Arsenic and Antimony in Hydrothermal Plumes from the Eastern Manus Basin, Papua New Guinea

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Received 27 December 2017; Accepted 18 February 2018; Published 15 April 2018

Academic Editor: Franco Tassi

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Studies on the concentrations of arsenic (As) and antimony (Sb) in seawater columns are very important for tracing hydrothermal plumes and understanding fluid characteristics of seafloor hydrothermal systems. The total As, Sb, Mn, and Cl$^-\$ concentrations of three hydrothermal plume seawater column samples have been studied at Stations 18G, 18K, and 18B in the eastern Manus back-arc basin, Bismarck Sea, Papua New Guinea. At Stations 18G and 18K, the plumes above North Su and near the Suzette site in the SuSu Knolls hydrothermal field are both enriched in As, Sb, and Mn and depleted in Cl$^-$, as a result of contribution of As-Sb-Mn-enriched and Cl-depleted vent fluid outputs to the hydrothermal plume, which is most likely generated in the subseafloor by fluid-rock interaction, magma degassing, or phase separation (boiling of hydrothermal fluid). The plume at Station 18B is enriched in As, Sb, Mn, and Cl, suggesting that As-Sb-Mn-Cl-enriched fluid discharges from vents, which have been generated by fluid-rock interaction. The concentrations of As and Sb anomalous layers, like manganese (Mn), are higher than those of the other layers in the three hydrothermal plume seawater columns. As and Sb with Mn showed a positive correlation ($R^2 > 0.8$, $p < 0.05$), and the distributions of As and Sb within the hydrothermal plume are not controlled by particle adsorption or biogeochemical cycles, suggesting that As and Sb, like Mn, can be used to detect and describe the characteristics of hydrothermal plumes in seawater environment. In addition, anomalous layer with As/Sb ratio lower than those of ambient seawater at the same temperature is found in the eastern Manus basin, suggesting that the As/Sb ratio may also act as an effective tracer reflecting the effect of hydrothermal activity on As and Sb in the seawater column.

1. Introduction

Hydrothermal plumes are potent tools for locating, characterizing, and quantifying seafloor hydrothermal discharge. A hydrothermal plume rises into the overlying seawater column until reaching a neutrally buoyant layer, at which point the buoyant driving force vanishes and the neutrally buoyant plume spreads laterally extending for many kilometers [1]. The physical and chemical characteristics of plumes are different from ambient seawater, thereby offering us an effective way for tracing their sources and distribution. Identifying hydrothermal plumes has mainly relied on a combination of temperature anomaly (e.g., [2–7]), turbidity or light transmission (e.g., [3, 5, 8–11]), and chemical anomalies of species such as iron (Fe), manganese (Mn), helium (He), and methane (CH$_4$) (e.g., [6, 12–19]).

Since 1990, studies on hydrothermal plumes in the eastern Manus back-arc basin have been carried out. For example, during the 21st cruise of Research Vessel (R/V) Akademik Mstislav Keldysh in April–June 1990, all seawater columns studied in the Manus basin showed turbidity anomalies (up to 1880 nephels, at 1600 m below sea level (BSL)), as well as anomalies in dissolved Mn (up to 44.8 nM, at 1975 m BSL) and in biogeochemical parameters (CO$_2$-assimilation up to 0.07 mM-day$^{-1}$, at 1950 m BSL; CH$_4$-oxidation up to 3.30 nM-day$^{-1}$, at 2150 m BSL) [14]. Later, in November–December 1990, large scale triple-layered buoyant plumes were revealed from seawater column anomalies of CH$_4$ (up
to 5.98 nM, at 1091 m BSL), Mn (up to 100 nM, at 1732 m BSL), Al (up to 1501 nM, at 1683 m BSL), and pH (up to 7.55, at 1700 m BSL) in the eastern Manus basin during KH-90-3 (AQUARIUS) expedition [12]. In 1993, the first indications of hydrothermal activity ~5 km NW of North Su (near Station 18G) were obtained, which showed a 0.7% transmissometer anomaly (% reduction in light transmission relative to background) at around 1450 m depth [11]. During the 1996 PACMANUS III expedition, the SuSu Knolls hydrothermal field was discovered by means of multiple real-time CTD (conductivity, temperature, depth) and transmissometry plume detection, leading to the mapping of two plume levels [22], and the depth range (1260–1460 m BSL) of the 1996 lower plume emanating [21] is different from that (1300–1600 m BSL) reported by McDonald et al. [11]. Further, during the 1997 PACMANUS IV cruise, the lower plume had disappeared and the upper plume had become more sharply cut off to the north and west, and samples from the plume peak showed transmissometer anomalies of up to 40% and temperatures of 0.05 °C above the ambient levels at 1050–1150 m BSL [11].

Arsenic (As)—though often present in significant amounts in hydrothermal phases (e.g., As₂O₃, AsO, AsS, AsCl₃, and As(OH)₃) throughout the fluid evolution (e.g., [23–25])—has been rarely investigated in seafloor hydrothermal system [26]. At higher temperatures (>400 °C), arsenic enrichment factors in the gas phase with respect to the magma phase are 100 to 1000, suggesting an important transfer of As into the hydrosphere during magma degassing [27]. Moreover, antimony (Sb) is easily mobilized by high-temperature hydrothermal fluids [28].

In back-arc basin, As and Sb contents in vent fluids (Vai Lili fluid in the Lau Basin and PACMANUS fluid in the Manus basin; [29]) associated with seawater-acidic rock interaction and/or magma degassing were high, about 10- to 100-fold higher than the values measured in midocean ridge fluids (fluid from the East Pacific Rise near 13° N and Lucky Strike fluid from the Mid-Atlantic Ridge; [29]), suggesting that these As and Sb contents are mostly controlled by the phase separation process of hydrothermal fluid, which is believed to be the primary mechanism causing large variations in the chlorinity of deep-sea hydrothermal fluids [30, 31], while some studies have shown that the concentration of Sb in the ocean is very low, with concentration of the order 1.64 nM [32], suggesting that Sb anomalies of the seawater column can be used to identify hydrothermal plumes.

However, there are no reports on the distribution of As and Sb anomalies in hydrothermal plume water column from the eastern Manus back-arc basin. In this study, As, Sb, Mn, and chloride (Cl⁻) concentrations have been measured, in the hydrothermal plume water column samples from the eastern Manus basin. We describe the concentration patterns of As, Sb, Mn, and Cl in hydrothermal plumes, characterize the correlations between As, Sb, Mn, and Cl, attempt to reveal the influencing factors on these elements, and attempt to understand the origin of hydrothermal plume in the eastern Manus basin.

2. Geological Setting

In the eastern Manus back-arc basin, extension is occurring within a remnant Eocene-Oligocene island-arc crust [33], spreading at <2 cm/year [34]. A series of en echelon volcanic ridges, 20 to 30 km long, <5 km wide, and 500–700 m high, occupies the zone of extension between the Djaul and Weitlin transform faults [34]. Moreover, this area has a variable basement composition, and lavas erupted along the ridges include the complete series from basalt to rhylolite [35–37].

There are four main hydrothermal fields: the PACMANUS field, DESMOS caldera (23 km east of PACMANUS), SuSu Knolls field (40 km east of PACMANUS), and Solwara 12 (3.7087°S, 151.8833°E, near Station 18B) [22, 35, 38–40] (Figure 1).

The PACMANUS field located on the Paul ridge is notable for its distinctly siliceous volcanic host rock (dacite and rhyodacite) [41–43] (Figure 1), and there are various sulfides and Fe-Si-Mn oxyhydroxides in this field (e.g., [35, 44]). Four high-temperature sites called Rogers Ruins, Roman Ruins, Satanic Mills, and Tsukushi and a low-temperature (6 °C) site called Snowcap were identified in this field [42, 45].

Ocean Drilling Program (ODP) Leg 193 investigated the PACMANUS field, finding that the highest vent temperature measurement at gray smokers was 280 °C [41] and that the salinities of the fluids are variable which indicates that phase separation (boiling of hydrothermal fluid) is occurring below the surface [33]. Moreover, the geochemical characteristics of PACMANUS fluids, such as negative δD_H2O values and δ³⁴S_H2S values, low pH (at 25 °C) values, high fluorine (F) concentration, and high CO₂ content, reflect the magmatic fluid input hydrothermal fluids [46]. In addition, the ⁸⁷Sr/⁸⁶Sr and δ³⁴S signatures of anhydrite recovered at Roman Ruins and Snowcap are very different, suggesting the PACMANUS system experiences a complex interplay between hydrothermal fluid, magmatic fluid, and seawater.

SuSu Knolls field is in the most eastern part of the eastern Manus basin (Figure 1), extending for approximately 4 km in a north-northwest to south-southeast direction [21, 47], and is characterized by porphyritic dacitic volcanics forming three prominent, moderately sedimented, steep sided conical peaks informally known as North Su, South Su, and Suzette [48]. At North Su, fluid boiling at the seafloor is evident, and the majority of fluids exhibit salinities lower or higher than seawater, consistent with phase separation of hydrothermal fluids below the seafloor [37].

DESMOS caldera, hosted by basaltic andesite [49] and located on the southeast ridge in the eastern Manus basin (Figure 1), emitted white-smoker fluids rich in sulfate with temperatures of 88 °C and 120 °C [38]. Like the North Su fluid, abundant CO₂ and excess F in the DESMOS fluid indicate magma degassing [37], and the basaltic andesite from the DESMOS caldera is altered by the interaction with hot acidic hydrothermal fluid (up to 340 °C) originating from the mixing of magmatic fluid and seawater [50].

Solwara 12 is located 25 km WNW of Solwara 1 (Suzette), on the SE edge of the DESMOS caldera on a distinctive knoll at around 1850 m to 1900 m BSL (Figure 1), and was discovered by Nautilus during the Fugro Solstice Target Generation
and Target Testing program in 2009 [40]. Moreover, there is extensive sediment cover in the Solwara 12, the mapped chimney field is around 200 m across and includes clusters of old sulfide deposit, and outcropping chimneys are large up to 10 m high [40]. In addition, it is known that the hydrothermal vent fluids at the seafloor in the eastern Manus basin have high As (up to 18500 nM) and Sb (up to 188 nM) concentrations [29].

3. Sampling and Analytical Methods

3.1. Sample Collection. During the KX08-973 cruise of R/V KEXUE YHAI in 2008, seawater column samples and temperature, salinity, and density data were collected at 3 hydrocast stations (18B 3.6827° S, 151.8636° E; 18G 3.7991° S, 152.1005° E; and 18K 3.7884° S, 152.1066° E) in the eastern Manus basin (Figure 1). At each station, seawater and hydrothermal plume samples were collected at different depths with a conductivity, temperature, and depth (CTD) aluminum rosette (Seabird) containing 24 10 L Niskin bottles. These stations were operated as on-line measurements with a Seabird 911 CTD coupled to a Carousel water sampler SBE 32. A total of 33 hydrothermal plume water samples were taken from different depths with a CTD rosette of 11 “Niskin” bottles. To ensure the highest possible purity of the samples, the Niskin bottles were cleaned thoroughly using 1% v/v HNO₃ solution and Milli-Q water before usage.

In general, hydrothermal plumes can rise tens to hundreds of meters to a level of neutral buoyancy. Therefore, seawater samples collected at water depths shallower than 1000 m were considered normal seawater. Upon recovery of the Niskin bottles, 30 cm long Teflon tubes were inserted through the outlet at the bottom of the Niskin bottles, and the first 200 ml of the liquid was discarded. The remaining aqueous samples were collected in 5 L precleaned HDPE bottles (the precleaning method is described in detail in Sampling and Sample-Handling Protocols for GEOTRACES Cruises).

The probes were obtained from the manufacturers and calibrated by the National Center of Ocean Standards and Metrology (NCOSM) in July 2007. The measurement accuracies were ±0.001°C for temperature, ±0.0003 S/m for conductivity, and ±0.015% of full-scale range for pressure, respectively.

Temperature anomaly (ΔT) of the plume relative to ambient seawater was calculated using the formula proposed by Baker and Lupton [2], which is suitable for the Pacific, and the potential density and potential temperature data required for the formula were also obtained using the CTD. Further, because the entrainment of seawater, which had been considered in the calculation of the potential temperature anomaly of the horizontally spreading fluid at the equilibrium height [51], and the calculation of the penetration height of the hydrothermal plume [52], was not considered in this
study, the calculated temperature anomaly value is lower than the actual value, but the trend with depth is significant. It is noteworthy that hydrothermal fluid samples could not be obtained due to the lack of sampling equipment during this cruise. However, we believe that the fluid data in the literature are reliable, and the hydrothermal activity in our survey field is steady [53].

3.2. Analytical Methods. A 250 ml aliquot of unfiltered seawater was transferred into a precleaned Naglen polypropylene bottle for measuring pH. In the ship laboratory, the pH of each aqueous sample was determined with a portable pH meter (JENCO 6010, resolution 0.01, automatic temperature compensation) immediately after collection at room temperature (approximately 25°C). The pH meter was calibrated with buffer solutions of pH 4.00 (potassium hydrogen phthalate (KHP) 0.1 M) and 6.86 (mixed phosphate 0.025 mol L⁻¹). The aqueous samples were filtered through 47 mm Merck Millipore 0.10 μm nitrocellulose membrane into 1L Naglen polypropylene bottles (previously soaked in 1:1 HNO₃ for 48 h, washed to neutral pH with deionized water and ultra-pure water) within the ship laboratory immediately after collection from the Niskin bottles. Filtered water samples were acidified to pH 1.8 using 2 M ultrapure HNO₃ (J. T. Baker), capped tightly, and resealed with Parafilm Sealing membrane.

The determination of total As and Sb concentrations was conducted at Qingdao Institute of Marine Geology, China Geological Survey Bureau. Following the analysis method in the national standards GB 17378.4-2007 and GB/T 5750.6-2006 of China, As and Sb were reduced to arsenic hydride in the Niskin bottles. The vertical column shows two distinct layers of temperature anomaly: the maximum temperature anomaly of the shallow layer (1070–1250 m BSL) is 0.056°C, occurring at 1126 m BSL, and the maximum occurrence at 1492 m BSL (Figure 2(b)). The shallower layer in the hydrothermal plume water column is thicker, and the depth of the peak of the deeper layer is identical to the transmissometer anomaly peak of the plume detected in 1993 (~1450 m) [11]. We are dealing with the lower plume, not the upper plume, because the upper plume water was not sampled at Station 18G. The profile of Mn concentration parallels that of the lower temperature anomaly at Station 18G, where the Mn concentration increases continuously from ~1300 m BSL to 1492 m BSL (Figure 2(b)), with the maximum occurring at 1492 m BSL and reaching 36.3 nM (Mn is about 4 times the ambient seawater value (9.3 nM), Table 1). Further, As and Sb in the lower anomaly layer (at 1492 m BSL) are also slightly enriched (As and Sb are enriched by ~12% and ~24%, resp., relative to ambient seawater) and depleted in Cl relative to ambient seawater at Station 18G (Table 1, Figure 3).

At Station 18K (lying 1.3 km to the east of Solwara 1, which is the name now used for the chimney field on the Suzette volcanic edifice), the vertical column also reveals two distinct anomalous temperature: the upper layer is at a depth of 1050–1300 m in which the maximum temperature anomaly is 0.041°C above ambient seawater, and the lower layer is at a depth of 1400–1550 m (ΔTmax is 0.042°C, at 1450 m BSL). The two anomalous layers are both deeper than those of the particulate plume discovered during the 1996 PACMANUS III marine expedition (1060–1140 m, 1260–1460 m) [12]; however, the depth of the maximum temperature anomaly of the deeper layer is identical to that of the transmissometer anomaly of the plume in 1993 above North Su (~1450 m) [11]. Furthermore, we are only concerned with the lower plume, because the upper plume was also not sampled at Station 18K. Here, the maximum concentration of Mn (110.8 nM) occurs at 1500 m BSL (Mn is about 10 times the ambient seawater value (14.8 nM)) and is also in the same layer as the maximum temperature anomaly (Figure 2(c)). Further, at Station 18K, the maximum anomalies of As and Sb also occur at 1500 m (Figure 3), where As and Sb are all significantly enriched (As and Sb are enriched by ~32% and ~46%, resp., relative to ambient seawater) (Table 1, Figure 3).

In addition, the water depth at Stations 18G and 18K is shallower than that at Station 18B (1400–1700 m), and the As and Sb concentrations in seawater were ~19 nM and ~2 nM, respectively. The variation in As at Station 18K is larger than that at Station 18G (Table 1, Figure 3(a)). At Station 18K, the maximum concentration of As (26.9 nM) is at 1500 m, but at Station 18G the concentration of As increases with depth similar to that of the temperature anomaly, and the maximum (79.3 nM) occurs at 1641 m BSL (Figure 2(a)). Further, at Station 18B, As, Sb, and Cl in the seawater profile are enriched relative to ambient seawater, and the maximum concentrations occur at 1641 m BSL, which is consistent with the Mn and temperature anomalies in the hydrothermal plume water column (Table 1, Figure 3).
Table 1: Concentrations of Mn, As, Sb, and Cl of the hydrothermal plume water columns in eastern Manus basin.

<table>
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<th>As (nM)</th>
<th>Sb (nM)</th>
<th>Cl (mM)</th>
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<td>61.3 ± 3.3</td>
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Note. The water sample is not filtered before acidification, so the As values in this table are the total dissolved concentration.
from 1400 m to 1600 m. The variation of Sb concentration in the seawater profile at these two stations is similar, with both reaching a maximum at depths of ~1500 m (Figure 3(b)).

5. Discussion

5.1 Anomalous Layers of Hydrothermal Plume Water Columns. At Station 18B, As, Sb, Mn, and Cl in the water column are significantly enriched (at 1641 m BSL, Mn is about 8 times the ambient seawater value (9.3 nM, Mn data from the minimum Mn content in the three water column samples), while As, Sb, and Cl are enriched by ~31%, ~47%, and ~4%, respectively, relative to ambient seawater (As (18.4 nM), Sb (2.33 nM), and Cl (546 mM) data from the respective As, Sb, and Cl content in the three water column samples)), suggesting that the As, Sb, and Cl anomalies in the water column is consistent with the Mn and temperature anomalies (see Figures 2 and 3). This is mainly caused by the input of hydrothermal fluid produced by fluid-rock (mainly andesite and dacite) interaction which can generate high contents of As, Sb, Mn, and Cl [29, 54]. Furthermore, Station 18B is located 1.8 km north-northwest of the DESMOS caldera rim, far away from the PACMANUS hydrothermal field and the Sb contents in the DESMOS fluid (Sb, <3.0 nM, [29]) are lower than those in the anomaly layer at Station 18B, suggesting that the chemical anomaly is not the result of hydrothermal plume drift from the DESMOS caldera (see Figure 1).

At Station 18G from the SuSu Knolls hydrothermal field, in the anomaly layer (60 m above the seafloor), Cl is slightly depleted relative to ambient seawater (lower than the
background seawater by 546 mM), while Mn, As, and Sb are slightly enriched (Mn is about 3 times the background seawater value, As and Sb are enriched by ~14% and ~31%, resp., relative to ambient seawater), reflecting the contribution of Mn-As-Sb-enriched, Cl-depleted fluid to the hydrothermal plume.

Discharge of Cl-depleted fluid to the SuSu Knolls hydrothermal field has been reported during the investigation of the plume in 1997 [11]. The plume may be related to the vapors produced by magma degassing and/or phase separation and emanation of the condensed vapor phase. Abundant CO₂ and excess fluorine in the North Su fluid are the indicators of magma degassing [37], and magma degassing [27, 38] may generate Cl-depleted and As-enriched magmatic fluid relative to ambient seawater. At North Su in the SuSu Knolls hydrothermal field, phase separation, with emanations rich in H₂S, very low in Cl in hydrothermal fluid, has taken place under the seafloor [37], generating Cl-depleted and slightly As-enriched (in the form of As(OH)₃) vapors [27, 29]. The enrichment of Sb may also be related to the above two processes, since Sb, OH⁻, and Cl⁻ components will partition into the vapor phase during boiling and vapor-brine separation processes occurring in magmatic-hydrothermal systems [28]. Furthermore, the enrichment of Sb would be more strongly controlled by fluid-rock interaction [29]. The enrichment of Mn is controlled more strongly by seawater-rock interaction, because it cannot form volatile species in the same way as those of As and Sb, which are controlled by magma degassing and phase separation of hydrothermal fluid under acidic hydrothermal conditions, all suggesting that the Mn-As-Sb-enriched, Cl-depleted fluid was most likely generated in the subsurface by mixing of different fluids that may be products of fluid-rock interaction, magma degassing, or phase separation (subcritical boiling). In addition, the lower plume at Station 18G may also be derived from South Su, according to the particulate plume investigation during the 1996 PACMANUS III and 1997 PACMANUS IV expeditions [21].

At Station 18K, the maximum anomalies of As, Sb, Mn, and Cl occur at about 70 m above the seafloor (Figures 2 and 3), where Cl is depleted relative to ambient seawater (lower than background seawater by 546 mM) while As, Sb, and Mn are all enriched significantly (As and Sb are enriched by ~46% and ~84%, resp., relative to background seawater; Mn is about 10 times the background seawater value). Like Station 18G, the depletion of Cl is an indication of Cl-depleted fluid input, which may be related to magmatic fluid (like DESMOS fluid; [38]) and vapors produced by subsurface boiling and phase separation of hydrothermal fluid with a lower Cl concentration than in seawater (similar to the Lucky Strike and EPR 17–19’S fluids; [55]). The Cl-depleted and gas-enriched fluids affected by subsurface boiling and phase separation of hydrothermal fluid exhibited relatively high As concentrations, consistent with the volatile character of H₂AsO₃ (aq) which is the dominating As species under these hydrothermal conditions [29], also indicating that the As-enriched and Cl-depleted fluid in the eastern Manus basin may be related to phase separation (enriched in vapor-derived low-chlorinity fluid) below the seafloor. The distinct enrichment of Mn is mainly due to seawater-rock interaction under the seafloor, and the enrichment of As and Sb may be linked to all of the above three processes: seawater-rock interaction, magma degassing, and boiling and phase separation of hydrothermal fluid (took place under subcritical conditions).

Moreover, there are two temperature anomalous layers in both casts at Stations 18G and 18K (Figures 2(b) and 2(c)), suggesting that the two distinct buoyant plumes are separated by seawater at ambient temperature (e.g., [40]). Compared to midocean ridge plumes, hydrothermal plumes in the eastern Manus basin are influenced by variable current directions and topography (e.g., [40]). Further, depending on the exact site within SuSu Knolls, the lower plume can include contributions from Solwara 1 (on Suzette), the crest of South Su (active black smokers), and small active sites (including Solwara 9) on the western flanks of North Su and South Su, hence influencing depth range of the lower plume (see Figure 1; Lipton, 2008 [40]). It is possible that the hydrothermal plumes can change with time as well as distance from source and deep currents which can swing through 180 degrees at SuSu Knolls [40].

At Stations 18G and 18K, the lower plume is also enriched in both As and Sb relative to ambient seawater, and the maximum anomaly layers are also close to the Mn and temperature anomaly maxima, at 1492 m BSL and 1500 m BSL, respectively (Table 1; Figures 3(a) and 3(b)). These results are clearly suggestive of simple dilution as a plume advection or of profiles made in different types of water (e.g., plume center and edge) of the same plume (e.g., [51]). The magnitude of the Sb anomaly at Station 18K was less than that at Station 18G, implying the Sb content possibly because the fluid at Station 18G leached considerable quantities of Sb from the upper dacite.

In the SuSu Knolls hydrothermal field, the vapors generated during magma degassing and boiling and phase separation of hydrothermal fluid are both rich in As and depleted in Cl⁻, and interactions between fluid and volcanic rock below the seafloor can produce high contents of As, Sb, and Cl⁻ in the fluid; however, the extent of enrichment of Cl⁻ during this process is less than that of the depletion of Cl⁻ in magmatic fluid and vapors generated during boiling and phase separation of hydrothermal fluid, which results in the formation of As-enriched and Cl-depleted fluid, thus the As-enriched and Cl-depleted fluid causing the anomaly in the seawater profile at Stations 18G and 18K may be a product of the influx of magmatic gases [37, 38, 56]. Because Sb is not easily enriched in the vapor phase and whether or not it can be enriched in the magmatic fluid is not known, we cannot confirm that the observation of higher Sb in the hydrothermal fluid than in the seawater is due to the influence of magmatic fluid. In addition, the Mn/ΔT ratios in the plume peak level at Stations 18G and 18K are significantly different, ~1820 and ~3640 nM/$^\circ$C, and Mn is more significantly enriched in the lower 18K plume than in the 18G plume (Figures 2(b) and 2(c)), which suggest 18K is closer than 18G to the hydrothermal vent fluid source of the lower plume.

5.2. Correlations between As, Sb, Mn, and Cl in the Hydrothermal Plume. The correlations between As, Sb, and Mn in the
hydrothermal plume peak level at all the stations are positive ($R^2 > 0.8$, $p < 0.05$) (Figure 4), suggesting that As, Sb, and Mn are derived from the hydrothermal vent fluid source and indicating that As and Sb can also be used as a tracer, similarly to Mn, to identify hydrothermal plumes (e.g., [57–60]). Further, the positive correlation between As and Sb ($R^2 > 0.5$, $p < 0.05$) in the plume peak level (Figure 5) demonstrates that the dissolved As and Sb remaining in the plume share similar characteristics during their dilution by seawater (e.g., [29]). However, because of the ongoing rock–fluid interaction, magma degassing, and boiling and phase separation of hydrothermal fluid in hydrothermal systems, the As/Sb ratios in plume peak levels at Station 18B, 8G, and 18K are slightly different (Figure 5) despite the fact that As and Sb have similar geochemical behavior in the hydrothermal plumes.

The correlations between Cl and Mn, As, and Sb in the plume at Station 18B are positive ($R^2 > 0.7$, $p < 0.05$) (Figure 6), indicating that Cl in the plume at Station 18B has the same fluid source as Mn, As, and Sb. At Stations 18K and 18G, the correlations between Cl and Mn, As, and Sb in the lower plume peak level are negative ($R^2 > 0.6$, $p < 0.05$) (Figure 6), implying that the correlations between Cl and Mn, As, and Sb in the lower plume peak level result from a Mn-As-Sb-enriched and Cl-depleted fluid.

### 5.3. As/Sb Ratios

The temperature varied widely (3–3.8°C) at Stations 18B, 18G, and 18K, where the As/Sb ratios in normal seawater decreased with increasing water temperature similarly to results reported in ocean surface water elsewhere [61], so, whether in the surface or in the deep water, the change of As/Sb ratio with temperature shows the same trend (Figure 7). Many studies have shown that the concentration of Sb is almost constant from the surface to the bottom of the ocean (e.g., [61]); thus the change of As/Sb ratio with temperature in normal seawater is dominated by the effect of temperature on As, possibly indicating that the biological

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**Figure 4:** Correlations between Mn and As at (a) Station 18B, (b) Station 18G, and (c) Station 18K; correlations between Mn and Sb at (d) Station 18B, (e) Station 18G, and (f) Station 18K in the plume in the eastern Manus basin.
uptake of seawater As increased at higher temperature (e.g., [61]).

However, since the increase in As concentration in the anomalous layer, relative to background seawater levels, is lower than that of Sb, As/Sb ratios in the anomalous layer are lower than those in normal seawater at the same temperature (Figures 3 and 7), suggesting that the As/Sb ratio may be a tracer reflecting anomalous As and Sb levels in the hydrothermal plume water profiles. Further, the As/Sb ratio in the anomalous layer at Station 18K is higher than that at Station 18G (Figure 7), possibly because the Sb content in the anomalous layer at Station 18K is similar to that at Station 18G, while the As content is higher than that at Station 18G (Figure 3).

5.4. A New Hydrothermal Vent May Exist Near Station 18B.
Station 18B (151°52'W, 3°41'S) is located at the northeast of the PACMANUS hydrothermal field and the DESMOS caldera, at about 35 km and 8 km, respectively. Station 18B is far away from the PACMANUS hydrothermal field, and the bottom current is from the southwest in this area [35], suggesting that the chemical anomaly of hydrothermal plume water column at Station 18B is not the result of the drift of the plume from the PACMANUS hydrothermal field. Further, the Cl and Sb contents in the DESMOS fluid (Cl 490 mM, Sb < 3.0 nM; [29]) are lower than those in the anomaly layer of hydrothermal plume water column at Station 18B, so the Cl and Sb anomaly of hydrothermal plume at Station 18B is also not the result of the drift of the plume from the DESMOS caldera, suggesting that there may be a new hydrothermal vent near Station 18B and that the characteristics of vent fluid from the new vent field are similar to those of the PACMANUS fluid: enriched in Mn, As, Sb, and Cl relative to ambient seawater.

6. Conclusions

In the SuSu Knolls hydrothermal field, the two plumes at Stations 18G and 18K are both enriched in As, Sb, and Mn and depleted in Cl, indicating that As-Sb-Mn-enriched and Cl-depleted vent fluid outputs to the hydrothermal plume water columns, which is most likely generated in the subseafloor by fluid-rock interaction, magma degassing, or boiling and phase separation of hydrothermal fluid. Further, the upper plume may emanate from near hydrothermal vent at Station 18G and the lower plume may have a hydrothermal source far from Station 18G.

The hydrothermal plume at Station 18B is slightly enriched in Cl and significantly enriched in As, Sb, and Mn, as a result of contribution of Mn-As-Sb-Cl-enriched vent fluid discharges into the hydrothermal plume water profile, which have been generated by fluid-rock interaction, and indicating that a new hydrothermal vent may have appeared in that area. The profile of As, Sb, and Mn content with water depth is similar to that of the temperature anomaly. The distributions of As and Sb within the hydrothermal plume are not controlled by particle adsorption or biogeochemical cycles, suggesting that As and Sb, like Mn, can act as tracers of hydrothermal plumes in the seawater environment.

In the eastern Manus basin, the As/Sb ratios in the anomalous layer caused by hydrothermal activity do not follow the relationship between As/Sb ratio and temperature for ambient seawater, suggesting that the As/Sb ratio may be a tracer reflecting the effect of hydrothermal activity on As and Sb in the hydrothermal plume.

Additional Points

Research Highlights. (i) Temperature and Mn, As, and Sb profiles in plume water columns are similar. (ii) There are positive correlations of As and Sb with Mn in the plumes. (iii) As and Sb can be used as tracers of hydrothermal plume. (iv) Plumes are enriched in As, Sb, Mn, and Cl or depleted in Cl. (v) As/Sb ratio may reflect hydrothermal effect on As and Sb in water column.
Figure 6: Correlations between Mn and Cl (a) at Station 18B, (b) at Station 18G, and (c) at Station 18K; correlations between As and Cl (d) at Station 18B, (e) at Station 18G, and (f) at Station 18K; and correlations between Sb and Cl (g) at Station 18B, (h) at Station 18G, and (i) at Station 18K in the plume in the eastern Manus basin.
These seabed depths at Stations 18B, 18G, and 18K are 1759 m, 1606 m, and 1615 m, respectively.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors would like to thank the crew of the “KX08-973” cruise in the eastern Manus basin in 2008 for their support during sampling. They are most grateful for the detailed and constructive comments and suggestions provided by Dr. Ray Binns, which significantly improved the content of this paper. International Science Editing checked the English in the manuscript. This work was supported by the National Natural Science Foundation of China (Grant nos. 41325021, 414776044), the National Key Basic Research Program of China (Grant no. 2015CB429700), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant no. XDA11030302), the International Partnership Program of Chinese Academy of Sciences (Grant no. 133137KYSB20170003), the Special Fund for the 13th Five-Year Plan of COMRA (Grant no. DY135-G2-1-02), the AoShan Talents Program Supported by the Qingdao National Laboratory for Marine Science and Technology (Grant no. 2015ASTP-0517), the Innovative Talent Promotion Program (Grant no. 2012RA2191), the Science and Technology Development Program of Shandong Province (Grant no. 2013GRC35020), the Scientific and Technological Innovation Project financially supported by the Qingdao National Laboratory for Marine Science and Technology (Grant nos. 2015ASKJ03, 2016ASKJ13), and the National High-Level Talent Special Support Program.

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