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# Gas discharges from the Kueishantao hydrothermal vents, offshore northeast Taiwan: Implications for drastic variations of magmatic/hydrothermal activities

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ABSTRACT

The chemical compositions of gas discharges from the Kueishantao (KST) hydrothermal field changed dramatically from 2000 to 2014. In this study, we established a gas mixing model for the KST gases. The $N_2$, Ar, and $CO_2$ contents were mixed from a magmatic endmember with $CO_2$ of about 990 mmol/mol, a hydrothermal and an atmospheric endmember enriched in $N_2$ and Ar. More than 71% KST gas components were mantle-derived/magmatic. The calculated endmember $N_2$/Ar ratio and Ar contents of the hydrothermal endmember (percolated fluid) are about 140 and 5.28–5.52 mmol/mol, respectively. This relatively elevated $N_2$/Ar ratio was probably caused by the thermogenic addition of $N_2$. The log($CH_4$/$CO_2$) values of the KST gas samples correlate well with the mixing temperature that estimated from the mixing ratio between the percolated fluid and the magmatic endmember. It is indicated that the KST $CH_4$ and $CO_2$ may have attained chemical equilibrium. The temporal variations of the KST gas compositions are determined by the mixing ratio, which is dependent on the magmatic activity underneath the KST field. With the decreasing of magmatic activity since 2005, the proportion of the hydrothermal endmember increased, along with the increasing of $N_2$, Ar, and $CH_4$ contents. This study proposed an effective model to quantitatively assess the sources of gas components discharged from submarine hydrothermal vents. In addition, it is suggested that the mixing between a magmatic and a hydrothermal endmember may play an important role in the concentrations of $CO_2$ and $CH_4$ in hydrothermal gas discharges.



## 1. Introduction

Submarine hydrothermal systems are usually driven by magmatic/volcanic activities and associated with seawater circulation (German and Von Damm, 2006; Von Damm, 1990; Yamaoka et al., 2015). Therefore, the chemical compositions of gas discharges from hydrothermal systems usually controlled by both magmatic degassing and fluid circulation (Caliro et al., 2015; Chiodini et al., 2006; Tassi et al., 2013). The mantle-derived/magmatic gas components mainly include $CO_2$, He, and $H_2S$/$SO_2$; while seawater circulation contributes $N_2$, $O_2$, and Ar for the hydrothermal gas discharges (Aiuppa et al., 2007; Caliro et al., 2015; Chen et al., 2016). $N_2$, Ar, and $CO_2$ can be either mantle-derived/magmatic, hydrothermal, or atmospheric components. In addition, $H_2$ and hydrocarbons can be generated during hydrothermal circulation via serpentinization and Fischer-Tropsch Type (FTT) reactions, respectively (Charlou et al., 1998; Giggenbach, 1997; Huang et al., 2016; McCollom, 2013; Proskurowski et al., 2008; Suda et al., 2014). Hydrocarbons can also be produced from thermogenic or biogenic processes (Botz et al., 2002; Oze et al., 2012). The boundaries between biotic and abiotic hydrocarbons, however, can be sometimes vague (Etiope and Schoell, 2014; Fiebig et al., 2015; Lang et al., 2012). The geochemical characteristics of gas discharges are critical for assessing/monitoring the magmatic/volcanic activity (Chiodini, 2009; Hilton et al., 1998; Jácome Paz et al., 2016) and the study on hydrocarbons can help investigating the global carbon cycle (Sephton and Hazen, 2013; Welhan and Craig, 1979) and discussing the origin of life (Holm and Charlou, 2001; Martin et al., 2008; McDermott et al., 2015). Therefore, it is important

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to study the evolution of gas components during hydrothermal circulation and to distinguish the mantle-derived/magmatic components from the hydrothermal sourced gases.

The Kueishantao (KST) submarine hydrothermal system is located offshore northeast Taiwan. There are >30 hydrothermal vents at depths of <30 m within this sediment-starved system (Chen et al., 2005b; Zeng et al., 2007, 2011). Preliminary studies suggested that the KST bubbling gases were dominated by $CO_2$ with contents higher than 900 mmol/mol (Chen et al., 2005b; Yang et al., 2005). The $CH_4$ and $N_2$ concentrations were <1 mmol/mol. Later studies by Zhang et al. (2013) and Chen et al. (2016), however, indicated that the KST $N_2$ and $CH_4$ concentrations have dramatically increased to >100 mmol/mol after 2010, accompanied by a significant decrease in $CO_2$ contents. Based on the chemical and isotopic compositions of the KST gases, it is suggested that the helium was mostly mantle-derived (Yang et al., 2005), while $CH_4$ may be derived from either a thermogenic or abiotic process, or a mixing of both. In addition, the KST $CH_4$ might be controlled by the $CO_2$-$CH_4$ equilibrium (Chen et al., 2016).

Nevertheless, some critical issues concerning the KST gases remain unsolved, including (1) the quantitative contributions for the KST components; (2) the mechanisms for the temporal variations of KST gas compositions; and (3) the evolution of KST gases during hydrothermal circulation. In this study, we established a gas mixing model and quantitatively assessed the sources of non-condensable gases ($N_2$, $CO_2$, Ar, and $O_2$). The mixing between a magmatic endmember, a hydrothermal endmember (percolated fluid), and an atmospheric endmember (air and/or seawater) was calculated and quantified by this model. In addition, we proposed a mechanism to explain the temporal variations of KST gas compositions during 2000 and 2014. Although it is known that some hydrothermal vents may cease to discharge (Chen et al., 2005b), this study shows for the first time that the existing shallow-water hydrothermal vents may also undergo drastic changes within a short time, which has been discovered in mid-Ocean ridge hydrothermal systems (Lilley et al., 2003).

## 2. Geological setting

KST (121.935–121.965° E, 24.835–24.850° N) is a Holocene volcanic island situates at the junction between the Okinawa Trough and the Philippine Plate (Fig. 1). The volcano last erupted at about 7000 years ago and the southern part of the island collapsed afterward (Chen et al., 2001; Kuo, 2001). However, because of the back-arc extending of the Okinawa Trough, the volcanic activity beneath the KST area is still vigorous. As a result, there are many submarine hydrothermal vents at depths of 5–30 m within this area. These vents can be classified as a group of vents with vent temperatures of 78–116 °C and fluid fluxes of up to 150 $m^3$/h, and a group of vents with temperatures of 30–65 °C and fluxes of <25 $m^3$/h (Chen et al., 2005a, 2005b). Both vents exhibited distinctive geochemical characteristics of vent fluids and gas discharges (Chen et al., 2005b; Chen et al., 2016), which provides an opportunity to study the processes controlling the geochemistry of the KST hydrothermal system. In this study, we selected the “yellow spring” (vent H, location: 24.83489° N, 121.96210° E, depth: 8 m) and the “white spring” (vent L, location: 24.83419° N, 121.96199° E, depth: 13 m) to study the temporal variations of KST gas compositions and their related magmatic/hydrothermal processes (Fig. 1).

## 3. Gas composition of the KST hydrothermal system

The bubbles discharged from the KST vents were collected and analyzed. The sampling during 2000 and 2003 was conducted by Kuo (2001), Chen et al. (2005b) and Yang et al. (2005). The sample collection during 2010 and 2014 was conducted and reported by Zhang et al. (2013) and Chen et al. (2016).

The compiled chemical compositions of the KST bubbling gases collected between 2000 and 2014 are shown in Table 1 of Chen et al. (2016). The most abundant gas components were $CO_2$ and $N_2$. $CO_2$ showed contents of 162–992 mmol/mol in the vent L gases and 366–987 mmol/mol in the vent H gases. The $N_2$ concentrations varied from 0.1 to 633.7 mmol/mol in the vent L gases and <0.1–429 mmol/mol in the vent H gases. The Ar contents fell in a range of between <0.1 and 6.3 mmol/mol in the vent L gases and <0.1–5.9 mmol/mol in the vent H gases. The predominant hydrocarbon, $CH_4$, also varied greatly from b.d.l. to 190 mmol/mol in the vent L gases and <0.1–44.3 mmol/mol in the vent H gases.

Because the KST $O_2$ was exclusively contributed by air contamination during/after sampling (Chen et al., 2016), we further corrected the data by removing the air components (Table 1). The results indicate that the KST gases were still dominated by $CO_2$ and $N_2$, which changed dramatically during the past decade. For instance, the contents of $N_2$, Ar, and $CH_4$ increased dramatically after 2010, accompanied with decreasing $CO_2$ contents. The vent L $CH_4$ concentrations increased from trace amounts to higher than 100 mmol/mol after 2010. Therefore, it is essential to understand the mechanism controlling the variation of KST gas compositions.

## 4. Discussion

### 4.1. Sources of non-condensable gases

Based on the $CO_2/^3He$ ratios of $10^8$–$10^{10}$ and $\delta^{13}C(CO_2)$ values of between −5.5 and −8.2‰, the contributions of each endmember for the KST $CO_2$ were preliminary estimated as: mantle (8–32%), sediment (14–27%), and limestone (54–72%) (Chen et al., 2016; Ishibashi et al.,

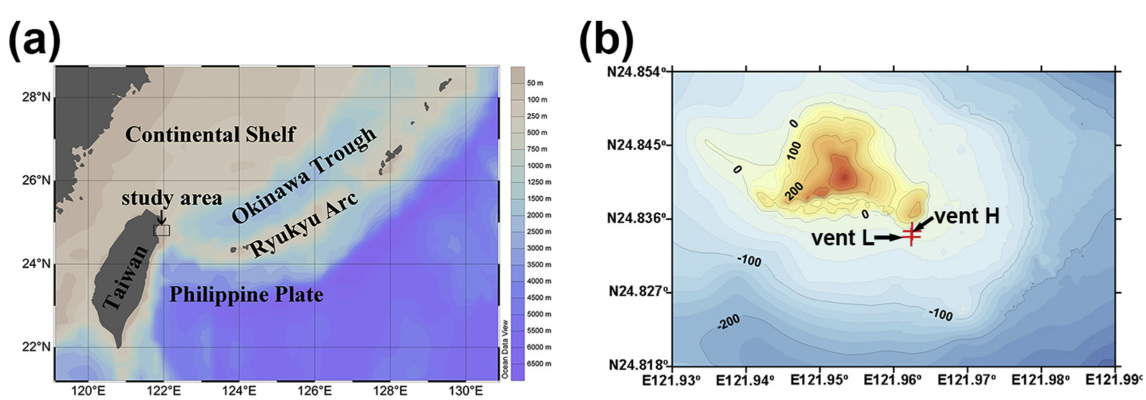


**Fig. 1.** (From Chen et al., 2016) (a) Geological setting of the Kueishantao (KST) hydrothermal field, which is located at the southwestern end of the Okinawa Trough. (b) Bathymetric map of the KST area (contours in meters). The studied higher-temperature vent (vent H) and lower-temperature vent (vent L) are marked as red crosses. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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