

Supplementary Table S1. Values for GEOTRACES Intercalibration for Dissolved Mn, Fe, Cu, and Zn in this study (nmol/kg) (<http://www.geotraces.org/sic/intercalibrate-a-lab/standards-and-reference-materials>).

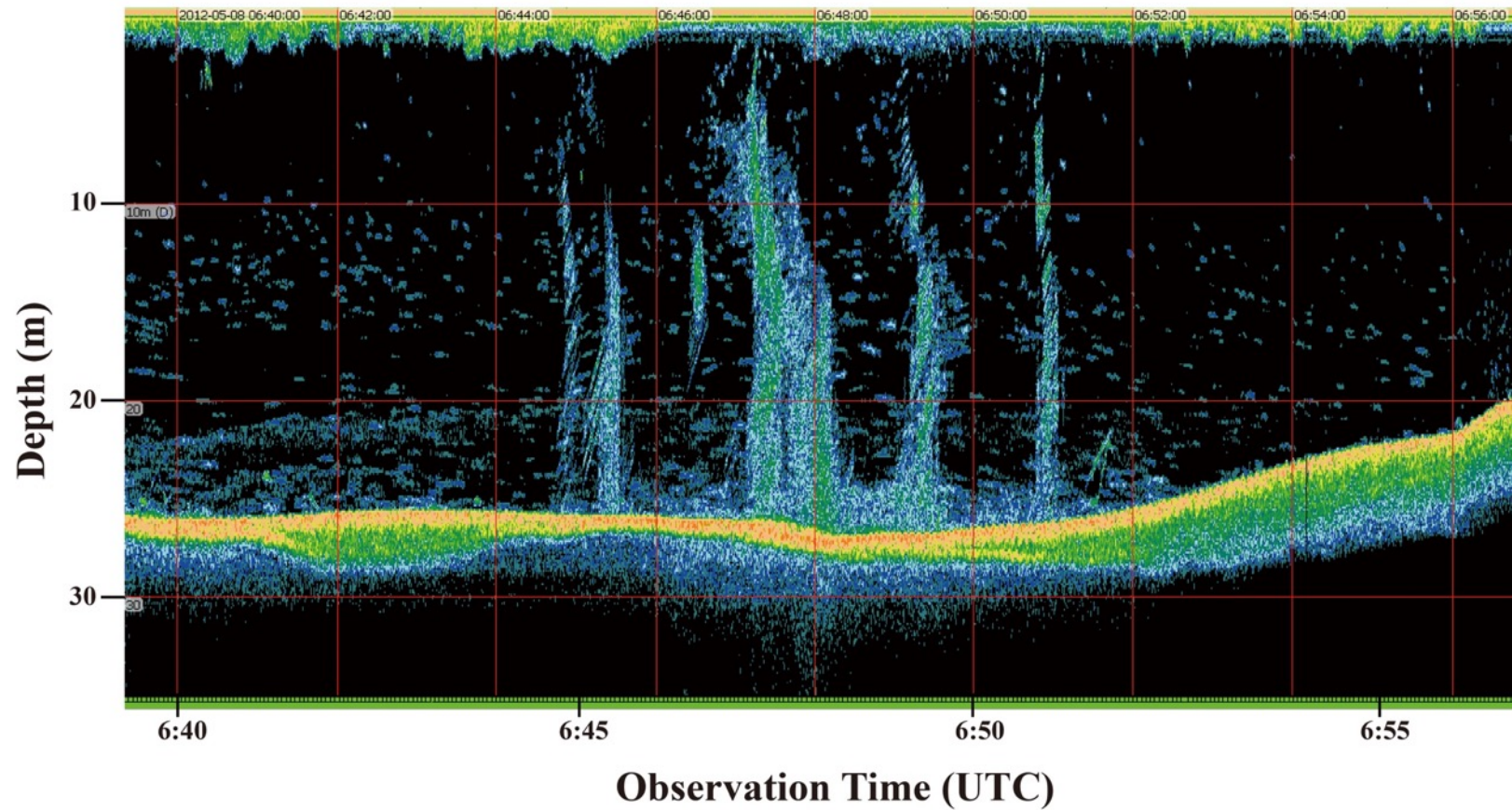
Sample		ICP-MS			CSV
		Mn	Fe	Cu	Zn
GS	This study				0.038±0.011
	Consensus value				0.041±0.007
GD	This study	0.25± 0.01	1.09±0.02	1.69±0.09	1.62±0.14
	Consensus value	0.21±0.03	1.00±0.10	1.62±0.07	1.71±0.07
SAFe D2	This study	0.42± 0.02	1.019±0.033	2.12±0.23	
	Consensus value	0.35±0.05	0.993±0.023	2.28±0.15	

Supplementary Table S2. Comparative data on the Tachibana Bay and other shallow coastal hydrothermal activity areas.

Location	Sampling methods	Potential Temp. (°C)	Salinity (PSU)	Mn	Fe	Cu	Zn	S	References
Tachibana Bay	Seawater sampler (OTE)	16.8–19.3	33.5–33.6	13.3–39.3 nM	1.8–16.5 nM	1.8–2.6 nM	0.3–3.1 nM	≤59.4 nM	This study
Bay of Plenty	Seawater sampler (Niskin)	13.0–20.6				0.5–1.0 nM			(Kleint <i>et al.</i> 2015)
Tachibana Bay	SCUBA diving	70.0–80.0	15.6–29.1	1.1–7.2 μM	0.1–1.3 μM				(Takeda 2018)
Santorini		22.0–30.0		4.9–25.5 μM	0.04–245.3 μM	28.3–86.6 nM	≤1.3 μM		(Smith and Cronan 1983)
				7.4 μM	94.2 μM				(Varnavas and Cronan 2005)
Milos	SCUBA diving	25.0–80.6				0.8–3.8 nM		≤0.5 mM	(Kleint <i>et al.</i> 2015)
	<i>in situ</i> sensor	31.6–46.4						0.5–1.3 mM	(Yücel <i>et al.</i> 2013)
				9.5 μM	5.8 μM				(Varnavas and Cronan 2005)
Dominica	SCUBA diving	25.0–75.0	10.9–34.0			0.6–21.5 nM			(Kleint <i>et al.</i> 2015)
	SCUBA diving	44.0–74.0		≤9.8 μM	≤113.7 μM				(McCarthy <i>et al.</i> 2005)
Tatum Bay	SCUBA diving	80.0–91.0		≤8.7 μM	≤30.0 μM				(Pichler <i>et al.</i> 1999)
Matupi Harbour	SCUBA diving	29.0–35.0	34.3–34.7	≤640.7 μM	≤30.4 μM		≤21.4 μM		(Tarasov <i>et al.</i> 1999)

Supplementary Table S3. Zn complexation data from other coastal areas. The values of $\log K'_{\text{ZnL,Zn}^{2+}}$ for previous studies (ASV method) are calculated by the equation ($K'_{\text{ZnL,Zn}^{2+}} = K'_{\text{ZnL,Zn}'} \times \alpha_{\text{Zn}'}$)

Location	C_{Zn} (nM)	C_{L} (nM)	$\log K'_{\text{ZnL,Zn}^{2+}}$	Organic Zn (%)	Zn^{2+} (nM)	References
Narragansett Bay	22–28	50–104	7.8–8.2	55–65	2.5–4.2	(Muller and Kester 1991)
	16–72	11–48	≥ 9.3	50–97	0.3–13	(Kozelka and Bruland 1998)
Chesapeake Bay	4–20	8–200	9.8–10.3	95–99	0.01–0.3	(Henry and Donat 1996)
Delaware Bay	3.5	15	≥ 11.2	98	0.04	(Lewis <i>et al.</i> 1995)
Tachibana Bay	0.3–3.1	0.9–1.6	9.9–10.3	88–95	0.02–0.17	This study



Supplementary Fig. S1. Example of the quantitative echosounder color image in the coastal area of Tachibana Bay near the Obama hot springs. Light blue streaks indicate fumarolic gas emissions.

Theory of Zn speciation analysis

Zn speciation was determined through titration by using competitive ligand equilibrium/adsorptive cathodic stripping voltammetry (CLE-ACSV) (van den Berg 1985; Donat and Bruland 1990; Kim *et al.* 2015), which uses a competitive equilibrium between Zn-complexing ligands naturally present in the sample and a competing ligand (APDC). A titration curve is produced by adding increasing concentrations of Zn. Once the natural ligands are saturated with Zn, the reduction peak current increases in proportion to the added Zn concentration. The dissolved Zn concentration (C_{Zn}) of a sample can be defined as

$$C_{Zn} = [Zn'] + [ZnL] + [ZnPDC] \quad , \quad (1)$$

where $[Zn']$ is the concentration of inorganic Zn, $[ZnPDC]$ is the concentration of Zn complexed with APDC (existing as either $ZnPDC^+$ or $Zn(PDC)_2$) (Donat and Bruland 1990), and $[ZnL]$ is the concentration of Zn complexed by natural ligands. By using a simple one-ligand model, the complexation of Zn in seawater by natural ligands can be defined as

$$K'_{ZnL,Zn^{2+}} = \frac{[ZnL]}{[Zn^{2+}][L']} \quad , \quad (2)$$

where $K'_{ZnL,Zn^{2+}}$ is the conditional stability constant of the Zn complex with respect to Zn^{2+} in seawater and $[L']$ is the concentration of the free ligand.

The total ligand concentration (C_L) of a sample can be defined as

$$C_L = [ZnL] + [L'] \quad . \quad (3)$$

Substitution for $[L']$ in Eq. (2) using Eq. (3) and rearranging terms gives the Van den Berg/Ružić linearization (Ružić 1982; van den Berg 1982). The equation for the resulting line is

$$\frac{[Zn^{2+}]}{[ZnL]} = \frac{[Zn^{2+}]}{C_L} + \frac{1}{(K'_{ZnL,Zn^{2+}} \times C_L)} \quad , \quad (4)$$

When values of $[Zn^{2+}]/[ZnL]$ are plotted against corresponding values of $[Zn^{2+}]$, a linear relationship with a slope equal to $1/C_L$ and with the intercept yielding $1/(K'_{ZnL,Zn^{2+}} \times C_L)$ is obtained.

The observed reduction peak current (i_p) is related to the concentration of Zn^{2+} by the equation

$$[Zn^{2+}] = \frac{i_p}{S \times \alpha'} \quad , \quad (5)$$

where S is the sensitivity, which is calibrated by standard additions to UV-irradiated seawater (UVSW) and α' is the overall side reaction coefficient for Zn:

$$\alpha' = \alpha_{Zn} + \alpha_{ZnPDC} \quad , \quad (6)$$

where α_{Zn} is the inorganic side reaction coefficient for Zn. A value of 2.2 (Turner *et al.* 1981) was used in this study. α_{ZnPDC} , the side reaction coefficient for Zn with APDC, is fixed by the concentration of APDC added to the sample. α_{ZnPDC} can be calculated as

$$\alpha_{ZnPDC} = K'_{ZnPDC}[APDC'] \quad , \quad (7)$$

where K'_{ZnPDC} is a conditional stability constant and $[APDC']$ is the concentration of APDC not complexed by Zn^{2+} . Because this $[APDC']$ is much greater than that of Zn, the total APDC concentration ($[APDC']_T$) can be selected for calculations. A K'_{ZnPDC} value of $10^{4.4}$ was used for seawaters of pH 8.2 with borate buffer (Ellwood and van den Berg 2000). $[ZnL]$ can be calculated as

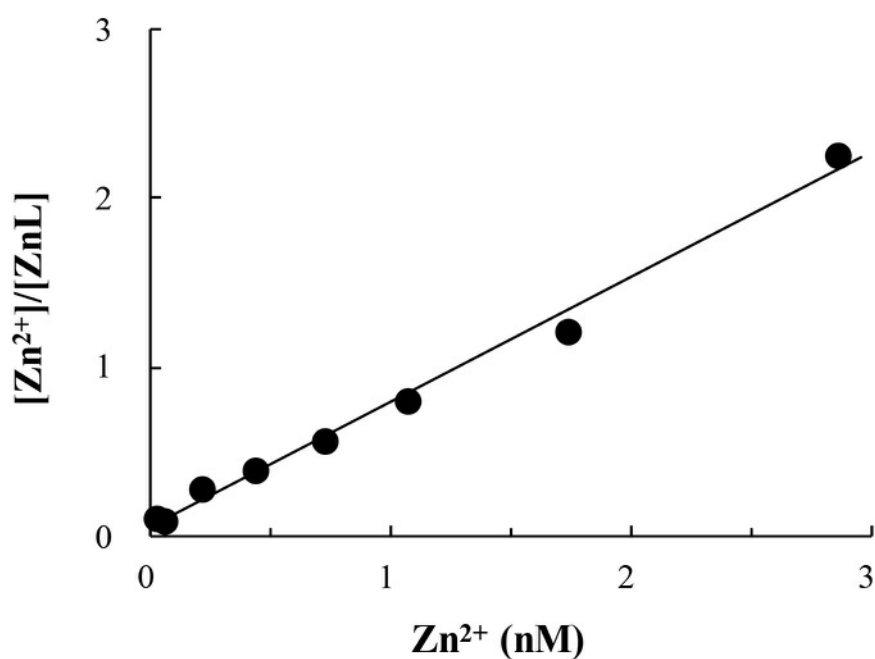
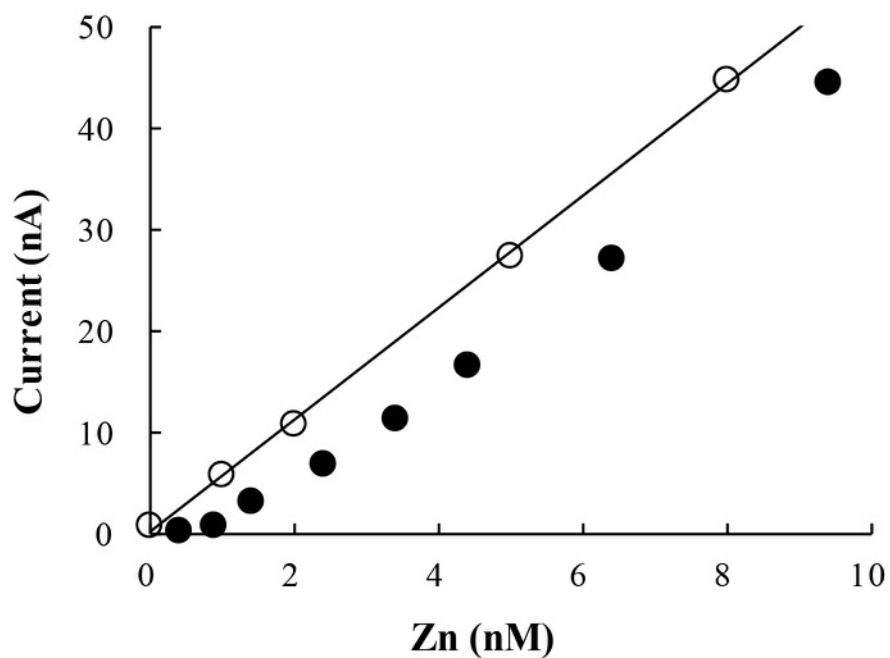
$$[ZnL] = C_{Zn} - \left(\frac{i_p}{S}\right) \quad , \quad (8)$$

where (i_p/S) is equal to labile Zn (Zn_{labile}) concentration ($= [Zn'] + [ZnPDC]$). Combining Eqs. (5) and (8), $[Zn^{2+}]/[ZnL]$ can be calculated as

$$\frac{[Zn^{2+}]}{[ZnL]} = \frac{i_p}{\alpha' \times (S \times C_{Zn} - i_p)} \quad , \quad (9)$$

Finally, once C_L and $K'_{ZnL,Zn^{2+}}$ have been determined, the concentration of Zn^{2+} can be calculated by the following quadratic equation (Ellwood and van den Berg 2000):

$$C_{Zn} = 0 \quad [Zn^{2+}]^2 \cdot \alpha_{Zn} \cdot K'_{ZnL,Zn^{2+}} + [Zn^{2+}](K'_{ZnL,Zn^{2+}} \cdot C_L - K'_{ZnL,Zn^{2+}} \cdot C_{Zn} + \alpha_{Zn}) - \quad (10)$$



Supplementary Fig. S2. Example of Zn titration data. (Top) The response of Zn peak current with increasing Zn additions (Stn. 6, 17 m). Black line and blank circles indicate the response of UV-irradiated seawater (UVSW) (Bottom) Linear relationship obtained by transforming the titration data. The calculated C_L and $\log K'_{ZnL,Zn^{2+}}$ were 1.4 nM and 10.2, respectively.

References for Supplemental Information

- Donat, J. R., and Bruland, K. W. (1990). A comparison of two voltammetric techniques for determining zinc speciation in Northeast Pacific Ocean waters. *Marine Chemistry* **28**, 301–323. doi:10.1016/0304-4203(90)90050-M
- Ellwood, M. J., and van den Berg, C. M. G. (2000). Zinc speciation in the Northeastern Atlantic Ocean. *Marine Chemistry* **68**, 295–306. doi:10.1016/S0304-4203(99)00085-7
- Henry, C. W., and Donat, J. R. (1996). Zinc complexation and speciation in the Chesapeake Bay. *EOS Trans. Am. Geophys. Union* **77**, 072.
- Kim, T., Obata, H., Kondo, Y., Ogawa, H., and Gamo, T. (2015). Distribution and speciation of dissolved zinc in the western North Pacific and its adjacent seas. *Marine Chemistry* **173**, 330–341. doi:10.1016/j.marchem.2014.10.016
- Kleint, C., Kuzmanovski, S., Powell, Z., Bühring, S. I., Sander, S. G., and Koschinsky, A. (2015). Organic Cu-complexation at the shallow marine hydrothermal vent fields off the coast of Milos (Greece), Dominica (Lesser Antilles) and the Bay of Plenty (New Zealand). *Marine Chemistry* **173**, 244–252. doi:10.1016/j.marchem.2014.10.012
- Kozelka, P. B., and Bruland, K. W. (1998). Chemical speciation of dissolved Cu, Zn, Cd, Pb in Narragansett Bay, Rhode Island. *Marine Chemistry* **60**, 267–282. doi:10.1016/S0304-4203(97)00107-2
- Lewis, B. L., Luther, G. W., III, Lane, H., and Church, T. M. (1995). Determination of metal–organic complexation in natural waters by SWASV with pseudopolarograms. *Electroanalysis* **7**, 166–177. doi:10.1002/elan.1140070213
- McCarthy, K. T., Pichler, T., and Price, R. E. (2005). Geochemistry of Champagne Hot Springs shallow hydrothermal vent field and associated sediments, Dominica, Lesser Antilles. *Chemical Geology* **224**, 55–68. doi:10.1016/j.chemgeo.2005.07.014
- Muller, F. L. L., and Kester, D. R. (1991). Measurement of the different forms of zinc in Narragansett Bay water based on the rate of uptake by a chelating resin. *Marine Chemistry* **33**, 171–186. doi:10.1016/0304-4203(91)90064-4
- Pichler, T., Veizer, J., and Hall, G. E. M. (1999). The chemical composition of shallow-water hydrothermal fluids in Tutum Bay, Ambitle Island, Papua New Guinea and their effect on ambient seawater. *Marine Chemistry* **64**, 229–252. doi:10.1016/S0304-4203(98)00076-0
- Ružić, I. (1982). Theoretical aspects of the direct titration of natural waters and its information yield for trace metal speciation. *Analytica Chimica Acta* **140**, 99–113. doi:10.1016/S0003-2670(01)95456-X
- Smith, P. A., and Cronan, D. S. (1983). The geochemistry of metalliferous sediments and waters associated with shallow submarine hydrothermal activity (Santorini, Aegean Sea). *Chemical Geology* **39**, 241–262. doi:10.1016/0009-2541(83)90017-7
- Takeda, S. (2018). Shallow submarine hydrothermal system in Tachibana Bay, Nagasaki, Japan-II: Chemical characteristics of submarine hot spring water. *Bulletin of the Faculty of Fisheries, Nagasaki University* **99**, 1–6.
- Tarasov, V. G., Gebruk, A. V., Shulkin, V. M., Kamenev, G. M., Fadeev, V. I., Kosmynin, V. N., Malakhov, V. V., Starynin, D. A., and Obzhairov, A. I. (1999). Effect of shallow-water hydrothermal venting on the biota of Matupi Harbour (Rabaul Caldera, New Britain Island, Papua New Guinea). *Continental Shelf Research* **19**, 79–116. doi:10.1016/S0278-4343(98)00073-9

- Turner, D. R., Whitfield, M., and Dickson, A. G. (1981). The equilibrium speciation of dissolved components in freshwater and sea water at 25°C and 1 atm pressure. *Geochimica et Cosmochimica Acta* **45**, 855–881. doi:10.1016/0016-7037(81)90115-0
- van den Berg, C. M. G. (1982). Determination of copper complexation with natural organic ligands in seawater by equilibration with MnO₂ I. Theory. *Marine Chemistry* **11**, 307–322. doi:10.1016/0304-4203(82)90028-7
- van den Berg, C. M. G. (1985). Determination of the zinc complexing capacity in seawater by cathodic stripping voltammetry of zinc—APDC complex ions. *Marine Chemistry* **16**, 121–130. doi:10.1016/0304-4203(85)90017-9
- Varnavas, S. P., and Cronan, D. S. (2005). Submarine hydrothermal activity off Santorini and Milos in the Central Hellenic Volcanic Arc: A synthesis. *Chemical Geology* **224**, 40–54. doi:10.1016/j.chemgeo.2005.07.013
- Yücel, M., Sievert, S. M., Vetriani, C., Foustoukos, D. I., Giovannelli, D., and Le Bris, N. (2013). Eco-geochemical dynamics of a shallow-water hydrothermal vent system at Milos Island, Aegean Sea (Eastern Mediterranean). *Chemical Geology* **356**, 11–20. doi:10.1016/j.chemgeo.2013.07.020