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Strontium, Hydrogen and Oxygen Behavior in Vent Fluids and Plumes from the Kueishantao Hydrothermal Field Offshore Northeast Taiwan: Constrained by Fluid Processes

Zhigang Zeng [1,2,3,*], Xiaoyuan Wang [1], Xuebo Yin [1], Shuai Chen [1,4], Haiyan Qi [1] and Chen-Tung Arthur Chen [5]

1 Seafloor Hydrothermal Activity Laboratory, CAS Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China; wangxiaoyuan@qdio.ac.cn (X.W.); re_hero@163.com (X.Y.); chenshuai@qdio.ac.cn (S.C.); qihaiyan@qdio.ac.cn (H.Q.)
2 Laboratory for Marine Mineral Resources, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China
3 University of Chinese Academy of Sciences, Beijing 101408, China
4 Center for Ocean Mega-Science, Chinese Academy of Sciences, Qingdao 266071, China
5 Department of Oceanography, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, China; ctchen@mail.nsysu.edu.tw
* Correspondence: zgzeng@ms.qdio.ac.cn

Abstract: Strontium (Sr), hydrogen (H) and oxygen (O) in vent fluids are important for understanding the water–rock interaction and hydrothermal flux in hydrothermal systems. We have analyzed the Sr, H and O isotopic compositions of seawater, vent fluid and hydrothermal plume samples in the Kueishantao hydrothermal field, as well as their calcium (Ca), total sulfur (S), Sr, arsenic (As), stibium (Sb), chlorine (Cl) and manganese (Mn) concentrations for understanding the origin and processes of fluids. The results suggest that most As, Sb and Mn are leached from andesitic rocks into the fluids, and most Ca and Cl remained in the deep reaction zone during the fluid–andesitic rock interaction. The ranges of $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values in the yellow spring, white spring and plumes are small. The $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values of fluids and plumes are like those of ambient seawater, indicating that the Sr, H and O of vent fluids and hydrothermal plumes are derived primarily from seawater. This suggests that the interaction of andesite and subseafloor fluid is of short duration and results in the majority of As, Sb and Mn being released into fluids, while most Ca and Cl remained in the deep reaction zone. In addition, there was no significant variation of Sr, H and O isotopic compositions in the upwelling fluid, keeping the similar isotopic compositions of seawater. There are obvious correlations among the pH values, As and Sb concentrations, and H isotopic compositions of the vent fluids and hydrothermal plumes, implying that the As and Sb concentrations and H isotopic compositions can trace the dispersion of plumes in the ambient seawater. According to the Sr concentrations and $^{87}Sr/^{86}Sr$ values, the water/rock ratios are 3076~8124, which is consistent with the idea that the interaction between fluid and andesite at the subseafloor is of short duration. The hydrothermal flux of Sr discharged from the yellow spring into the seawater is between 2.06×10^4 and 2.26×10^4 mol/yr, and the white spring discharges 1.18×10^4~1.26×10^4 mol/yr Sr if just andesites appear in the reaction zone.

Keywords: strontium-hydrogen-oxygen isotopes; vent fluid; hydrothermal plume; Kueishantao hydrothermal field

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1. Introduction

Extensive strontium (Sr), hydrogen (H), and oxygen (O) isotopic and chemical exchange depending on fluid temperatures, hydrothermal alteration and the water/rock ratios can be caused by hydrothermal circulation [1–5]. The intensity of the water–rock

interaction has been recorded by these isotopes in the hydrothermal fluids, and they are particularly useful in the research of fluid origin and hydrothermal processes in subseafloor hydrothermal systems [1,6,7]. The mobile Sr, H and O isotopes are good markers of host rock composition and subseafloor alteration processes in hydrothermal systems [2,4,8,9]. Sr, H and O in hydrothermal fluids come from different sources, relying on the hydrothermal circulation system, seawater and fluid mixing, host rocks and magma [2,4,10,11]. Their isotopic ratios are used to identify different sources (rock, seawater and sediment) [2,4,12] and mixing versus conductive cooling or heating processes and may be valuable for constraining the phase separation conditions in seafloor hydrothermal systems.

However, it has been implied that the high-temperature hydrothermal circulation is insufficient to balance the other Sr input fluxes, as an increase of ~5.4×10^{-5} Myr^{-1} [13] has been observed in oceanic $^{87}Sr/^{86}Sr$ over the past few million years [14–16]. Many explanations have been put forward to explain the missing unradiogenic $^{87}Sr/^{86}Sr$ flux, such as hydrothermal systems occurring on the ridge flank [16], low-temperature alteration processes and the precipitation of carbonate [17,18]. The reactions happening in the hydrothermal systems are of great importance and are believed to be the main source of unradiogenic $^{87}Sr/^{86}Sr$ in seawater; however, the Sr flux into the oceans from high- and particularly low-temperature hydrothermal systems remain poorly quantified [14,17].

During subcritical phase separation, H isotope fractionation has been shown to depend on both temperature and salinity [19]. Furthermore, H isotope ratios of fluids are relatively insensitive to reactions with the host rock because H is abundant in the fluid relative to the mineral content. However, the H isotope fractionation data of brine and vapor coexisting in the two-phase supercritical region of seawater is completely lacking. The H isotope fractionation related to the phase separation of NaCl-H_2O fluid has only been obtained up to 350 °C [19]. Although the temperature of the vent fluid is generally close to 350 °C [20], phase separation occurs in the deep reaction zones at temperatures significantly higher than this. Many hydrothermal experiments studying the fractionation of seawater phase separation at 450 °C had obtained H isotopic fractionation factors, and these data were then used to explain the phase separation and segregation in deep-sea hydrothermal systems [2].

The first O isotope studies of black smoker hydrothermal fluids were published by the East Pacific Rise Study Group [21] and Welhan and Craig [22], which showed that the $\delta^{18}O$ values are close to that of ambient seawater; however, they increase by 1–2‰ owing to the reaction between basalt and seawater at elevated temperatures. Furthermore, Teagle et al. [23] used Sr and O isotope systematics to confirm that anhydrite on the Trans-Atlantic Geotraverse (TAG) Mound forms through the mixing between fluids and seawater, which is conductively heated to 100–180 °C before mixing; thus, anhydrite forms by a mixture of heated seawater and vent fluid at 230–320 °C. According to Bach and Humphris [24], the $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ of the vent fluids on the oceanic ridge show a global correction with the rate of spreading (or the rate of magma supply). They believe that at low spreading rates (or low magma supply rates), there is significantly less Sr from seawater and higher $\delta^{18}O$ from seawater in vent fluids. This is due to a greater exchange of Sr and O with the crust during hydrothermal fluid circulation, possibly because of longer reaction paths under slow-spreading ridges. Using the datasets of hydrothermal vent fluids associated with ridges, linear regression equations and R2 values show that the $\delta^{18}O$ proposed by Bach and Humphris [24] is not statistically related to the spreading rate.

Field and experimental studies, as well as isotopic exchange computations [25–31], have clearly shown that both O and H isotope values increase due to water/rock interactions with the igneous crust. Due to the decrease of water/rock mass ratios caused by the evolution of hydrothermal fluids, the O and H isotope values of end-member vent fluids follow the calculated seawater/basalt reaction vector [25]. For slower spreading ridges, higher δD values are consistent with longer fluid paths and more fluid-rock interactions. However, $\delta^{18}O$ values would be even more responsive to fluid–rock interactions and have insignificant variation with the rate of spreading. With the increase of the hydrothermal

vent fluid database, the short-term time variation in each field becomes more and more important.

The chemical characteristics of deep-sea hydrothermal fluids from mid-ocean ridges and back-arc basins, including Sr, H and O isotopic compositions, have been described by [20,32–35]. However, little is known about the chemical and Sr, H and O isotopic compositions of shallow hydrothermal vents fluids. The quantification of global hydrothermal flux into the ocean is also biased due to the lack of budget caused by the interaction of seawater and andesite. To better understand the fluid–andesitic rock interaction, the fluid and plume samples in the Kueishantao shallow hydrothermal field were collected and analyzed. The main purposes of this study are (1) to investigate the geochemistry characteristics and evolution of hydrothermal fluids and their plumes, (2) to study the rock–fluid interactions recorded by fluids and plumes, and (3) to assess the hydrothermal flux of Sr in the shallow hydrothermal field.

2. Geologic Setting

The Kueishantao shallow hydrothermal field (121°55′ E, 24°50′ N) is in the southeast of Kueishantao, northeastern Taiwan, and near the southern Okinawa Trough. The hydrothermal field covers an area of about 0.5 square kilometers (Figure 1). Kueishantao's last major eruption occurred about 7000 years ago [36], and the area around the hydrothermal vents is characterized by andesitic lava and pyroclastic flows. The andesitic magma is thought to be produced by a MORB-type magma with an assimilated 30% local continental crust [37]. The difference in Fe-Cu-Zn isotopic compositions between the Kueishantao andesites and the MORBs and the continental crust might indicate entrainment of carbonate sediment components into the andesitic magma [38].

The Kueishantao hydrothermal field has more than 30 hydrothermal vents at water depths of 10–30 m. The hydrothermal products in the form of chimneys, mounds and balls are mainly composed of natural sulfur. On 12 August 2000, a large yellow chimney approximately 6 m high was discovered at a water depth of 20 m. The geochemical study of the native sulfur chimneys and balls indicated that trace elements are derived primarily from the andesite and partly from seawater, and the interaction between the subseafloor fluid and the andesite has a short duration [39,40].

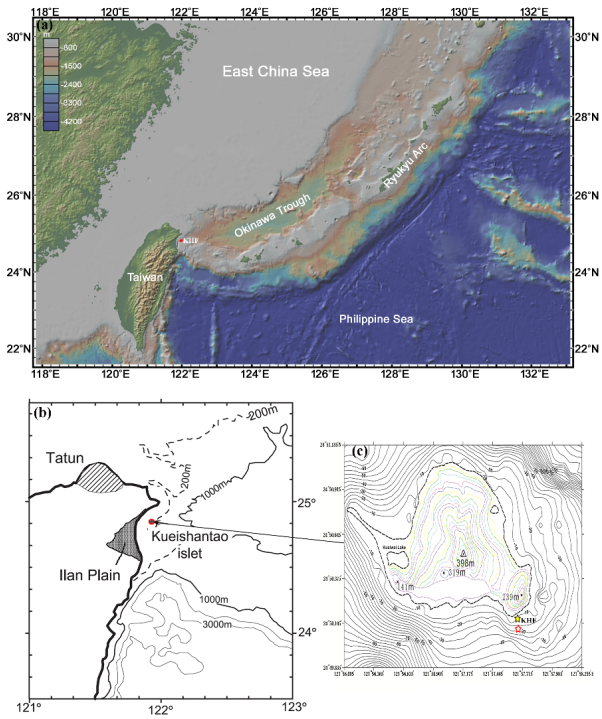

Figure 1. (**a**) The bathymetric map of Taiwan and the Okinawa Trough (based on [41]). (**b**) The tectonic map with the location of Kueishantao island (from [42]). (**c**) The location of the yellow spring

(yellow star, 108 °C) and white spring (red star, 51 °C) in the Kueishantao hydrothermal field (based on [41]).

There are two types of vents, "yellow spring" (78~116 °C) and "white spring" (30~65 °C) [42]. The yellow spring fluids are characterized by very low pH (~1.52) and a wide range of chemical compositions. The white spring fluids have a relatively low content of methane, iron and copper [42]. The temperature of the vent fluids varied with tides and reached the maximum temperature approximately 3.5 h after each high tide [42–44]. The Ca, Mg and K are significantly correlated with each other, indicating the same source of seawater [45]. The gas component is mainly CO_2, followed by N_2, CH_4 and H_2S [46].

3. Sampling and Methods

3.1. Sample Collection

On 31 May 2011, the samples of hydrothermal fluids and plumes were collected from the Kueishantao hydrothermal field by divers (Table 1, Figure 1). Four liter Pyrex bottles were used to sample the hydrothermal fluids at and in the vent. Two-valve polyethylene tubes were also employed to sample the fluids in order to assess the reliability of the data gained by the Pyrex bottles. The hydrothermal plume was sampled in 1 L Nalgene polypropylene bottles at approximately 2, 5 and 7 m below sea level above the yellow spring vent (water depth, 7.2 m) and approximately 5, 10, 13 and 15 m below sea level above the white spring vent (water depth, 15.1 m). Shallow seawater was sampled at a depth of 10 m near Kueiwei to eliminate the effect of hydrothermal activity. The fluid fluxes and temperatures were determined in situ. Kuo [43] described in detail the methods of fluid collection and the measurement of temperature and flux in situ.

Table 1. Location of the yellow and white springs in the Kueishantao hydrothermal field as well as the fluid temperature and flux [45].

Spring Type	Latitude (°N)	Longitude (°E)	Depth (m)	Fluid Temperature (°C)	Fluid Flux (m^3/h)
Yellow spring	24.8349	121.96194	7.2	108	35.1
White spring	24.83412	121.96196	15.1	51	19.3

3.2. Analytical Methods

In the lab on the shore, the pH of the liquid was analyzed by a portable pH meter with a resolution of 0.01 (JENCO 6010, San Diego, CA, USA). Before measurement, calibrate the pH meter with buffer solutions of pH 4.00 and 6.86 (i.e., 0.05 mol/L potassium hydrogen phthalate (25 °C, pH = 4.00) and 0.025 mol/L mixed phosphate (25 °C, pH = 6.86) buffers). All liquids were filtered into 1 L Nalgene polypropylene bottles, which were previously soaked in 1:1 HNO_3 for 48 h, washed with distilled water, and then dried.

Calcium (Ca), total sulfur (S) and Sr were analyzed by the inductively coupled plasma optical emission spectrometer at the Shandong Institute of Geophysical and Geochemical Exploration, and the precision was <±5%. Arsenic (As) and stibium (Sb) were determined using atomic fluorescence spectrophotometer at the Qingdao Institute of Marine Geology, China Geological Survey Bureau. Manganese (Mn) was analyzed by inductively coupled plasma mass spectrometer, and chlorine (Cl) was determined using ion chromatography at the Institute of Oceanology, Chinese Academy of Sciences. The detailed chemical separation and measurement procedures of As, Sb, Mn and Cl were described in previous studies [47]. Seawater standard NASS-5 was used. The analytical precision of As, Sb and Mn was better than 5%, and that of Cl was ±1%.

The $^{87}Sr/^{86}Sr$ was measured using thermal ionization mass spectrometry (TIMS; Triton) at the State Key Laboratory of Geological Processes and Mineral Resources, China

University of Geosciences. The procedures of chemical separation and determination were described in detail in previous studies [48,49]. For Sr, the procedural blanks were less than 50 pg. The determination of the NBS987 Sr isotopic standard gained over one year yielded an average value of $^{87}Sr/^{86}Sr$ = 0.710266 ± 0.000009 (2σ, *n* = 38). Rock standard AGV-2 was used for $^{87}Sr/^{86}Sr$. The analytical precision was <0.006%.

H and O isotopic ratios were measured by the stable isotope ratio mass spectrometer (MAT-253, Thermo Fisher, USA) at the Institute of Mineral Resources, Chinese Academy of Geological Sciences. Fluid samples were prepared for H isotope analyses using the Zn-reduction method and for O isotope analyses using the CO_2 equilibration technique. Values of H and O isotopes are calibrated relative to the V-SMOW standard. The analytical precision of the δD and $\delta^{18}O$ are better than 1.0‰ and 0.1‰, respectively.

4. Results

We report the element (Ca, total S, Sr, As, Sb, Cl and Mn) concentrations and $^{87}Sr/^{86}Sr$, δD and $\delta^{18}O$compositions of fluid and plume samples collected from the Kueishantao hydrothermal field. At both yellow and white spring sites, the hydrothermal fluids are released directly from the andesite host rock due to an absence of sediment cover. Figure 1 displays the sample locations and element concentrations, and the $^{87}Sr/^{86}Sr$, δD and $\delta^{18}O$ values are listed in Table 2.

Table 2. pH, Ca, total S, Sr, As, Sb, Cl and Mn concentrations and $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values of fluid and plume samples collected from the Kueishantao hydrothermal field.

Sample	Depth (m)	pH	Ca (mg/L)	Total S (mg/L)	Sr (mg/L)	As (μg/L)	Sb (μg/L)	Cl (mg/L)	Mn (μg/L)	$^{87}Sr/^{86}Sr$	2σ(±)	$\delta D_{V\text{-}SMOW}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)
Ambient seawater	10	8.02	372.6	835	6.62	1.15	0.20	19,352	0.91	0.709177	0.000008	2	0.1
YSP, 0 m	0	6.15	381.3	829	6.37	5.59	0.29	20,814	10.8	0.709147	0.000008	2	0.1
YSP, −2 m	2	6.12	385.0	840	6.36	3.81	0.23	20,422	3.93	0.709156	0.000007	3	0.2
YSP, −5 m	5	5.60	382.2	833	6.34	6.01	0.28	20,810	3.45	0.709168	0.000006	5	0.2
YSF, out, bottle	7.2	2.81	371.2	810	5.87	22.4	0.77	18,052	4.55	-	-	1	0.1
YSF, in, bottle	>7.2	2.29	378.9	812	6.12	46.4	1.22	18,254	3.58	-	-	1	0.1
YSF, out, tube	7.2	-	345.0	838	6.32	-	0.03	17,380	18.5	-	-	-	-
YSF, in, tube	>7.2	-	359.1	1069	6.43	0.29	-	18,323	14.2	-	-	-	-
WSP, 0 m	0	6.14	381.3	832	6.35	5.65	0.27	19,068	6.24	0.709202	0.000006	0	0.1
WSP, −2 m	2	6.12	383.0	833	6.35	4.08	0.29	18,925	3.48	0.709186	0.000005	0	0.1
WSP, −5 m	5	5.91	379.3	823	6.30	6.46	0.32	20,205	4.34	0.709171	0.000006	2	0.1
WSP, −10 m	10	5.51	376.2	823	6.27	14.5	0.48	20,454	10.4	0.709178	0.000005	0	0.2
WSF, out, bottle	15.1	5.11	380.5	826	6.42	10.5	0.36	16,529	7.48	0.709158	0.000004	−4	0.2

Table 2. *Cont.*

Sample	Depth (m)	pH	Ca (mg/L)	Total S (mg/L)	Sr (mg/L)	As (μg/L)	Sb (μg/L)	Cl (mg/L)	Mn (μg/L)	$^{87}Sr/^{86}Sr$	2σ(±)	$\delta D_{V\text{-}SMOW}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)
WSF, in, bottle	15.1	4.67	369.4	963	6.12	15.8	0.36	16,951	23.3	-	-	−2	0.2
WSF, out, tube	15.1	5.10	383.2	802	6.56	27.6	0.47	17,811	14.4	0.709154	0.000007	1	0.2
WSF, in, tube	15.1	4.67	372.5	805	6.23	21.1	0.39	17,309	13.2	0.709164	0.000006	1	0.3
Sample	Range of Sr (ppm)				Average of Sr (ppm)								
Kueishantao andesite	175–264				206 (n = 41)								

"-" no detect; YSP represents yellow spring plume; YSF represents yellow spring fluid; WSP represents white spring plume; WSF represents white spring fluid.

The Ca, total S, Sr As, Sb, Cl and Mn concentrations in the yellow spring varied from 381.3 mg/L, 892 mg/L, 6.37 mg/L, 5.59 μg/L, 0.29 μg/L, 20,814 mg/L and 10.8 μg/L at 0 mbsl (meters below sea level) to 371.2 mg/L, 810 mg/L, 5.87 mg/L, 22.4 μg/L, 0.77 μg/L, 18,052 mg/L and 4.55 μg/L at 7.2 mbsl (Figure 2), respectively. The Ca, total S, Sr As, Sb, Cl and Mn concentrations in the white spring varied from 381.3 mg/L, 832 mg/L, 6.3 mg/L, 5.65 μg/L, 0.27 μg/L, 19,068 mg/L and 6.24 μg/L at 0 mbsl to 369.4 mg/L, 963 mg/L, 6.12 mg/L, 15.8 μg/L, 0.36 μg/L, 16,951 mg/L and 23.3 μg/L at 15.1 mbsl (Figure 2), respectively.

Compared with the Ca, Sr As and Cl concentrations in the yellow spring hydrothermal plumes (381.3 to 385.0 mg/L, 6.34 to 6.37 mg/L, 3.81 to 6.01 μg/L and 20,422 to 20,814 mg/L), those in the white spring hydrothermal plumes have a slightly wider range of variation (376.2 to 383.0 mg/L, 6.27 to 6.35 mg/L, 4.08 to 14.5 μg/L and 18,925 to 20,454 mg/L) than in (Figure 3). Most of the total S and Sr concentrations for both hydrothermal plumes are slightly lower than that of shallow seawater (835 and 6.62 mg/L) (Figure 2). The Ca, Sr and Cl concentrations of most hydrothermal fluids are clearly lower than that of shallow seawater and consistent with those (Cl 15,811–19,888 mg/L) of [39,42].

The $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values in the yellow spring range from 1‰ and 0.1‰ in fluid to 5‰ and 0.2‰ in the plume, and the $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values in the white spring range from 0.709154, −4‰, and 0.2‰ in fluid to 0.709202, 2‰ and 0.2‰ in the plume (Table 2). The $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values of the two hydrothermal plumes were similar (Table 2), and near the 0.709177, 2‰ and 0.1‰ values of ambient seawater (Figure 3). The $^{87}Sr/^{86}Sr$ values of the white spring hydrothermal fluids are distinctly lower than those of shallow seawater and the white spring hydrothermal plume (Figure 3).

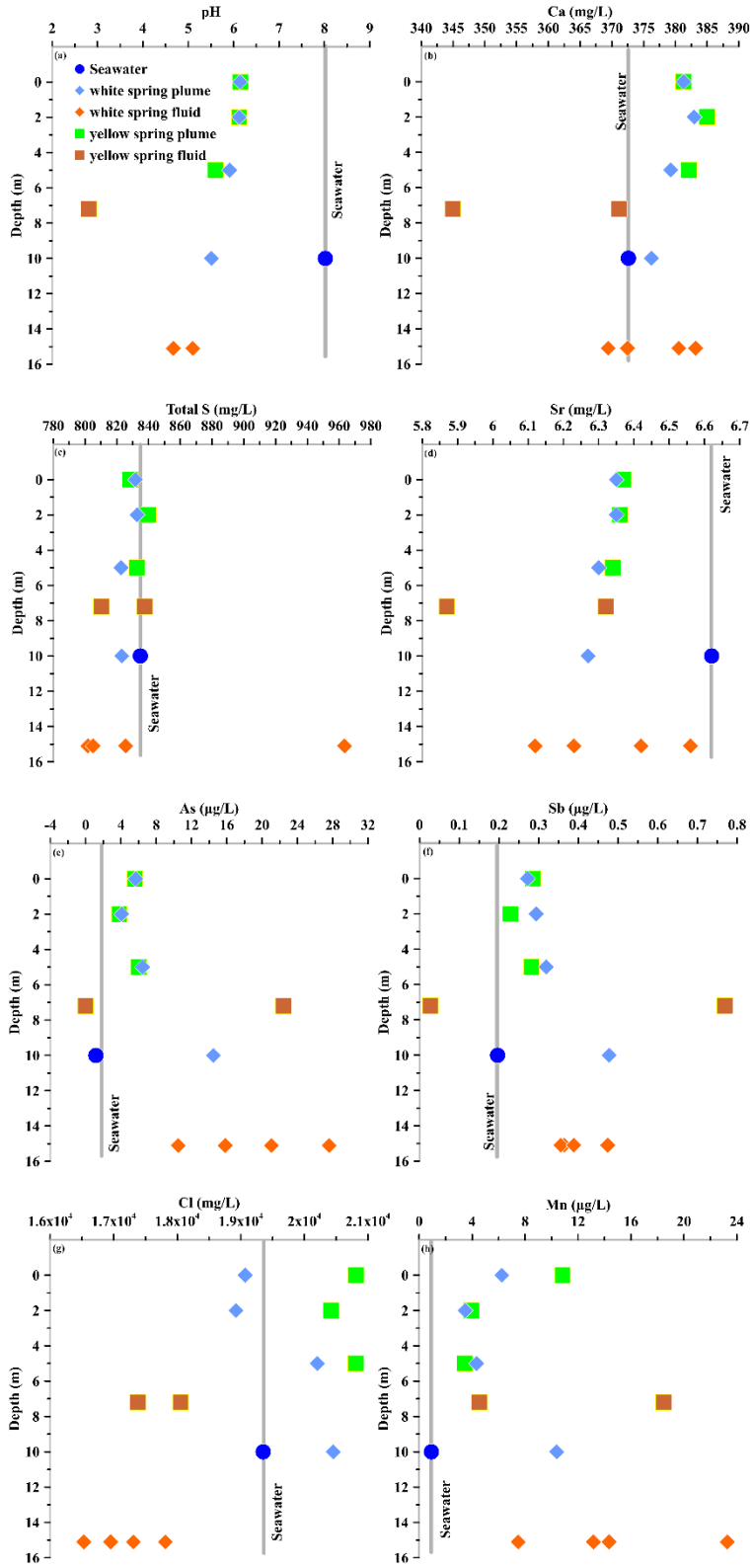

Figure 2. Changes in pH (**a**), Ca (**b**), total S (**c**), Sr (**d**), As (**e**), Sb (**f**), Cl (**g**) and Mn (**h**) concentrations from hydrothermal fluid to plume at the yellow and white spring sites.

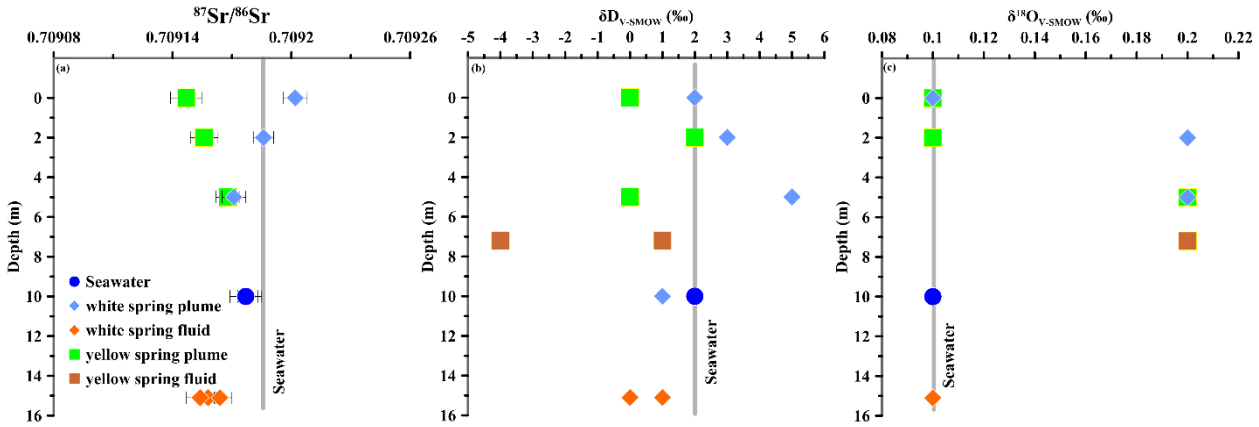

Figure 3. Variation of $^{87}Sr/^{86}Sr$ (**a**), δD (**b**) and $\delta^{18}O$ (**c**) values from hydrothermal fluid to plume at the yellow and white spring sites.

The hydrothermal fluids have a pH range of 2.29 to 5.11, and those of the plumes are 5.51~6.15. The pH values of the hydrothermal fluids and plumes are distinctly lower than that of shallow seawater (8.02), and from the hydrothermal fluids to the hydrothermal plumes, the pH value increases gradually as the water depth decreases (Figure 2). The As, Sb and Mn concentrations and $\delta D_{V\text{-}SMOW}$ values of the hydrothermal fluids and plumes display a good positive and negative correlation with pH values (Figure 4).

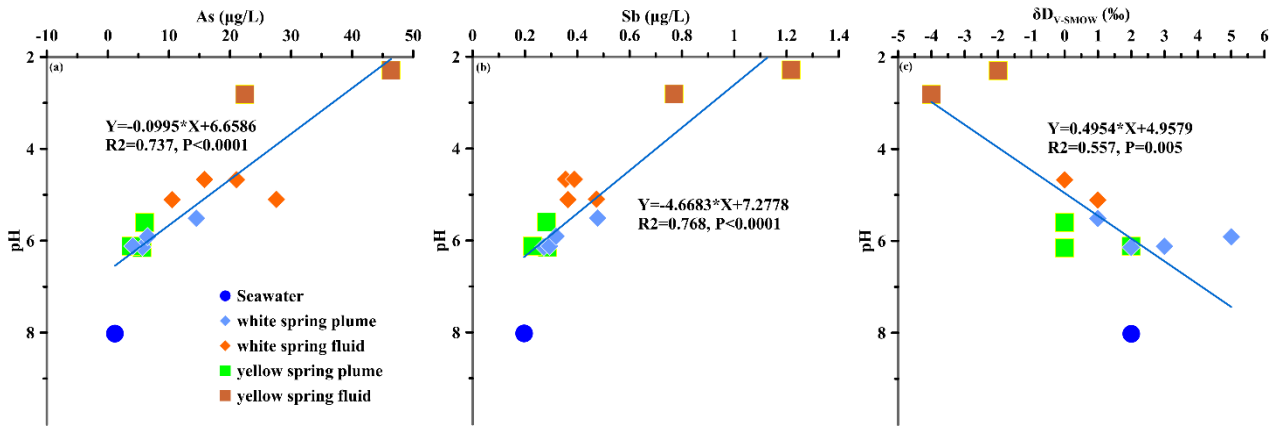

Figure 4. pH vs. As concentration (**a**), pH vs. Sb concentration (**b**) and pH vs. δD (**c**) values for fluids and plumes in the yellow and white springs.

From vent fluids to hydrothermal plumes, the pH values, As and Sb concentrations and H isotope compositions have a good correlation, and the concentrations of As and Sb decrease with the increase of pH value (Figure 4), which is like the boron (B) concentrations and isotopic compositions [42], indicating that the As and Sb concentrations and H isotopic compositions can be used to trace the variation of chemical characteristics during the hydrothermal plumes that disperse in the seawater.

Moreover, from the surface to the water depth of 5 m, the Cl and total S concentrations and $\delta^{18}O_{V\text{-}SMOW}$ values in the hydrothermal plumes are similar (Figure 2), which is due to the mixing of the hydrothermal plumes with shallow seawater (Figure 4B,C).

5. Discussion

5.1. Sources of Strontium, Hydrogen and Oxygen

Because Sr, H and O isotopes in seawater and andesite are different, the Sr, H and O in hydrothermal fluids might be derived from two components: seawater and andesite. In the Kueishantao hydrothermal field, the $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values in

ambient seawater are 0.709177, 2‰ and 0.1‰ with a Sr concentration of 6.62 mg/L, and an average Sr content in the andesite is 206 ppm (Table 2). The andesite in the Kueishantao hydrothermal field have a large range of $^{87}Sr/^{86}Sr$ (from 0.70577 to 0.70688) and $\delta^{18}O_{SMOW}$ (from 7.1‰ to 7.9‰) values, with Sr concentrations of 221–317 ppm [37].

However, the hydrothermal plumes have similar values of $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ to those of the shallow seawater (Table 2) (Figure 3), and the $^{87}Sr/^{86}Sr$ ratios of the hydrothermal fluids and plumes in the Kueishantao hydrothermal field were significantly higher than those (from 0.70382 to 0.7056) of hydrothermal fluids from the Eastern Lau spreading center [35], suggesting that the hydrothermal plumes and fluids are derived primarily from seawater.

A simple two-end-member mixing model using an equation:

$$M_{mix} = X \times M_{seawater} + (1 - X) \times M_{andesite} \quad (1)$$

where X is the amount of the seawater component; M is the $^{87}Sr/^{86}Sr$ and $\delta^{18}O$; M_{mix}, $M_{seawater}$ ($^{87}Sr/^{86}Sr_{seawater}$ 0.709177, $\delta^{18}O_{seawater}$ 0.1‰) and $M_{andesite}$ ($^{87}Sr/^{86}Sr_{andesite}$ from 0.70577 to 0.70688, $\delta^{18}O_{andesite}$ from 7.1‰ to 7.9‰) are the Sr and O isotopic compositions of hydrothermal plumes and fluids, seawater and andesite, respectively. The model shows that approximately 99% and 97% of the Sr and O are derived from seawater (Table 3).

Table 3. Calculated water/rock ratios, Sr and O source contributions and Sr fluxes in the Kueishantao hydrothermal field.

Sping Fluid	Water/Rock Ratio		Strontium Source Contributions (%)				Strontium Flux (mole/yr)	Oxygen Source Contributions (%)			
	$^{87}Sr/^{86}Sr_{andesite}$ = 0.70577	$^{87}Sr/^{86}Sr_{andesite}$ = 0.70688	Andesite [1]	Seawater [2]	Andesite [3]	Seawater [2]		Andesite [4]	Seawater [5]	Andesite [6]	Seawater [5]
YSF, out, bottle	-	-	-	-	-	-	2.06×10^4	1.43	98.57	1.28	98.72
YSF, in, bottle	-	-	-	-	-	-	2.15×10^4	1.43	98.57	1.28	98.72
YSF, out, tube	-	-	-	-	-	-	2.22×10^4	1.43	98.57	1.28	98.72
YSF, in, tube	-	-	-	-	-	-	2.26×10^4	2.86	97.14	2.56	97.44
WSF, out, bottle	5548	3730	0.56	99.41	0.83	99.17	1.24×10^4	0.00	100	0.00	100
WSF, in, bottle	-	-	-	-	-	-	1.18×10^4	-	-	-	-
WSF, out, tube	4578	3076	0.68	99.32	1.00	99.00	1.26×10^4	-	-	-	-
WSF, in, tube	8124	5467	0.38	99.62	0.57	99.43	1.20×10^4	0.00	100	0.00	100

"-" no data. Sr of spring fluid from andesite and seawater. Sr source contribution (X) can be calculated by using the simple two endmember mixing method: $X = ((^{87}Sr/^{86}Sr_{spring\ fluid} - {}^{87}Sr/^{86}Sr_{seawater})/(^{87}Sr/^{86}Sr_{andesite} - {}^{87}Sr/^{86}Sr_{seawater}) \times 100)$; YSF represents yellow spring fluid; WSF represents white spring fluid; [1] represents $^{87}Sr/^{86}Sr_{andesite}$ = 0.70577 from [37]; [2] represents $^{87}Sr/^{86}Sr_{seawater}$ = 0.709177; [3] represents $^{87}Sr/^{86}Sr_{andesite}$ = 0.70688 from [37]. O source contribution (Y) can be calculated by using simple two end-member mixing method: $Y = ((\delta^{18}O_{spring\ fluid} - \delta^{18}O_{seawater})/(\delta^{18}O_{andesite} - \delta^{18}O_{seawater}) \times 100)$; [4] represents $\delta^{18}O_{andesite}$ = 7.1‰ from [40]; [5] represents $\delta^{18}O_{seawater}$ = 0.1; [6] means $\delta^{18}O_{andesite}$ = 7.9‰ from [37].

5.2. Seawater-Rock Interaction

Sr, H and O behave conservatively, as their behavior during hydrothermal alteration demonstrates [6]. The geochemistry of Sr, H and O in submarine hydrothermal systems has been used to constrain subseafloor fluid-rock interaction processes [23,30]. When high-temperature fluids reacted with fresh basalt in mid-ocean ridges [50,51], Sr is believed to be extracted from basalt quantitatively during hydrothermal reactions without subsequent re-equilibration with secondary mineral phases [6,23,30], while O and H may be primarily derived from seawater. The relative concentrations of Sr, As, Sb and Mn in the hydrothermal fluids could reflect those in the volcanic rocks where they were leached [52,53].

Past studies of seafloor hydrothermal fields imply that hydrothermal fluids often have similar $^{87}Sr/^{86}Sr$, δD and $\delta^{18}O$ values to those of the nearby rocks ($^{87}Sr/^{86}Sr$) and seawater (δD and $\delta^{18}O$), indicating the leaching of Sr from the host rocks or mixing of H and O from seawater [6,23,30]. Therefore, the Sr, H and O isotopic compositions of hydrothermal fluids can be used to clarify different source rocks.

In both springs, the $^{87}Sr/^{86}Sr$ values of the hydrothermal fluids are obviously higher than that in hydrothermal fluids at the mid-ocean ridge (the East Pacific Rise near 9°N 0.70381–0.70790, [7]) and back-arc basin (Lau basin 0.70382–0.7056, [20]) (Figure 3), and the $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values of Kueishantao vent fluids and hydrothermal plumes are like those of the ambient seawater, indicating a short-term interaction between subseafloor fluids and andesite.

Most As, Sb and Mn concentrations in hydrothermal fluids are much higher than those in sea level hydrothermal plumes, which have lower temperatures. However, the high As, Sb and Mn concentrations cannot be produced solely by local seawater contributions. The apparently higher concentrations of As, Sb and Mn in the hydrothermal fluids may show an extra source from the andesite basement. The seawater-andesite interaction will result in higher exchangeable As, Sb and Mn concentrations. The high As, Sb and Mn concentrations of most hydrothermal fluids (above seawater, Table 2) partly reflect the constraints by the andesite, which reacts with source fluids. These As-, Sb- and Mn-enriched fluids in both springs have low pH values and can be interpreted by the interaction between seawater and andesite, which explains the difference between Kueishantao and mid-ocean ridge hydrothermal systems. The $^{87}Sr/^{86}Sr$ values in the Kueishantao hydrothermal fluids are obviously higher than those in the hydrothermal fluids on the Valu Fa ridge in the Lau basin (Figure 3), indicating a short interaction between the andesite basement and seawater.

In the Kueishantao hydrothermal field, the concentrations of As, Sb and Mn in the hydrothermal plume and fluid are enriched relative to those in the seawater. This is different from the basalt-hosted hydrothermal systems in which As, Sb and Mn losses are caused by the entrainment of seawater during the formation of altered minerals at low temperatures, and subsequently, the mobilization of As, Sb and Mn in the high-temperature reaction zone [52,53], usually resulting in the slight enrichment of As, Sb and Mn in high-temperature hydrothermal fluids. The concentrations of As, Sb and Mn in the Kueishantao hydrothermal system are like those in the back-arc basins. At these two locations, the weak water–rock interaction results in the smaller removal of As, Sb and Mn in the hydrothermal fluid circulation. However, the unique enrichment of As, Sb and Mn in the hydrothermal fluids is a feature of hydrothermal systems with andesite basements because trace As, Sb and Mn have been leached out by seawater.

We calculated the water/rock ratios of the fluid-rock reaction as follows:

$$W/R = ((^{87}Sr/^{86}Sr_h - {}^{87}Sr/^{86}Sr_{andesite}) \times Sr_{andesite})/((^{87}Sr/^{86}Sr_{sw} - {}^{87}Sr/^{86}Sr_h) \times Sr_{sw}) \quad (2)$$

where $^{87}Sr/^{86}Sr_h$, $^{87}Sr/^{86}Sr_{andesite}$ and $^{87}Sr/^{86}Sr_{sw}$ (0.709177) are the isotopic ratios in hydrothermal fluids, andesite and seawater, respectively, and $Sr_{andesite}$ (206 ppm) and Sr_{sw} (6.62 mg/L) are the Sr concentrations of andesite and seawater, respectively. The water/rock ratios for $^{87}Sr/^{86}Sr$ andesite = 0.70577 and 0.70688 are listed in Table 3, ranging from 4578 to 8124 and 3076 to 5467, respectively. The significant difference between these results and those (approximately 1.6) from fluids from the DSDP Hole 504B, Costa Rica Rift reported by Kawahata et al. [6] is ascribed to the shorter fluid pathways and seawater–rock interaction. However, the Sr/Ca ratio of KHF hydrothermal fluids and plumes (0.0165–0.0171, n = 15) is like that (0.0178) of ambient seawater and significantly higher than that (0.0042–0.0068, n = 35) of KHF andesites, which indicates the precipitation of anhydrite is negligible in the subseafloor recharge zone. This suggests that the fluids in the Kueishantao hydrothermal field have weaker water and rock interactions and shorter reaction paths, and the isotopic fractionation seems to decrease accompanying the increasing water/rock ratio, resulting in the $^{87}Sr/^{86}Sr$, δD and $\delta^{18}O$ values of upwelling fluids in the Kueishantao hydrothermal field like those of ambient seawater.

5.3. From Vent Fluid to Plume

The Ca and Cl concentrations of vent fluids are less than those of hydrothermal plumes and ambient seawater (Table 2), and the Ca and Cl concentrations of hydrothermal plumes are higher than those of shallow seawater. This suggests that the mixing of hydrothermal fluids and seawater leads to the enrichment of Ca and Cl in the hydrothermal plumes, and most Ca and Cl are retained in the deep reaction zone during the fluid-andesite interaction. Thus, the resulting Ca and Cl concentrations of upwelling and vent fluids are less than that of shallow seawater.

The As, Sb and Mn concentrations of most vent fluids are higher than those of hydrothermal plumes and shallow seawater (Table 2), and the As, Sb and Mn concentrations of most vent fluids are higher than those of hydrothermal plumes. This suggests that As, Sb and Mn in the hydrothermal fluids are leached from andesite during the fluid–rock interaction, and the mixing of the hydrothermal fluid and shallow seawater leads to the leaching of the As, Sb and Mn in the fluids into hydrothermal plumes.

In a plot of pH versus As, Sb and $\delta D_{V\text{-}SMOW}$, the linear correlation (Figure 4) indicates that the hydrothermal plumes are a two-component mixture of seawater and fluid. Therefore, the As, Sb and $\delta D_{V\text{-}SMOW}$ values of the Kueishantao hydrothermal fluids and plumes can be interpreted as the result of mixing seawater As, Sb and $\delta D_{V\text{-}SMOW}$ with fluid As and Sb extracted from the andesitic rocks.

5.4. Strontium Flux

The hydrothermal circulation under the sea floor leads to extensive chemical and isotopic exchange due to changes in fluid temperature. For Sr, the reaction direction changes from uptake by the rock at low temperature to release from the rock at high temperature [51]. However, the Sr and Cl are clearly like those of the hydrothermal fluids in the North Cleft segment on the Juan de Fuca Ridge [54] and those vented from the Plume vent at the South Cleft [55] (Figure 2). The Sr concentrations and $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values of the white spring (51 °C) are like those of the yellow spring (108 °C), indicating that the exchange magnitude of Sr, H and O between the andesite and seawater is consistent within these two types of springs.

For calculating the Sr flux, it was presumed that the yellow and white springs have stable flow rates and that andesite is the only host rock in the reaction zone. Using measured Sr concentrations in hydrothermal fluids, the Sr flux calculated for the white spring vent into the ocean is between 2.06×10^4 and 2.26×10^4 mol/yr, and the Sr flux for the yellow spring vent is between 1.18×10^4 and 1.26×10^4 mol/yr (Table 3). Therefore, the Sr flux from the yellow spring is slightly higher than that from the white spring. Assuming that more than 30 vents occur in the Kueishantao hydrothermal field [42], the hydrothermal Sr flux is about 6×10^5 mol/yr with $F_{sr}{}^{sw}$ (fraction of Sr from seawater) values from 0.990 to 0.996, much higher than the $F_{sr}{}^{sw}$ values of 0.083—0.318 at hydrothermal vent fields on the Lau basin, Mariana Trough, Mid-Atlantic Ridge, Juan de Fuca Ridge and East Pacific Rise [24]. The difference also shows that there is a short lifetime of subseafloor fluid–rock interaction and/or short reaction paths at the Kueishantao hydrothermal field.

6. Conclusions

The element concentrations and $^{87}Sr/^{86}Sr$, $\delta D_{V\text{-}SMOW}$ and $\delta^{18}O_{V\text{-}SMOW}$ values of the Kueishantao hydrothermal fluids and plumes have smaller ranges of variation than those of fluids released from back-arc basins and mid-ocean ridges. The $^{87}Sr/^{86}Sr$ values and Sr concentrations of fluids range from 0.709154 to 0.709164 and 5.87 to 6.56 mg/L, respectively. For the plumes, the $^{87}Sr/^{86}Sr$ values range from 0.709147 to 0.709202, and the Sr concentrations range from 6.27 to 6.37 mg/L. From hydrothermal fluid to hydrothermal plume, the As, Sb and Mn concentrations decrease with the reduction of water depth, whereas Cl and Ca concentrations tend to increase. The As, Sb and Mn concentrations of the hydrothermal fluids and plumes of both yellow and white springs are higher than those of shallow seawater (As, Sb and Mn are 1.15, 0.20 and 0.91 mg/L), and the $^{87}Sr/^{86}Sr$ values

of most vent fluids of the white spring are obviously less than that of shallow seawater. The variations of As, Sb and Mn concentration and $\delta D_{V\text{-}SMOW}$ values of the hydrothermal plumes can be interpreted by the mixing of vent fluids with seawater. Using As, Sb and H isotopes of hydrothermal plumes can describe their diffusive processes.

Sr, H and O in Kueishantao vent fluids are primarily derived from the ambient seawater. The As, Sb, Mn, Ca and Cl concentrations of hydrothermal fluid are influenced slightly by weak interactions between seawater and rock in the deep reaction zones, which is characterized by leaching of As, Sb and Mn from andesite. The hydrothermal flux of Sr in the Kueishantao hydrothermal field is between 1.18×10^4 and 2.26×10^4 mol/yr. Compared with the fluxes in other hydrothermal fields, the low flux might be caused by lower formation temperatures, higher seawater/andesite ratios (3076–8124), the shorter duration of seawater–andesite interaction and/or the shorter fluid paths.

However, most As, Sb, and Mn in the Kueishantao hydrothermal fluids are leached from andesitic rocks into the fluids. Most Ca and Cl remained in the reaction zone of the subseafloor hydrothermal field during seawater and rock interactions. At present, the sampling numbers of hydrothermal fluids, plumes and andesite are not enough. In the future, it will be possible to understand the material and heat flux of hydrothermal fluids and plumes formed by subseafloor magma chambers to seawater and their effect on seawater and ecologic environments by carrying out long-term continual observations.

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