

1 **Supplementary information to**

2 **Copper-rich deep-sea hydrothermal vent minerals facilitate**
3 **hydrogen cyanide formation from glycine**

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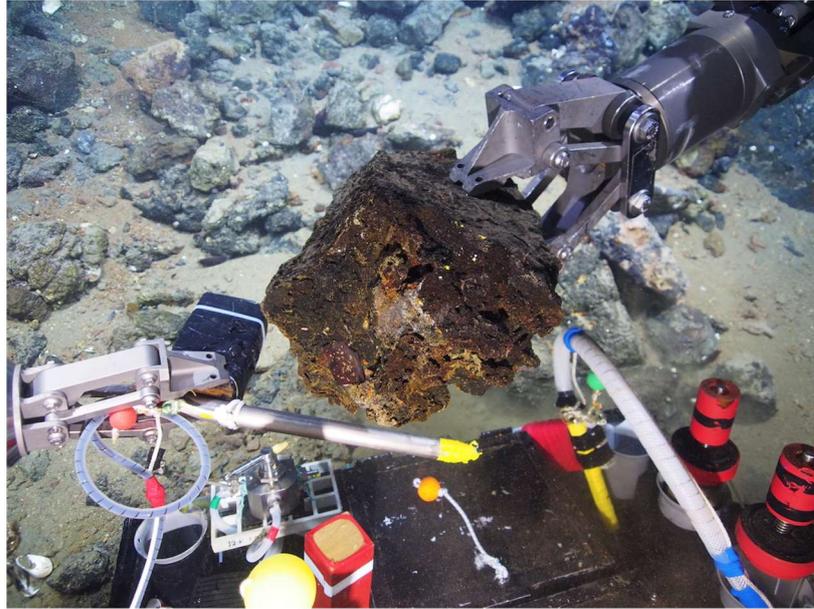
This file contains:

Supplementary Figure Fig. S1 to S7

Supplementary Table S1

Reference list

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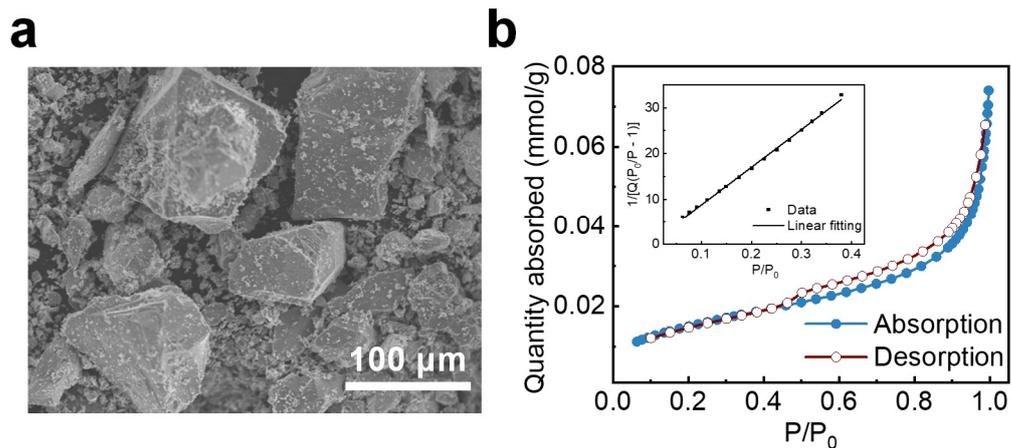


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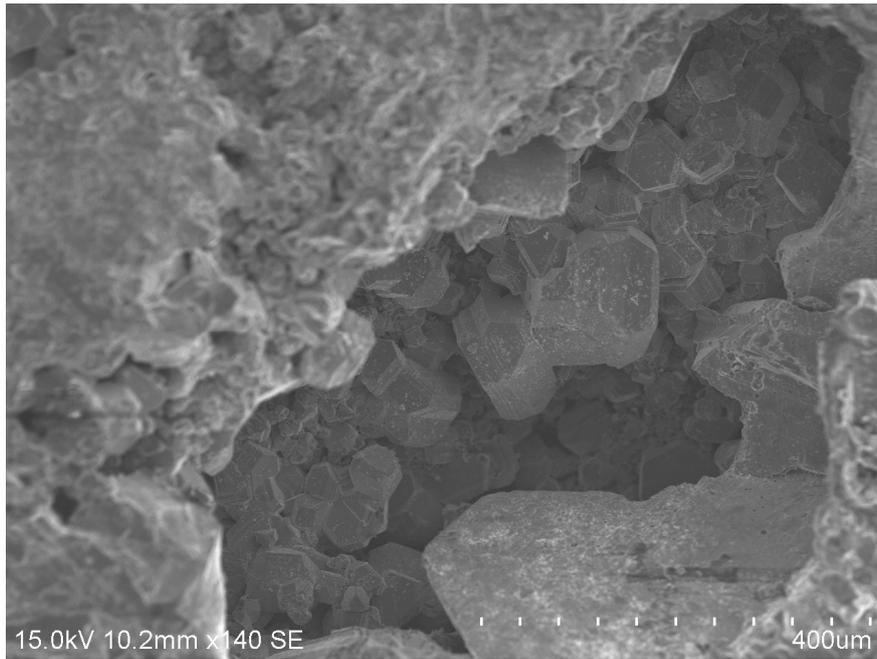
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Figure S1. Collection of chimney sample KK805#R02. (a) The sample was collected robotically from the Iheya Okinawa Trough in 2018/11/6 by vessel Kaiko / Kairei with cruise code KR18-14 Leg2. The sample was collected from the sea floor at an active NBC chimney. (b) A portion of the rock (right) that contained a golden band, while oxidized iron species appeared as red rust on the surface. The cut slice (left) showed a region of golden color that corresponded to chalcopyrite, as identified by XRD.



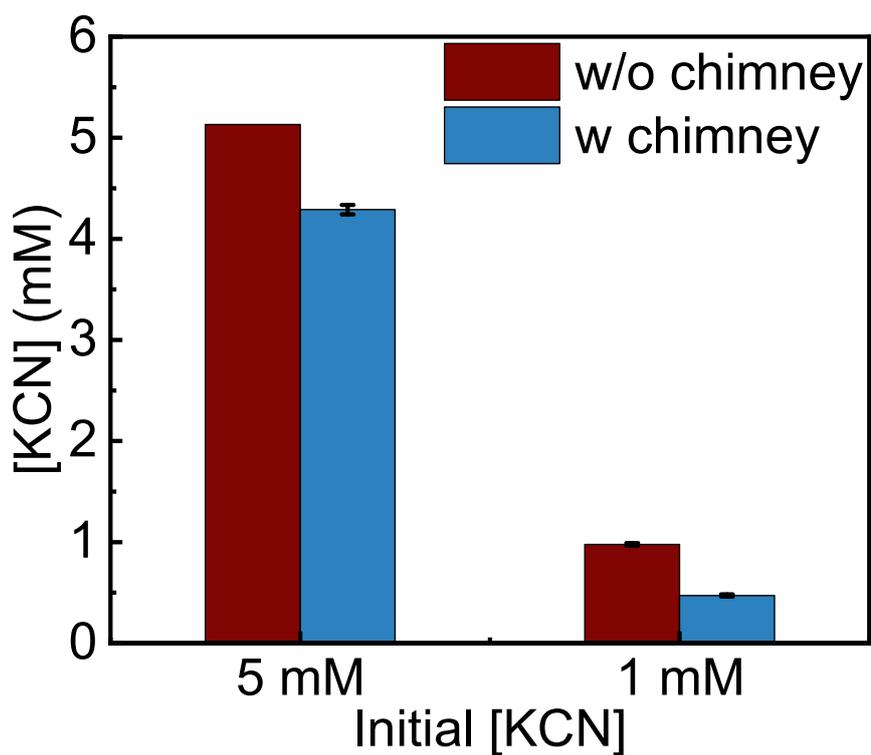
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Figure S2. Particle size and surface area characterization of the chimney powder used for glycine oxidation reactions. (a) Scanning electron microscopy image of the ground powder, showing particle diameters of approximately 100 μm. (b) Nitrogen adsorption-desorption isotherm of the powder. Blue filled circles represent the adsorption branch, and red open circles represent the desorption branch. The inset shows the linear fitting of the Brunauer-Emmett-Teller (BET) region, confirming the validity of the BET surface area determination.



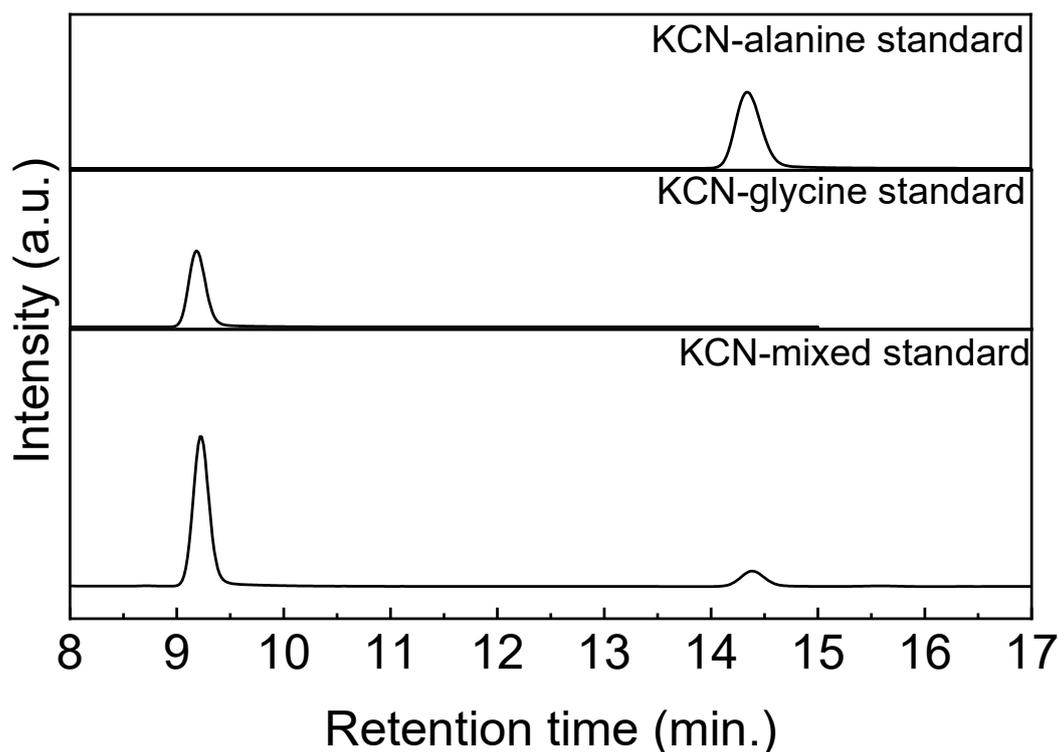
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Figure S3. Scanning electron microscopy image of a sliced chimney sample showing the presence of microcrystals on the surface. The surface fissure was approximately 800 μm in width, and the crystal diameters were generally smaller than 200 μm .



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Figure S4. Adsorption experiment of KCN stock solutions by chimney powder. Reactions were conducted using 50 mg chimney powder in 2.5 mL KCN solution with initial concentrations of 5 or 1 mM. Adsorption was performed under an Ar/H₂ atmosphere at 25 °C for 24 h. After reaction, the solutions were diluted 500-fold with 0.1 M NaOH prior to derivatization. When the initial KCN concentration was 5 mM, a decrease in the KCN concentration of 0.72 mM was observed. In contrast, when the initial concentration was 1 mM, the final KCN concentration was 0.47 mM. Given that 50 mg chimney powder was used in both experiments, the amount of KCN adsorbed by the chimney sample was estimated to be approximately 10-14 mM/g.



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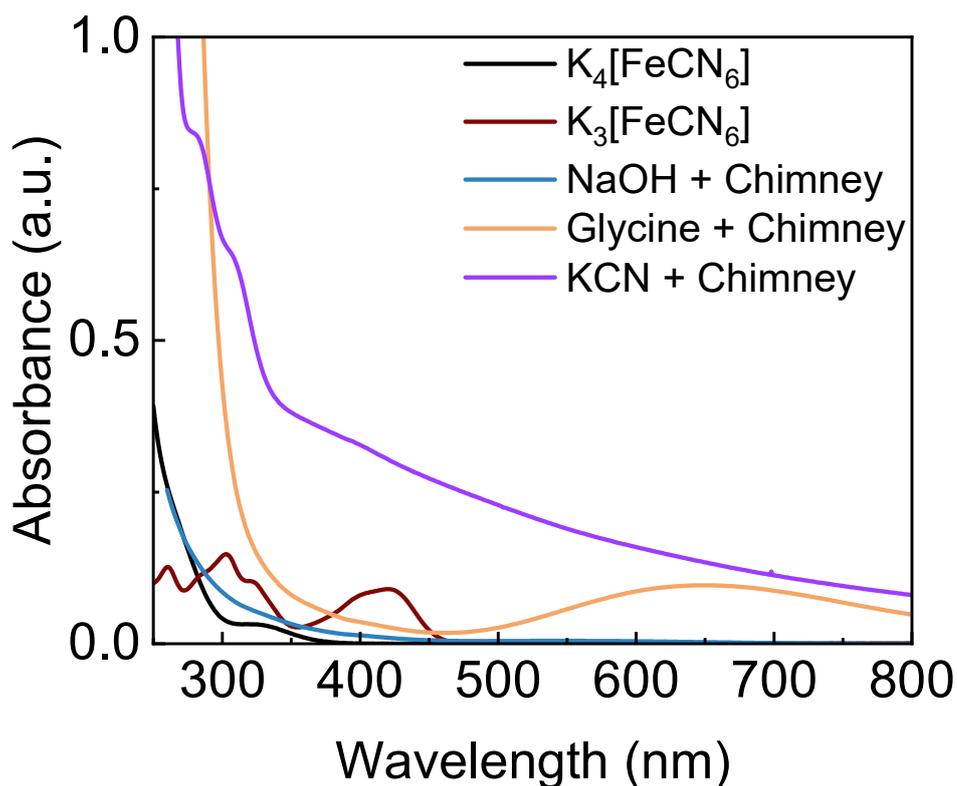
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Figure S5. Qualitative evaluation of competition between glycine and *L*-alanine in reactions with 2,3-naphthalenedicarboxaldehyde and KCN based on fluorescence intensity. In this experiment, 400 μL of 10 mM Na_3BO_3 buffer (pH 9.21), 200 μL of 100 mM glycine, 200 μL of 100 mM *L*-alanine in Milli-Q water, and 400 μL of 200 μM KCN were mixed in a 2-mL vial. The reaction was initiated by adding 400 μL of 1 mM 2,3-naphthalenedicarboxaldehyde in methanol. After shaking for 30 min, the reaction mixtures were analyzed by UPLC. As shown in the first and second panels, glycine and *L*-alanine independently reacted with 2,3-naphthalenedicarboxaldehyde to form fluorescent derivatives, with retention times of 9.17 min for glycine and 14.34 min for *L*-alanine, respectively. When equimolar amounts of glycine and *L*-alanine were present simultaneously, 2,3-naphthalenedicarboxaldehyde preferentially reacted with glycine, resulting in reduced peak intensity for the *L*-alanine derivative and increased background signals in the corresponding LC-MS spectra.



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Figure S6. Photographs of reaction solutions after reacting 50 mg chimney powder with or without glycine. The three tubes on the left correspond to solutions containing 50 mM glycine after filtration, whereas the three tubes on the right correspond to glycine-free solutions (0.1 M NaOH). These samples are identical to those used for the ICP-OES analysis. Solutions containing glycine exhibited a light blue color, whereas glycine-free solutions appeared colorless. Based on the ICP-OES results, the observed blue coloration was attributed to dissolved Cu(II) species. Both conditions yielded transparent solutions after filtration. Given that the solution pH was 12.6, the blue color was unlikely to have originated from copper hydroxide.



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Figure S7. Detection of soluble iron-cyanide complexes in filtered reaction solutions. Standard solutions of potassium ferrocyanide and potassium ferricyanide (1 mM) were used as references. No peaks attributable to iron-cyanide complexes were detected in either reaction solutions containing chimney powder and NaOH mixed with/without glycine. The spectrum of 5 mM KCN with chimney powder showed shoulder peaks at 283 and 308 nm. However, the peaks could not be assigned to any iron-cyanide complex at this stage. The glycine concentration was 50 mM and NaOH concentration was 0.1 M, and all reactions were conducted under the standard conditions described in the Methods section. Spectra were plotted using the average absorbance from three repeated scans.

116 **Table S1. EDS elemental analysis of spots A-C indicated in Figure 3.**

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Spot A						
Element	Atomic number	Line series	Net counts	Mass Concentration /%	Norm. mass concentration /%	Norm. atomic concentration /%
S	16	K	127154	46.8	49.2	62.8
Fe	26	K	25703	48.2	50.8	37.2
Sum				95.0	100	100
Spot B						
Element	Atomic number	Line series	Net counts	Mass Concentration /%	Norm. mass concentration /%	Norm. atomic concentration /%
S	16	K	63135	31.0	31.3	48.0
Fe	26	K	1674	2.5	2.5	2.2
Cu	29	K	922	2.8	2.8	2.2
Zn	30	K	13975	62.7	63.4	47.6
Sum				99.0	100	100
Spot C						
Element	Atomic number	Line series	Net counts	Mass Concentration /%	Norm. mass concentration /%	Norm. atomic concentration /%
S	16	K	83600	29.0	29.8	44.8
Fe	26	K	12063	18.9	19.4	16.8
Cu	29	K	14925	49.4	50.8	38.4
Sum				97.3	100	100

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