth and Planetary Science Letters, 101(2-4): 388-403, doi: 10.1016/0012-821X(90)90168-W
- Sinton J M, Ford L L, Chappell B, et al. 2003. Magma genesis and mantle heterogeneity in the Manus back-arc basin, Papua New Guinea. Journal of Petrology, 44(1): 159–195, doi: 10.1093/petrology/44.1.159
- Stanton R L. 1991. Understanding volcanic massive sulfides: past, present, and future. In: Hutchinson R W, Grauch R I, eds. Historical Perspectives of Genetic Concepts and Case Histories of Famous Discoveries. Society of Economic Geologists, 8: 82–95
- Stanton R L. 1994. Ore Elements in Arc Lavas. Oxford: Clarendon Press
- Sun Weidong, Huang Ruifang, Li He, et al. 2015. Porphyry deposits and oxidized magmas. Ore Geology Reviews, 65: 97–131, doi: 10.1016/j.oregeorev.2014.09.004
- Symonds R B, Reed M H, Rose W I. 1992. Origin, speciation, and

fluxes of trace-element gases at Augustine volcano, Alaska: Insights into magma degassing and fumarolic processes. Geochimica et Cosmochimica Acta, 56(2): 633–657, doi: 10.1016/0016-7037(92)90087-Y

- Symonds R B, Rose W I, Reed M H, et al. 1987. Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia. Geochimica et Cosmochimica Acta, 51(8): 2083–2101, doi: 10.1016/0016-7037(87)90258-4
- Taylor B. 1979. Bismarck Sea: Evolution of a back-arc basin. Geology, 7(4): 171–174, doi: 10.1130/0091-7613(1979)7<171:BSEOAB> 2.0.CO;2
- Taylor H P Jr. 1997. Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In: Barnes H L, ed. Geochemistry of Hydrothermal Ore Deposits. 3rd ed. New York: John Wiley & Sons, 229-302
- Thal J, Tivey M, Yoerger D, et al. 2014. Geologic setting of PAC-MANUS hydrothermal area-high resolution mapping and in situ observations. Marine Geology, 355: 98–114, doi: 10.1016/j. margeo.2014.05.011
- Yang Kaihui, Scott S D. 1996. Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. Nature, 383(6599): 420-423, doi: 10.1038/383420a0

- Yang Kaihui, Scott S D. 2002. Magmatic degassing of volatiles and ore metals into a hydrothermal system on the modern sea floor of the eastern Manus back-arc basin, western Pacific. Economic Geology, 97(5): 1079–1100, doi: 10.2113/gsecongeo.97.5.1079
- Yang Kaihui, Scott S D. 2005. Vigorous exsolution of volatiles in the magma chamber beneath a hydrothermal system on the modern sea floor of the eastern Manus back-arc basin, western Pacific: evidence from melt inclusions. Economic Geology, 100(6): 1085–1096, doi: 10.2113/gsecongeo.100.6.1085
- Yang Kaihui, Scott S D. 2006. Magmatic fluids as a source of metals in seafloor hydrothermal systems. In: Christie D M, Fischer C R, Lee S M, et al., eds. Back-Arc Spreading Systems: Geological, Biological, Chemical, and Physical Interactions. New York: American Geophysical Union, 166: 163–184
- Yeats C J, Parr J M, Binns R A, et al. 2014. The SuSu Knolls hydrothermal field, eastern Manus Basin, Papua New Guinea: an Active submarine high-sulfidation copper-gold system. Economic Geology, 109(8): 2207–2226, doi: 10.2113/econgeo.109.8.2207
- Zajacz Z, Halter W. 2009. Copper transport by high temperature, sulfur-rich magmatic vapor: evidence from silicate melt and vapor inclusions in a basaltic andesite from the Villarrica volcano (Chile). Earth and Planetary Science Letters, 282(1-4): 115–121, doi: 10.1016/j.epsl.2009.03.006