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Dissolved metals' transformation, fluxes from shallow water hydrothermal vents off Kueishantao Islet, Taiwan, China and potential impacts on nearby ecosystem

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Abstract: Shallow water hydrothermal vents are one of important sources of trace elements in the ocean, which potentially impact coastal ecosystem. We investigated two shallow water hydrothermal vents (white and yellow vents) for siderophile and chalcophile elements (Fe/Mn/V/Cu/Mo) off Kueishantao islet, Taiwan, China. The results show that dissolved metals were generally lower in the yellow vent than that in the white vent. Especially waters inside the white vent was enriched with dissolved metals such as Mn and Fe. High abundance of sulfide particles was identified both in hydrothermal plumes. The fluxes of dissolved elements was estimated from the KSI hydrothermal vents were as the following annually: 0.10–1.23 kg Fe, 0.08–28 kg Mn, 33.4–306 g V, 2.89–77.7 g Cu, and 54.3–664 g Mo. In summary, our study identified a large number of acid-reducible sulfides, ore-forming metals in these shallow water hydrothermal vents along with those highly toxic and acidic hydrothermal fluids. The unique ecosystem nearby further suggests such release of chemical substances from these vents play a key role in moderating the evolution of marine environment nearby.

Introduction

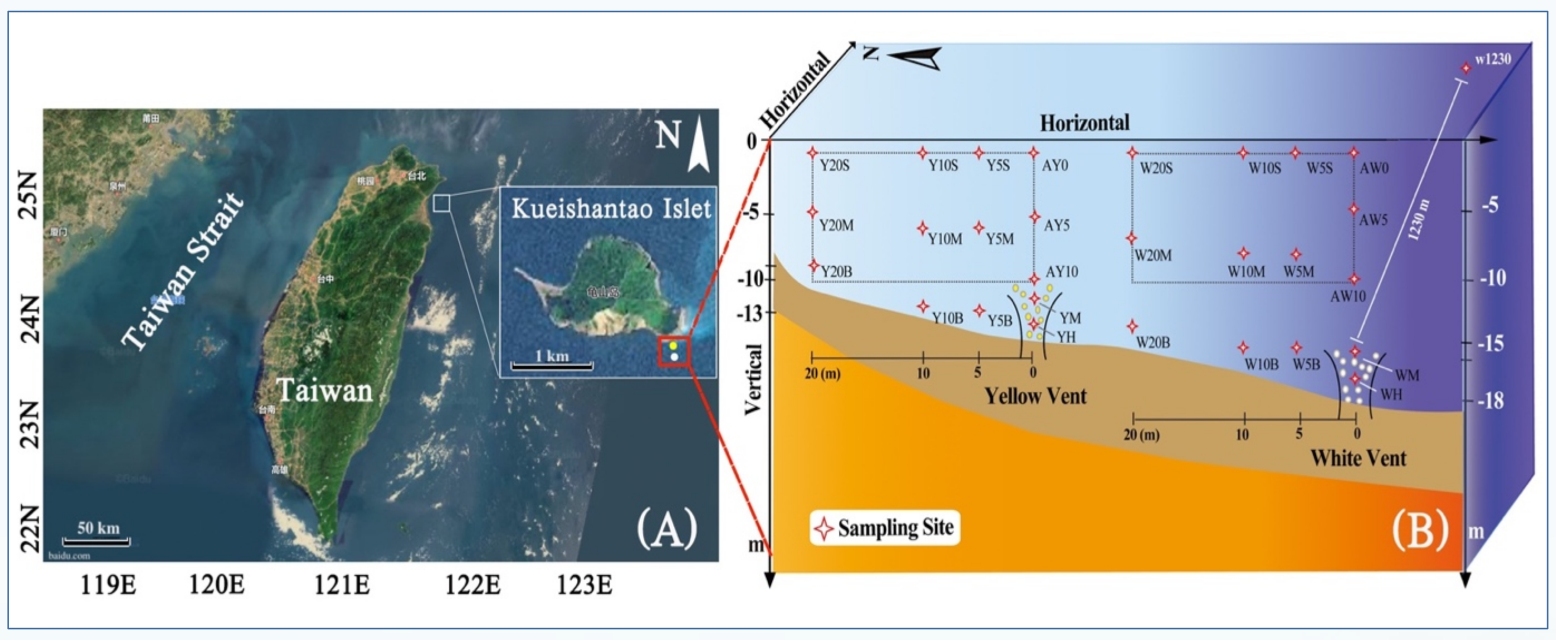
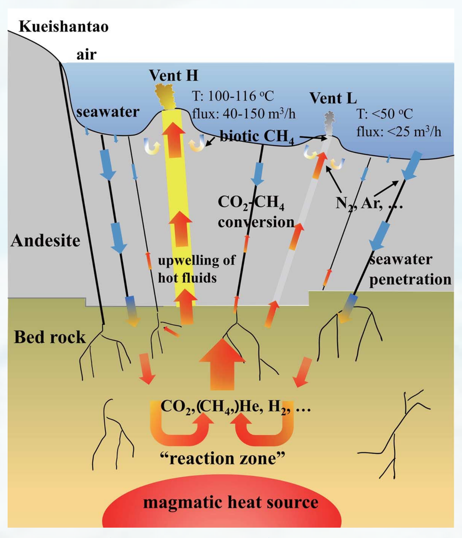


Figure 1. Satellite image (A) and sampling sites (B) in Kueishantao area

➢ Kueishantao Islet (KSI) shallow hydrothermal ecosystems are sources of chemical elements and gases to the ambient coastal ocean (Chen et al, 2011).

➢ Discharge of metallic minerals, accumulation of sulfide, distinct microbial communities appeared in vent (Tang et al., 2018).

➢ Vent-fluid discharges and the harmful effects of hydrothermal substances on autotrophic activities have been underestimated (Lin et al., 2021).



(Chen et al., 2016)

Experimental method

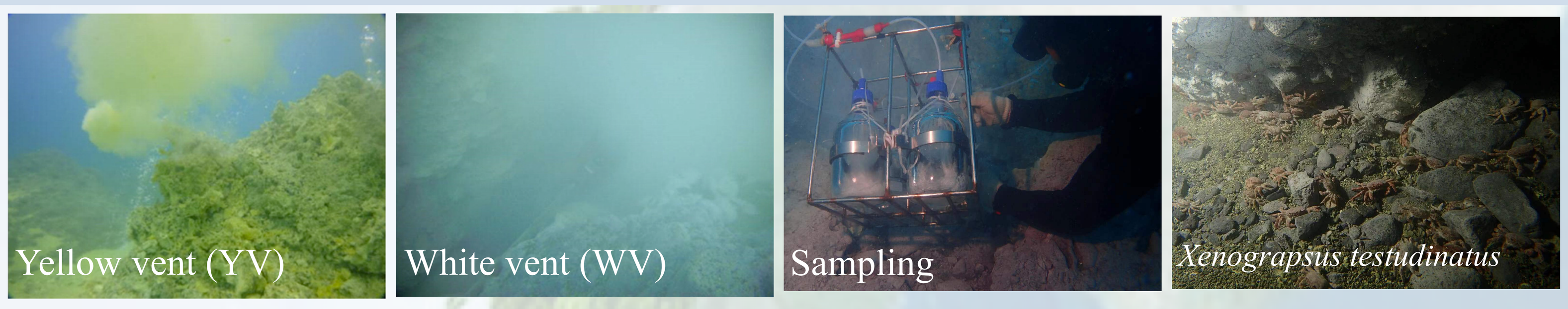
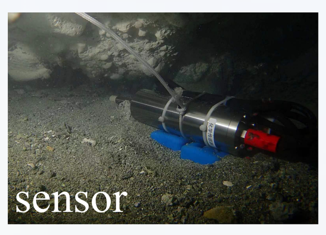


Figure 2. Sampling and crabs near hydrothermal vents (Photos by Seawatch Co.)

➢ Water samples were collected in titanium-made automatic gas-tight hydrothermal samplers with a volume of 5 L (Fig. 2).

➢ Samples were acidified, demineralized, and then enriched with Chelex-100 resins followed the previous procedure (Wang et al., 2012).

➢ Enriched samples were used to determine trace metal elements in Fe, Mn, V, Cu, and Mo by ICP-MS (Agilent 7700)



➢ $Annual\ Flux = f \times C \times 24 \times 365$

Where f is flow rate (m^3/hour) of hydrothermal vents, C is the concentration of dissolved trace metals (nmol/L).

Results and discussion

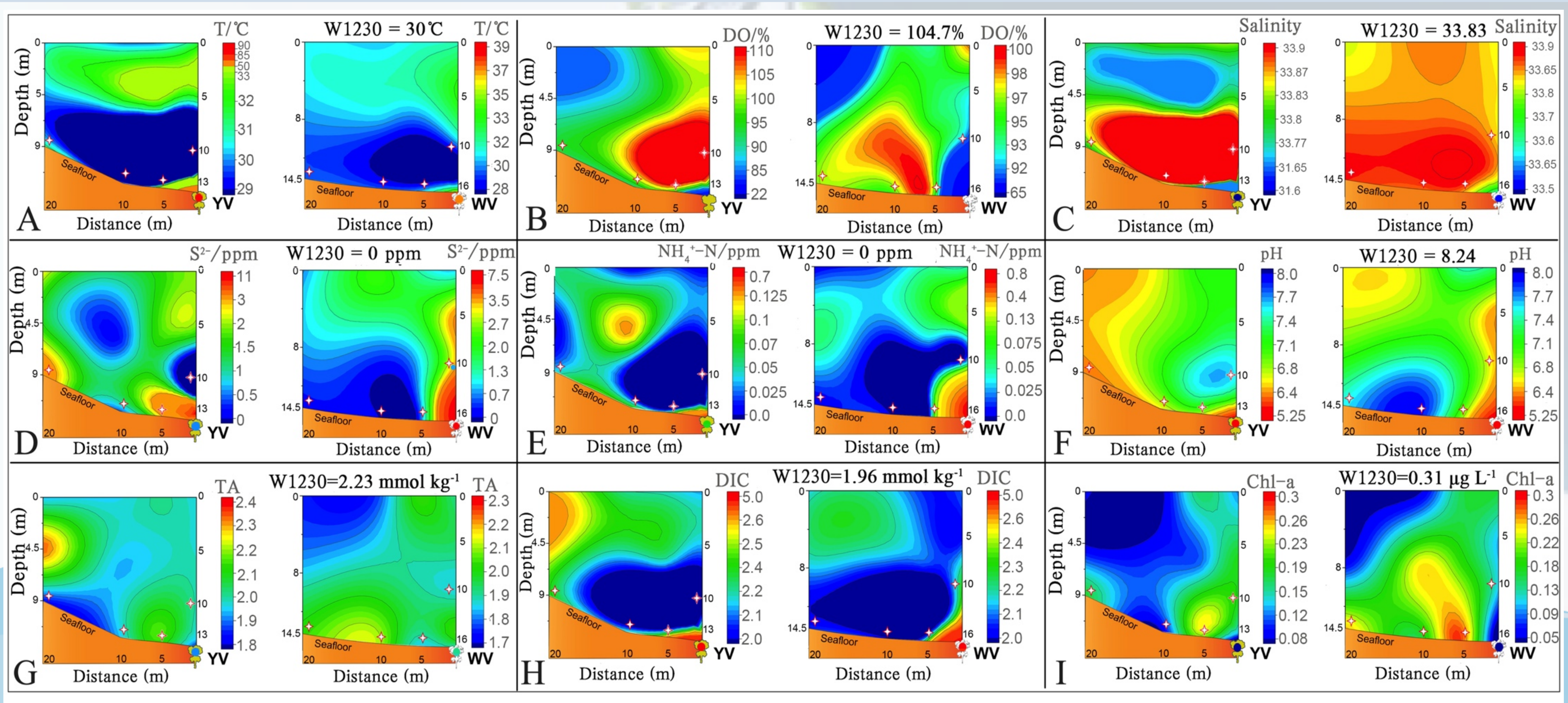


Figure 3. Environmental characteristics of two hydrothermal vents and background site (W1230)

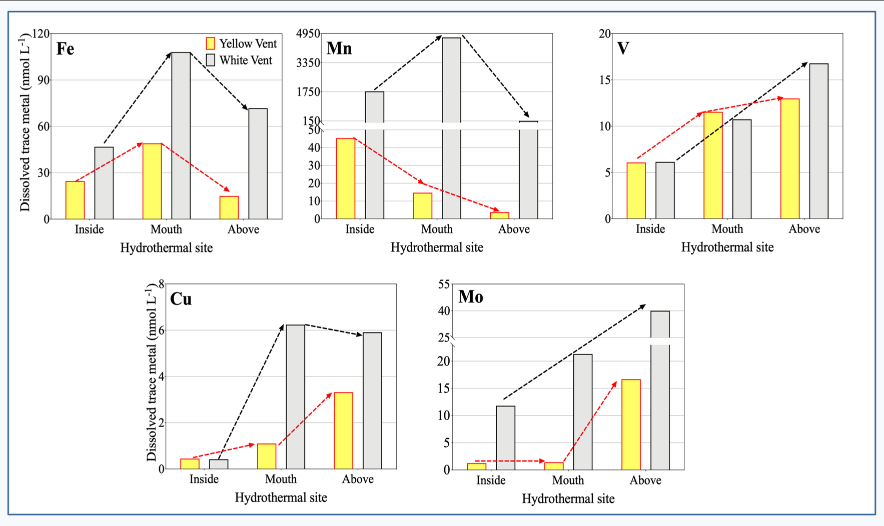


Figure 4. Dissolved heavy metal concentration

	Sality	S	NH4+	pH	TA	DIC	Chl-a	Fe	Mn	V	Cu
Sality	1										
S	0.143	1									
NH_4^+	**-0.771**	0.314	1								
pH	**0.943[b]**	0.086	**-0.714**	1							
TA	**0.657**	0.371	-0.086	**0.600**	1						
DIC	**-0.943[b]**	-0.086	**0.714**	**-1.00[b]**	**-0.600**	1					
Chl-a	**0.812[a]**	0.174	**-0.638**	**0.928[b]**	0.464	**-0.928[b]**	1				
Fe	-0.429	**0.771**	**0.771**	-0.486	0.143	0.486	-0.348	1			
Mn	-0.486	0.143	**0.829[a]**	-0.314	0.143	0.314	-0.319	0.429	1		
V	**0.943[b]**	0.086	**-0.714**	**1.00[b]**	**0.600**	**-1.00[b]**	**0.928[b]**	-0.486	-0.314	1	
Cu	**0.543**	0.143	-0.086	**0.600**	**0.886[a]**	**-0.600**	**0.580**	0.029	0.200	**0.600**	1
Mo	**0.600**	0.029	-0.143	**0.714**	**0.771**	**-0.714**	**0.551**	-0.257	0.371	**0.714**	**0.771**

[a] Correlation is significant at 0.05 level (two-tailed).
[b] Correlation is significant at 0.01 level (two-tailed).

Table 1. Correlations among determined parameters

➢The environmental parameters include the following: temperature (T), dissolved oxygen (DO), salinity, sulfide (S), nutrients (NH_4^+), pH, total alkalinity (TA), dissolved inorganic carbon (DIC), and chlorophyll a (Chl-a) are shown in Fig. 3.

➢Most elevated metals (Fig. 4) were resulting from geochemical reaction: chloride-induced desorption from the suspended sediments (Fig. 3C), oxidation of metal sulfides (Fig. 3D), and the partial dissolution of minerals (Wang et al., 2012).

➢V, Cu, and Mo showed similar correlations among each other, which may originated from the same source (seawater). Mn acted as major ions but co-precipitated in the white vent (Fig. 4).

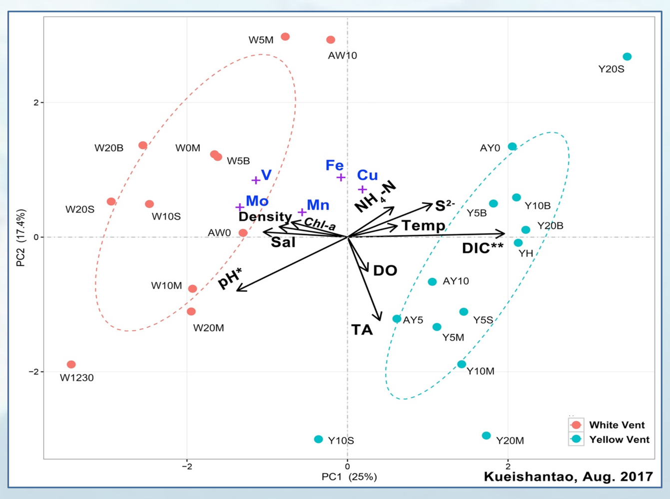


Figure 5. PCA results

Study area	Sampling site	Type	Fe	Mn	V	Cu	Mo	Ca	Mg
Kueishantao [A]	Yellow vent fluids	Hot T(°C) in total	22.3±32.8 μM	1.31±2.43 μM	-	218 ± 862 μM	-	9.43±0.50 mM	48.7±2.25 mM
(Chen et al, 2005)	Yellow vent fluids	Low T(°C) in total	7.92±6.55 μM	0.58±0.51 μM	-	5.25±8.52 μM	-	9.64±0.36 mM	49.8±1.52 mM
Kueishantao [B]	*Xenograpsus testudinatus*	Gill (ug/g DW)	159 ± 71.0	3.31 ± 1.31	-	290 ± 91.41	-	-	-
(Peng et al, 2011)	(crab in dry weight)	Hepatopancreas (ug/g)	175 ± 99.2	3.95 ± 2.35	-	53.4 ± 37.6	-	-	-
		Muscle (ug/g DW)	37.04 ± 21.72	0.69 ± 0.5	-	74.6 ± 27.1	-	-	-
Kueishantao [C]	surface seawater	Total (unfiltered)	1.96-7.74 μM	0.78-1.19 μM	-	-	-	10.6-12.5 mM	51.1-55.5 mM
(Chen et al., 2018)	Yellow vent fluids	Total (unfiltered)	7.13-7.86 μM	1.14-1.15 μM	-	-	-	10.0-10.3 mM	50.1-50.9 mM
	Yellow vent plume	Total (unfiltered)	9.13-13.6 μM	1.37-1.43 μM	-	-	-	10.3-10.5 mM	50.5-50.6 mM
	White vent fluids	Total (unfiltered)	35.7 μM	2.01 μM	-	-	-	9.2 mM	48.4 mM
	White vent plume	Total (unfiltered)	4.19-6.54 μM	0.96-1.42 μM	-	-	-	10-10.2 mM	50.2-52.4 mM
This study (2017)	fluids	Dissolved (nM) / Flux	24.6 / 0.62 kg	45.4 /1.13 kg	6.07 / 139 g	0.45 / 12.9 g	1.25 / 54.3 g	-	0.99 / 42.8 g
Yellow vent	plume	Dissolved (nM) / Flux	49.0 /1.24 kg	14.7 / 0.36 kg	11.5 / 266 g	1.10 / 31.7 g	1.42 / 61.6 g	-	1.29 / 55.9 g
	seawater	Dissolved (nM) / Flux	19.2 / 0.49 kg	3.14 / 0.08 kg	13.3 / 306 g	2.69 / 77.7 g	21.1 / 915 g	-	1.62 / 70.2 g
	fluids	Dissolved (nM) / Flux	46.8 / 0.28 kg	1770 /10.5 kg	6.13 / 33.7 g	0.42 / 2.89g	11.8 / 122 g	-	1.09 / 11.3 g
White vent	plume	Dissolved (nM) / Flux	108 / 0.65 kg	4730 / 28.0 kg	10.7 / 59.0 g	6.24 / 43.1g	21.3 / 221 g	-	2.33 / 24.1 g
	seawater	Dissolved (nM) / Flux	15.8 / 0.1 kg	80.5 / 0.48 kg	14.6 / 80.2 g	4.04 / 27.9 g	64.16 / 664 g	-	1.34 / 13.9 g

Table 2. Heavy metals comparison and annual fluxes

➢The determined parameters of the two vents can be classified into two components with a total cumulative variance of 42.4% based on PCA (Fig. 5).

➢The explanation of DIC (p <0.01) and pH (p <0.05) to environmental differentiation are both significant.

➢ The estimated annual fluxes of dissolved elements emanating from the hydrothermal vents were: 0.10–1.23 kg Fe, 0.08–28 kg Mn, 33.4–306 g V, 2.89–77.7 g Cu, and 54.3–664 g Mo (Table. 2).

Graphic abstract

➢The temperature of YV (90°C) is nearly twice as high as that of WV (50°C).

➢YV contains more yellowish sulfur particles (average pH≈5.25), while WV discharged ivory-white fluids with higher pH (≈5.35) .

➢The YV has a large flow rate and a large change in salinity, and chemical reactions are severely affected by sulfide, in comparison with the WV.

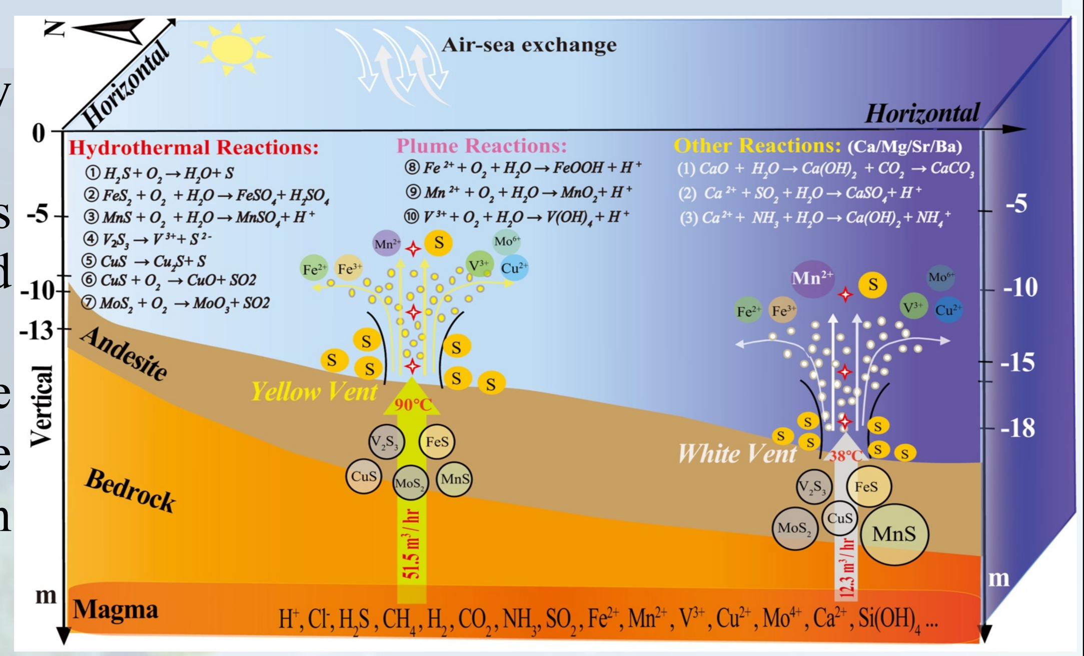


Figure 6. Schematic of chemical reactions

Summary

☐ Dissolved metal Fe and Mn contribute to ambient environment significantly; V, Cu, and Mo may originate from the source of seawater.

☐ The release of dissolved metals in hydrothermal fluids of WV is much higher than that of YV.

☐ The study found that a large number of acid-reducible sulfides, ore-forming metals, and highly toxic and acidic hydrothermal fluids constitute a distinct ecosystem affected by hydrothermal activities

Acknowledgements

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