

# Thioester synthesis through geoelectrochemical CO<sub>2</sub> fixation on Ni sulfides

Norio Kitadai<sup>1,2\*</sup>, Ryuhei Nakamura<sup>2,3</sup>, Masahiro Yamamoto<sup>1</sup>, Satoshi Okada<sup>1</sup>, Wataru Takahagi<sup>1,4</sup>, Yuko Nakano<sup>2</sup>, Yoshio Takahashi<sup>5</sup>, Ken Takai<sup>1</sup>, Yoshi Oono<sup>6</sup>

**Thioester synthesis by CO dehydrogenase/acetyl-CoA synthase is among the most ancient autotrophic metabolisms. Although the preceding prebiotic CO<sub>2</sub> fixation routes to thioesters are often suggested, none has any experimentally supported evidence. Here we demonstrate that, under an electrochemical condition realizable in early ocean hydrothermal systems, nickel sulfide (NiS) gradually reduces to Ni<sup>0</sup>, while accumulating surface-bound CO due to CO<sub>2</sub> electroreduction. The resultant partially reduced NiS facilitates thioester (S-methyl thioacetate) formation from CO and methanethiol even at room temperature and neutral pH. This thioester formation can further be enhanced up to a selectivity of 56% by NiS coprecipitating with FeS or CoS. Considering the central role of Ni in the enzymatic process mentioned above, our demonstrated thioester synthesis with the partially reduced NiS could have a direct implication to the autotrophic origin of life.**

Thioester synthesis via acetylation of coenzyme A is a universal metabolic strategy of energy and carbon conservation. Molecular phylogenetics suggests that this biological reaction already functioned in the last universal common ancestor with carbon monoxide dehydrogenase (CODH) and acetyl-CoA synthase (ACS) as the prime catalysts<sup>1</sup>. At the Ni-based active centers bridged to an (or multiple) Fe–S cluster(s), CODH reduces CO<sub>2</sub> to CO using electrons typically taken from hydrogen (H<sub>2</sub>), whereas ACS reacts CO with a methyl group to form acetyl, transferring it to CoA to form acetyl-CoA. These enzymatic processes often remind us of their prebiotic origins in a hydrothermal vent environment rich in CO<sub>2</sub>, H<sub>2</sub>, and (Fe,Ni)S minerals on the Hadean ocean floor<sup>2,3</sup>.

However, nonenzymatic realization of the two reaction steps remains an experimental challenge. The CO<sub>2</sub>-to-CO reduction requires a highly reducing potential that is inaccessible by the H<sup>+</sup>/H<sub>2</sub> redox couple in the absence of flavin-based electron bifurcation<sup>4</sup> (Supplementary Fig. 1). In the ACS catalytic cycle, the active Ni site serves as both the electron donor and acceptor through changing its oxidation state between +1 and +3, facilitating both the reduction and oxidation intermediate steps<sup>5</sup>. Such redox bifunctionality of Ni has never been observed in natural Ni-bearing minerals. Although Huber and Wächtershäuser demonstrated S-methyl thioacetate (MTA) synthesis from CO and methanethiol in the presence of NiS as a potential prebiotic precursor of the ACS reaction<sup>6</sup>, the yield was very low (0.2% based on the initial amount of CO) even under their optimum condition (pH 1.6 and 100°C), which is uncommon in nature.

How were CO<sub>2</sub>-to-CO reduction and CO conversion realized under primordial realistic conditions? A clue is an *on-site* observation by Yamamoto et al.<sup>6</sup> of electricity generation in deep-sea hydrothermal vent chimneys and mineral deposits. The geoelectricity arises from the redox coupling between hydrothermal fluid chemicals and seawater-dissolved species via electrically conducting yet thermally insulating sulfide rocks<sup>8</sup> (Supplementary Fig. 1). Considering cool (0–50 °C) and slightly acidic (pH 6–7) character of the ancient seawater<sup>9</sup>, together with pH and temperature dependences of the H<sup>+</sup>/H<sub>2</sub> and CO<sub>2</sub>/CO redox potentials<sup>10,11</sup>, H<sub>2</sub>-rich alkaline hydrothermal systems must have readily provided negative electric potentials favorable for the CO<sub>2</sub>-to-CO reduction at the chimney-ancient seawater interface. We previously demonstrated efficient CO<sub>2</sub> electroreduction to CO on some metal sulfide catalysts (for example, cadmium sulfide) under a simulated early ocean geoelectrochemical condition<sup>12</sup>. It was later found that FeS undergoes day-scale electroreduction to Fe<sup>0</sup><sup>13</sup>. The resultant

<sup>1</sup>Super-cutting-edge Grand and Advanced Research (SUGAR) Program, Institute for Extra-cutting-edge Science and Technology Avant-garde Research (X-star), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan.

<sup>2</sup>Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

<sup>3</sup>Biofunctional Catalyst Research Team, RIKEN Center for Sustainable Resource Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.

<sup>4</sup>Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

<sup>5</sup>Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

<sup>6</sup>Department of Physics, University of Illinois at Urbana-Champaign, 1110W. Green Street, Urbana, IL 61801-3080, USA (retired).

\*Correspondence to: nkitadai@jamstec.go.jp

FeS-Fe<sup>0</sup> assemblage, named FeS\_PERM (FeS partially electroreduced to metal), showed exceptional capability of promoting various prebiotically important reactions owing to synergy between surface Fe sites with different oxidation states (Fe<sup>2+</sup> and Fe<sup>0</sup>)<sup>14,15</sup>.

In our previous works<sup>12,13</sup>, NiS exhibited neither CO evolution nor Ni<sup>0</sup> formation detectable by X-ray diffraction (XRD) analysis. However, our further investigation presented below found non-crystalline growth of Ni<sup>0</sup> under geochemically feasible potential conditions, with a substantial amount of CO bound on the resultant surface Ni<sup>0</sup> sites. It is furthermore shown below that the partially reduced NiS, that is, NiS\_PERM realizes efficient conversion of CO and methanethiol to MTA even at room temperature and neutral pH. Notice that the accumulation of surface-bound CO during CO<sub>2</sub> electroreduction is generally recognized as a poisoning of surface (electro)catalytic activity<sup>16,17</sup>, but our results suggest that the CO accumulation process on NiS\_PERM was rather a crucial step for subsequent primordial thioester formation in early ocean hydrothermal systems. Thioesters are versatile compounds in organic chemical synthesis as well as in biosynthesis, enabling diverse coupling reactions including C-C bond formation, esterification, and amide bond formation owing to the activated acyl unit<sup>18–20</sup>. To the best of our knowledge, our study provides the first experimental demonstration of thioester synthesis from CO and thiol under mild aqueous condition. Thus, besides rendering a realistic support for autotrophic scenarios of the origin of life<sup>2,3</sup>, our demonstrated CO-thiol reaction on NiS\_PERM could be a practical approach to CO utilization<sup>21</sup>.

## Results

### Metal sulfide electroreduction

We prepared metal sulfides including NiS by simply mixing an aqueous solution of the corresponding metal chloride and an aqueous solution of sodium sulfide. The obtained sulfides were exposed to a constant electric potential for 7 days in 100 mM NaCl at room temperature (25 ± 2°C) under continuous CO<sub>2</sub> bubbling that maintained the solution pH at 6 ± 0.25 (Supplementary Figs. 2 and 3). The electrolyzed sulfides were then separated from the supernatant solution, dried under vacuum, and used for the following experiments.

The NiS consists of aggregated nanoparticles with an average particle diameter of 15 ± 11 nm (Supplementary Fig. 6). Although no significant morphological change was caused (Supplementary Fig. 6), exposure at –0.5 V<sub>SHE</sub> (volt versus the standard hydrogen electrode) led to the desulfurization of NiS to heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>) (Fig. 1a), consistent with thermodynamic calculation (Fig. 1b). Further reduction of Ni<sub>3</sub>S<sub>2</sub> at lower electric potentials was indicated

by energy dispersive X-ray spectroscopy (EDS) mapping on the NiS particles electrolyzed at –1.0 V<sub>SHE</sub> (Fig. 1c), where a clear decrease in the sulfur signal intensity relative to nickel was observed in comparison with pure NiS, and with the NiS electrolyzed at –0.5 V<sub>SHE</sub> (Fig. 1d). In agreement with the EDS result, nickel K-edge X-ray absorption near-edge structure (XANES) of the NiS samples showed spectral changes with decreasing potential from –0.5 to –1.0 V<sub>SHE</sub> (Fig. 1e) attributable to the occurrence and growth of Ni<sup>0</sup> in Ni<sub>3</sub>S<sub>2</sub> up to the Ni<sup>0</sup> percentage of 12% at –1.0 V<sub>SHE</sub> (Fig. 1f and Supplementary Fig. 11). Similarly, XANES analysis allowed us to estimate 7% conversion of CoS to Co<sup>0</sup> at –1.0 V<sub>SHE</sub> (Supplementary Fig. 12). Thus, NiS\_PERM and CoS\_PERM are formed at –1.0 V<sub>SHE</sub> and even less negative potentials near their sulfide/metal equilibria (Fig. 1b and f, Supplementary Figs. 11 and 12) just as in the FeS case. However, in contrast to FeS that exhibited broad but clear XRD signals for Fe<sup>0</sup> even at –0.7 V<sub>SHE</sub> (Supplementary Fig. 8)<sup>13</sup>, NiS showed no XRD signal for Ni<sup>0</sup> in the examined potential range (≤ –1.0 V<sub>SHE</sub>) (Fig. 1a). The Ni<sup>0</sup> percentage up to 12% (Fig. 1f) is well above the detection limit of XRD (Supplementary Fig. 10) if the formation of meso- or macroscopic crystalline structure is assumed. Thus, NiS\_PERM would be with more finely dispersed zerovalent metal than FeS\_PERM.

### CO production and accumulation on the metal-sulfide PERMs

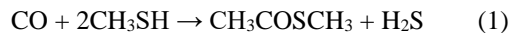
To explore the possibility of CO production and accumulation on the metal-sulfide PERMs formed under CO<sub>2</sub> atmosphere, we dissolved the resultant metal-sulfide PERMs completely in 35% hydrogen chloride, and quantified the released CO by gas chromatography (Supplementary Fig. 18 and Supplementary Movie 1). Except for FeS, all the sulfides exposed at ≤ –0.6 V<sub>SHE</sub> were found to retain CO (Fig. 2a and Supplementary Table 2). The threshold potential is close to the sulfide/metal equilibrium potentials for Ni and Co (–0.57 V<sub>SHE</sub> for both; Fig. 1b and Supplementary Fig. 4), and is also near the thermodynamic CO<sub>2</sub>/CO redox potential at the condition of sulfide electrolysis (–0.50 V<sub>SHE</sub>; Supplementary Fig. 1). The amount of CO increased with decreasing the potential, up to 180 ± 40 μmol g<sup>–1</sup> for the case of NiS. Because sulfurized Ni binds CO considerably more weakly than pure Ni<sup>0</sup><sup>22</sup>, the observed CO should mostly derive from the CO bound on the surface Ni<sup>0</sup> sites. In fact, the maximum adsorption (180 ± 40 μmol g<sup>–1</sup>) corresponds to the surface coverage of one CO molecule per 8 ± 3 surface Ni atoms (Supplementary Fig. 13), consistent with the percentage of Ni<sup>0</sup> grown at –1.0 V<sub>SHE</sub> (Fig. 1f). The similar interpretation should be applicable to the adsorption behavior of CO on the CoS\_PERM<sup>23</sup>. Coprecipitation with FeS led to decline of the amounts of CO

on NiS and CoS (Fig. 2a) probably because of the decrease in the surface reactive sites.

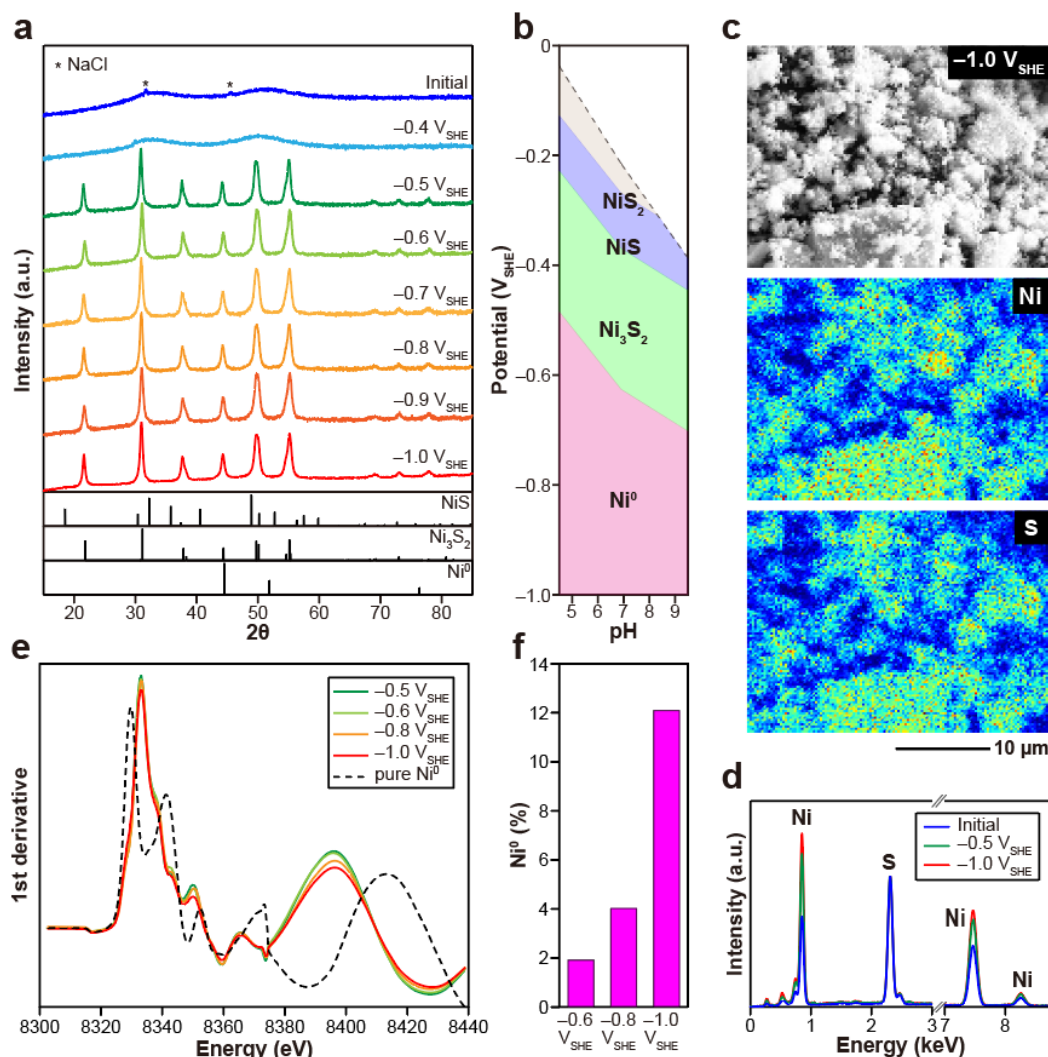
### Nonenzymatic thioester synthesis

We mixed the metal-sulfide PERMs retaining the surface-bound CO (Fig. 2a) (50 mg for each) with an aqueous solution of sodium methanethiolate (75  $\mu\text{mol}$ ) in a serum bottle (13.8 ml), and agitated at room temperature ( $25 \pm 2^\circ\text{C}$ ) for up to 7 days without externally imposing electric potential. pH was buffered at neutral ( $7.0 \pm 0.5$ ) by filling the gas space with  $\text{CO}_2$  (1 atm). Despite this very mild condition, gas chromatograph–mass spectrometry analysis revealed

efficient MTA formation in the presence of specific electrolyzed sulfides (Fig. 2b and c). Organosulfur compounds detected with the amount higher than 0.01  $\mu\text{mol}$  were methanethiol, MTA, dimethyl sulfide and dimethyl disulfide (Supplementary Figs. 19 and 20), among which MTA was the sole product built from CO and methanethiol



Experiments with the NiS\_PERM prepared at  $-1.0 V_{\text{SHE}}$  exhibited the following product characteristics. The yield of MTA increased over one week, while the amounts of CO and



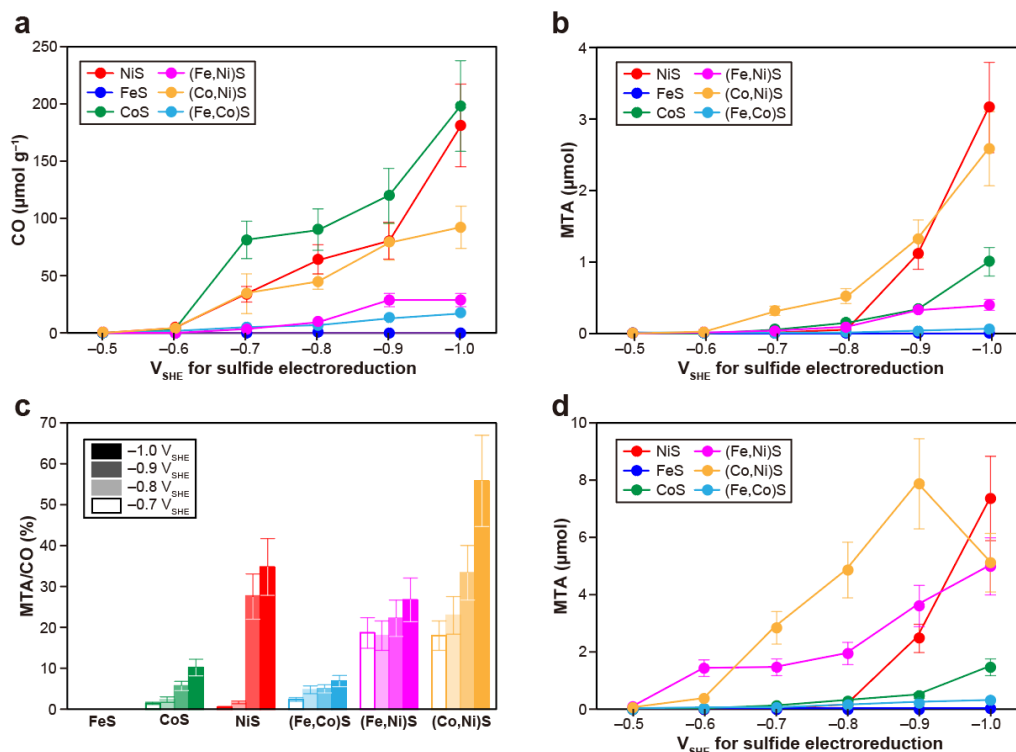
**Fig. 1. | NiS electroreduction characterized by (a) XRD patterns, (b) thermodynamic calculation, (c and d) SEM-EDX mapping data, and (e and f) nickel K-edge XANES spectra. (c) presents the EDX mapping data for the NiS electrolyzed at  $-1.0 V_{\text{SHE}}$ . In (d), the S signal intensities (2.3 keV) for NiS before (blue) and after the electrolysis at  $-0.5 V_{\text{SHE}}$  (green) or  $-1.0 V_{\text{SHE}}$  (red) are matched with each other for comparison. (e) The first derivative XANES spectra is shown.**

methanethiol decreased from their maxima at the beginning (Supplementary Fig. 24). CO appeared in the gas-phase through competitive adsorption with methanethiol: in the absence of methanethiol under otherwise identical condition, few CO gas was detected ( $0.03 \mu\text{mol}$ ) and no MTA was observed (Supplementary Fig. S21a). As long as methanethiol was available, replacement of  $\text{CO}_2$  in the gas space with helium (He), and dissolution of 1 M phosphate (pH 7.0) into the sample solution had no significant influence on the yield of MTA ( $3.2 \pm 0.6 \mu\text{mol}$ ; Fig. 2b  $\rightarrow 3.6 \pm 0.7 \mu\text{mol}$ ). It was also confirmed with  $^{13}\text{C}$ -labeled  $\text{CO}_2$  that the  $\text{CO}_2$  filled in the serum bottle did not serve as a component of MTA. The MTA formed under  $^{13}\text{CO}_2$  atmosphere showed the mass spectrum identical to that of the standard MTA with normal carbon isotopic composition.

In aqueous solutions, acetate ( $0.19 \pm 0.04 \mu\text{mol}$  or  $0.25 \pm 0.05 \text{ mM}$ ) and formate ( $0.03 \pm 0.01 \mu\text{mol}$  or  $0.035 \pm 0.01 \text{ mM}$ ) were observed (Supplementary Fig. 25). The acetate concentration increased to  $2.0 \pm 0.4 \text{ mM}$  when the product solution was basified by 1 M sodium hydroxide due to MTA hydrolysis. Because MTA hydrolysis is accelerated at

elevated temperatures<sup>24</sup>, a one-day experiment at  $80^\circ\text{C}$  resulted in a higher yield of acetate ( $2.4 \pm 0.5 \mu\text{mol}$  or  $3.2 \pm 0.6 \text{ mM}$ ) and a lower yield of MTA ( $0.68 \pm 0.14 \mu\text{mol}$ ) (Supplementary Fig. 25). Other biologically relevant organic acids such as pyruvate and lactate were not detected in any product solutions with concentrations higher than  $0.01 \text{ mM}$ . We also treated solid samples with 8 M potassium hydroxide after the reaction, but neither pyruvate nor lactate was observed.

When CO, as well as methanethiol, were initially introduced with equal amounts ( $75 \mu\text{mol}$ , or  $0.14 \text{ bar}$  in the gas space) in the presence of NiS\_PERM formed at  $-1.0 \text{ V}_{\text{SHE}}$ , the yield of MTA more than doubled, compared with the case without CO in the initial gas phase ( $3.2 \pm 0.6 \rightarrow 7.4 \pm 1.5 \mu\text{mol}$ ; Fig. 2d and Supplementary Fig. 21a). In contrast, under the same initial condition with CO, few or no detectable MTA was formed in the presence of pure NiS, the  $\text{Ni}_3\text{S}_2$  prepared at  $-0.5 \text{ V}_{\text{SHE}}$ , or pure  $\text{Ni}^0$  (Supplementary Fig. 21 and Supplementary Table 4), indicating the necessity of the coexistence of zerovalent and non-zerovalent Ni surface sites for efficient MTA production. It is also notable that the



**Fig. 2. | CO accumulation through  $\text{CO}_2$  electroreduction (a) and CO conversion to S-methyl thioacetate (MTA) (b–d) on the metal-sulfide PERMs.** The surface-bound CO on the electrolyzed sulfides were quantified (a) and used as a carbon source for the MTA synthesis in the presence of methanethiol ( $75 \mu\text{mol}$  per  $50 \text{ mg}$  of sulfide) (b). The percentages of CO to form MTA are shown in (c). (d) The MTA synthesis were examined with CO and methanethiol externally added ( $75 \mu\text{mol}$  for each). The yield of MTA on (Co,Ni)S declined at the lowest potential ( $-1.0 \text{ V}_{\text{SHE}}$ ) because of depletion of methanethiol (Supplementary Table 4).

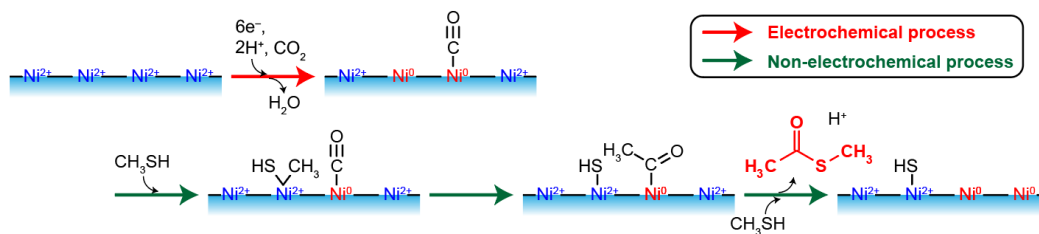
MTA yield decreased steeply as the NiS electroreduction potential was positively changed from  $-1.0$  to  $-0.8$  V<sub>SHE</sub> (Fig. 2b to d) although  $-0.8$  V<sub>SHE</sub> is still sufficient for the Ni<sup>0</sup> generation (Fig. 1f). In light of reported chemical functions of Ni and other metals in organometallic analogues of ACS<sup>25, 26</sup>, one possible interpretation is that the MTA synthesis involves at least two adjacent surface Ni<sup>0</sup> sites (Fig. 3): one Ni<sup>0</sup> serves as an electron donor for the reductive cleavage of methanethiol C-S bond. Close location of another Ni<sup>0</sup> (the closest Ni-Ni distance = 2.48 Å; supplementary Fig. 13) allows transfer of the generated electrophilic methyl onto the nucleophilic carbon of adsorbed CO. After the formation of C-C bond to make the acetyl-Ni<sup>0</sup>, its oxidative thiolysis to form MTA occurs through coupling with the reduction of neighboring non-zerovalent Ni atoms. The cleavage of methanethiol C-S bond also accounts for the formations of CH<sub>4</sub> and dimethyl sulfide (Supplementary Table 3 and 4), where the resultant methyl converts to CH<sub>4</sub> via protonation, while thiolysis of the methyl generates dimethyl sulfide. If a random Ni<sup>0</sup> distribution is assumed, a 12% conversion of Ni<sup>2+</sup> to Ni<sup>0</sup> achieved at  $-1.0$  V<sub>SHE</sub> (Fig. 1f) results in 1.4% occurrence of the adjacent Ni<sup>0</sup>-Ni<sup>0</sup> surface pair, while this percentage drops to 0.16% with a 4% conversion achieved at  $-0.8$  V<sub>SHE</sub>. Thus, our proposed process taking multiple Ni sites into account (Fig. 3) explains the large potential dependence in MTA productivity of NiS\_PERM (Fig. 2b to d) as well as the few or no MTA formation on Ni<sub>3</sub>S<sub>2</sub> and pure Ni<sup>0</sup>, although this mechanism is different from the ACS-reaction. This nonenzymatic process is expected to be eventually deactivated due to cumulative surface sulfurization (Fig. 3), but the surface activity may be restored by additional solid electrolysis.

Interestingly, even greater CO-to-MTA reaction efficiencies were obtained with the NiS coprecipitating with FeS or CoS (Fig. 2c). Up to  $56 \pm 10\%$  of the surface-bound CO, produced by CO<sub>2</sub> electroreduction, was converted to MTA on the electrolyzed (Co,Ni)S. (Fe,Ni)S produced a considerable amount of MTA from initially introduced CO and methanethiol even after the  $-0.6$  V<sub>SHE</sub> electrolysis (Fig. 2d). Given FeS's electroreduction reactivity higher than that of NiS (Supplementary Figs. 7 and 8), Fe in the electrolyzed (Fe,Ni)S possibly assists the Ni's performance as an electron

donor at an intermediate reduction step. The Fe's supportive role is also seen in the ACS-reaction as the form of ferredoxin serving as the redox mediator<sup>5</sup>. Co is also involved in the enzymatic process as a transporter of the methyl group<sup>5</sup>.

## Discussion

Our experiments revealed that partial electroreduction product of NiS, that is, NiS\_PERM, promotes thioester synthesis from CO and methanethiol. NiS\_PERM accumulates surface-bound CO during the formation under CO<sub>2</sub> atmosphere, so NiS offers a two-step CO<sub>2</sub> fixation route to thioester with the aid of electric energy. Ancient seawater was rich in Ni<sup>2+</sup> owing to much greater mantle activity than the present level<sup>27</sup>. Because Ni<sup>2+</sup> is almost insoluble in alkaline sulfide condition, Ni-bearing sulfides must have precipitated at the vent-seawater interface in early ocean alkaline hydrothermal systems, and has been exposed to a sustained negative potential by the geoelectrochemical processes (Supplementary Fig. 1). The potential level required for the Ni<sup>0</sup> formation and the surface-catalyzed CO production ( $\leq -0.6$  V<sub>SHE</sub>; Figs. 1 and 2) is attainable under moderately hot, H<sub>2</sub>-rich, and alkaline conditions as observed even in the present-day hydrothermal systems<sup>28</sup>. The surface-bound CO is stable in NaCl aqueous solution, but is largely and quickly released in the presence of adsorption competitors such as methanethiol and hydrogen sulfide (see Methods, Supplementary Figs. 26 and 27). Thus, considering dynamic mixing of hydrothermal fluids with seawater observed in the present-day deep-sea vent chimneys through the pore systems<sup>29</sup>, continuous CO production, concentration, desorption, and advection are likely to have occurred within the pore spaces of ancient hydrothermal mineral deposits (Fig. 4). Such fluid-mediated materials transport favors the occurrence and combination of multiple reactions including the formation of thiols from CO (or CO<sub>2</sub>) and H<sub>2</sub>S<sup>30,31</sup>, the reaction of CO with methanethiol to form MTA (Fig. 2b to d), and the accumulation of organic products<sup>32</sup>. Thus, the thioester synthesis via the formation of Ni sulfide\_PERMs should have been robustly concomitant with ubiquitous hydrothermal activities on the primordial seafloor.



**Fig. 3. | Possible intermediate steps in the MTA formation via the formation of NiS\_PERM with the surface-bound CO (red arrow) and the CO-methanethiol reaction on NiS\_PERM (green arrows).**



Nowadays, growing consensus for CO<sub>2</sub> as the dominant carbon species on the Hadean Earth has stimulated exploration of geo- and astro-chemical events that could have transiently realized highly reducing early atmosphere<sup>33</sup>. Subsequent photochemical and aqueous-phase processes with reactive carbon sources, powerful oxidizing/reducing agents, and/or UV light might have realized abiotic thioester synthesis<sup>34,35</sup>. Although these reactions might have played a role in enrichment of a prebiotic soup, their relevance to biosynthesis is ambiguous. Consequently, numerous questions remain unanswered by the transient scenario regarding the gap between prebiotic chemistry and early biochemistry conserved in the metabolic and phylogenetic architectures of life.—

The two key facts: CO<sub>2</sub> fixation utilizing various states of Ni due to our experiments (Fig. 2) and the well-known central role of Ni at the active sites of CODH/ACS<sup>5</sup> may lead to a plausible scenario for the emergence of protometabolism prior to the origin of life. Sustained occurrence of electrochemical energy adequate for the Ni sulfide\_PERM formation,  $\leq -0.6$  V<sub>SHE</sub> in the ancient seawater condition (Figs. 1 and 2), is limited in nature except for deep-sea hydrothermal settings (Supplementary Fig. 1). This environmental specificity with the known necessity of Ni in both biological and chemical CO<sub>2</sub> fixation suggest that the Ni sulfide\_PERM-promoted thioester synthesis in early ocean hydrothermal systems (Fig. 4) is a primordial precursor of the CODH/ACS reaction. The CO production on metal-sulfide\_PERMs (Fig. 2a) may also have served as crucial carbon and energy sources for the early chemolithotrophic ecosystem, thereby supporting, or even

directing, the origin and early evolution of autotrophs as suggested from the autotrophic metabolism core<sup>36</sup>.

## Methods

### Preparation of metal sulfides

All metal sulfides were prepared by adding 100 mM sodium sulfide (Na<sub>2</sub>S) dropwisely into the corresponding 100 mM metal chlorides (NiCl<sub>2</sub>, FeCl<sub>2</sub>, or CoCl<sub>2</sub>) or their binary mixtures (for example, 50 mM NiCl<sub>2</sub> plus 50 mM FeCl<sub>2</sub>) under vigorous stirring to a final volume ratio of 1:1. Solid precipitates were then separated from the supernatant solutions by centrifugation (8000 rpm, 10 min) and were dried under vacuum. To prevent oxidation by atmospheric O<sub>2</sub>, the sample preparation was conducted in a glove box filled with N<sub>2</sub> gas (>99.9995%), with 4% H<sub>2</sub> being added (the Coy system). All chemicals were purchased from FUJIFILM Wako Pure Chemical Corporation as reagent grade. Deaerated Milli-Q water (18.2 megohms) was used as the solvent.

Pure metals (Fe<sup>0</sup>, Co<sup>0</sup>, and Ni<sup>0</sup>) were obtained from EM Japan. Their reported characteristics and XRD patterns measured in this study are presented in Supplementary Table 1 and Supplementary Fig. 9, respectively.

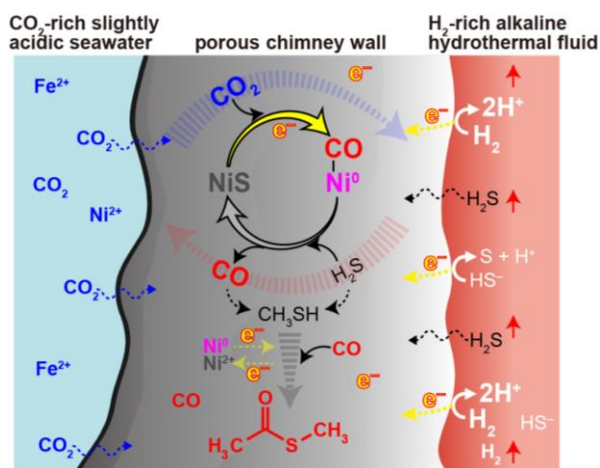
### Sulfide electrolysis

Metal sulfide electrolysis was conducted under a simulated early ocean condition in accordance with the procedure reported previously<sup>13</sup>. Briefly, 400 mg of sulfide samples was deposited on a carbon working electrode (5.7 cm<sup>2</sup>) in a H-type cell (Supplementary Fig. 2), immersed in a deaerated 100 mM NaCl, and exposed to a flow (20 ml min<sup>-1</sup>) of CO<sub>2</sub> (>99.995%) containing 4 ppm of H<sub>2</sub>S. The CO<sub>2</sub> gas buffered the solution pH at slightly acidic (6.0 ± 0.25). The H<sub>2</sub>S partial pressure was determined by thermodynamic calculation to supply H<sub>2</sub>S and HS<sup>-</sup> into solution with the equilibrium total concentration of 0.5 μmol kg<sup>-1</sup>. Although the ionic strength and pressure conditions adopted in this experiment are different from the ancient deep-sea hydrothermal settings<sup>38,39</sup>, a thermodynamic calculation indicates that these differences have no significant influence on the redox potentials for the sulfide/metal and the CO<sub>2</sub>/CO systems (Supplementary Fig. 5)<sup>13</sup>.

While keeping the CO<sub>2</sub> gas flow that was started at least 1 hour before each experiment, a constant potential was applied on the carbon electrode for 7 days by using a multi-potentiostat (PS-08; Toho Technical Research). All potentials were measured against an Ag/AgCl reference electrode in saturated KCl and were converted to the SHE scale by the following equation

$$E \text{ (versus SHE)} = E \text{ (versus Ag/AgCl)} + 0.198 \text{ V} \quad (1)$$

After the electrolysis, the electrochemical cell was immediately transferred into a glove box filled with N<sub>2</sub> and



**Fig. 4. | Schematic cross-section of a vent chimney in an early ocean alkaline hydrothermal system showing possible abiotic thioester synthesis promoted by Ni sulfide\_PERM.**

H<sub>2</sub> gases (volume ratio, 96:4). The solid sample was then separated from the supernatant solution, dried under vacuum for 1 hour, and stored inside the glove box. A dry vacuum pump (RDA-281H, ULVAC) with the reported ultimate pressure of 0.08 Pa was used for the dehydration. The surface-bound CO was expected to be intact at this vacuum condition<sup>22,40,41</sup>.

### Solid characterization

Scanning electron microscopy (SEM) imaging was performed on a Helios G4 UX (Thermo Fisher Scientific) equipped with a PP-3010 cryo preparation system (Quorum) and an Octane Super C5 EDS detector (AMTEC). An acceleration voltage of 2 kV was applied for secondary electron imaging and 20 kV for energy dispersive X-ray spectroscopy (EDS) analysis under a reduced pressure of  $< 1 \times 10^{-4}$  Pa at room temperature ( $23 \pm 2^\circ\text{C}$ ). Samples were prepared as follows. First, sulfide sample sealed in a serum bottle was placed in a vacuum chamber of the cryo-preparation system, whose internal atmosphere was replaced with N<sub>2</sub> gas from liquid N<sub>2</sub> vaporization by three times of evacuation-purge cycles. Under flow of N<sub>2</sub> gas, the serum bottle was opened, and the sulfide was rubbed onto a carbon tape (Nisshin EM) attached on a transfer shuttle by a plastic spatula. The shuttle was transferred into a transfer device under  $\sim 10^2$  Pa, and then to the SEM chamber via a cryo-preparation chamber ( $< 10^{-4}$  Pa).

Particle size distribution (Supplementary Fig. 6) was determined by manual segmentation on Affinity Photo for iPad 1.6.8.77 (Serif (Europe) Ltd.) followed by image analysis with Image-Pro 3D v9.3 (Media Cybernetics). Particle diameters were calculated from the segmented areas assuming spherical morphology.

X-ray diffraction (XRD) patterns of sulfide samples were measured by using an X-ray diffractometer with Cu K $\alpha$  radiation (MiniFlex 600, Rigaku). All runs were conducted with  $2\theta$  ranging from  $10^\circ$  to  $90^\circ$  using  $0.02^\circ$   $2\theta$  step with a scan rate of 0.1 or  $1^\circ \text{ min}^{-1}$ . To prevent oxidation by atmospheric O<sub>2</sub> during the measurement, the solid samples were shielded in an air-sensitive sample holder (Rigaku). Peak identifications were made on the basis of the reference patterns reported in the Powder Diffraction File published by the International Centre for Diffraction Data. The reference patterns are presented in Fig. 1a and Supplementary Figs. 8–11 with the measured XRD data.

X-ray absorption near-edge structure (XANES) spectra at Ni and Co K-edges were measured at BL-12C (bending magnet beamline) in a synchrotron radiation facility (Photon Factory) in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. In the beamline, X-ray from a synchrotron operated at 2.5 GeV (current: 450 mA) was monochromatized with a Si(111) double-crystal

monochromator, and focused to an area of  $0.5 \times 0.5 \text{ mm}^2$  with a bent cylindrical mirror, which also reduced the higher order. XANES spectra were obtained in transmission mode using two ion chambers to measure intensities of incident ( $I_0$ ) and transmitted ( $I$ ) X-rays. Energy step within the XANES region was 0.25 eV, and the absorbance by the sample ( $\mu t$ ) was obtained as  $\mu t = \ln(I/I_0)$ . Sulfide samples were diluted with boron nitride (BN,  $< 150 \text{ nm}$ , 99% purity) to yield the metal/BN molar ratio of 1:25, and shielded by an O<sub>2</sub>-impermeable polyethylene film. Measurement was conducted for a part of the sample with uniform thickness within the area of the X-ray beam.

### Search for the surface-bound CO on electrolyzed sulfides

Each sulfide sample (50 mg for each) was sealed in a serum bottle (124.7 ml) with a Teflon-laminated butyl rubber cap and an aluminum stopper in a glove box filled with N<sub>2</sub> and H<sub>2</sub> gases (volume ratio, 96:4). The bottle was then filled with pure He gas ( $> 99.99995\%$ ) by flowing the He through a stainless needle at a rate of  $100 \text{ ml min}^{-1}$  over 10 min. This was followed by the addition of 5 ml of 35% HCl (super special grade; FUJIFILM) under vigorous agitation. After the sulfide sample dissolved completely under 60 rpm rotation of the bottle at room temperature ( $25 \pm 2^\circ\text{C}$ ) (typically, within 30 min), the headspace gas was analyzed by gas chromatography (GC) (Fig. 2a, Supplementary Fig. 18 and Supplementary Table 2). To ensure reproducibility, we carried out multiple independent runs, using several sulfide samples for each metal. Differences among the data obtained at the identical condition were less than 20%. The same was true for the following two experiments “Nonenzymatic thioester synthesis” and “competitive adsorption of CO with H<sub>2</sub>S”.

To verify the CO production and accumulation on the NiS\_PERM, we conducted the following experiment with isotopically labeled sodium bicarbonate (NaH<sup>13</sup>CO<sub>3</sub>, 99% purity) provided by Cambridge Isotope Laboratories, Inc. First, 400 mg of NiS was electrolyzed at  $-1.0 \text{ V}_{\text{SHE}}$  for 7 days in 60 ml of 0.5 M phosphate buffer solution (pH 6.0) under pure N<sub>2</sub> gas flow ( $> 99.9998\%$ ). Then, the gas headspace of the electrochemical cell ( $\sim 40 \text{ ml}$ ) was purged with <sup>13</sup>CO<sub>2</sub> gas that was provided by a dropwise addition of 0.1 M phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) onto NaH<sup>13</sup>CO<sub>3</sub> powder under vigorous stirring in a closed vial connected with the electrochemical cell with a polyvinyl chloride tube and stainless needles. After additional two-hour electrolysis with the gas inlet and outlet closed, the NiS\_PERM on the carbon paper was collected, dried under vacuum, and dissolved completely in 35% HCl. GC-MS analysis of the released gas revealed the formation of <sup>13</sup>CO with the  $m/z = 29$  (Supplementary Fig. 18c). No <sup>13</sup>CO was detected in the

$^{13}\text{CO}_2$  formed by the  $\text{H}_3\text{PO}_4$  addition to  $\text{NaH}^{13}\text{CO}_3$  (Supplementary Fig. S18).

In the normal  $\text{CO}_2$  gas bubbled during the sulfide electrolysis, we detected no CO with our GC's maximum performance (detection limit;  $\sim 1$  ppm). Even if a very slight amount of CO impurity is present in the  $\text{CO}_2$ , its contribution to the surface-bound CO (Fig. 2a and Supplementary Table 2) must be negligible because the electrolyzed FeS released almost no CO despite the fact that  $\text{Fe}^0$  has an even stronger CO binding energy than  $\text{Ni}^0$  and  $\text{CO}^0$ <sup>42</sup>.

Supplementary Movie 1 presents a demonstration of the surface-bound CO on the NiS electrolyzed at  $-1.0\text{ V}_{\text{SHE}}$ . A weak acid ( $1\text{ M H}_3\text{PO}_4$ ) was used here to make sure that the gas bubble formation is not due to NiS dissolution but from the purging of the electrolyzed surface.

### Nonenzymatic thioester synthesis

Each sulfide sample (50 mg for each) was sealed in a serum bottle (13.8 ml) with a Teflon-laminated butyl rubber cap and an aluminum stopper in a glove box filled with  $\text{N}_2$  and  $\text{H}_2$  gases (volume ratio, 96:4). The bottle was then filled with pure  $\text{CO}_2$  gas ( $>99.995\%$ ) by flowing the  $\text{CO}_2$  through a stainless needle at a rate of  $100\text{ ml min}^{-1}$  over 5 min. This was followed by the addition of 0.75 ml of 100 mM sodium methanethiolate ( $\text{CH}_3\text{SNa}$ ) with or without 1.86 ml of CO gas (1 atm, 99.9% purity). After rotating the bottle at 60 rpm for 7 days at room temperature ( $25 \pm 2^\circ\text{C}$ ), the headspace gas was analyzed by GC (Fig. 2b–d, Supplementary Figs. 19–23 and Supplementary Tables 3 and 4). The aqueous suspension was then centrifuged (10000 rpm, 2 min) and measured for pH by a portable pH meter (Seven2Go Pro, Mettler Toledo).

We did not carry out “one-pot” organic synthesis in an electrochemical cell because  $\text{H}_2$  evolution during sulfide electrolysis<sup>12</sup> prevented us from keeping methanethiol in the cell in the reaction period due to pressurization. As discussed in the main text, however, occurrence and combination of multiple reactions are likely to be more realistic than a single-pot reaction in natural hydrothermal vent environments.

### Competitive adsorption of CO with $\text{H}_2\text{S}$

Sulfide sample (50 mg for each) was sealed in a serum bottle (19.5 ml) with a Teflon-laminated butyl rubber cap and an aluminum stopper in a glove box filled with  $\text{N}_2$  and  $\text{H}_2$  gases (volume ratio, 96:4). The bottle was then filled with pure He gas ( $>99.99995\%$ ) by flowing the He through a stainless needle at a rate of  $100\text{ ml min}^{-1}$  over 5 min. This was followed by the addition of 1 ml of 300 mM  $\text{Na}_2\text{S}$  and the subsequent addition of 1 ml of 450 mM HCl. After rotating the bottle at 60 rpm for one day at room temperature ( $25 \pm 2^\circ\text{C}$ ), the headspace gas was analyzed by GC (Supplementary Figs. 26 and 27 and Supplementary Table 5). No carbon-

sulfur compounds (for example, methanethiol, carbon disulfide, carbonyl sulfide) were detected.

From the pH values of aqueous suspensions (7.5–8.0; Supplementary Table 5), the initial dissolved  $\text{H}_2\text{S}$  and  $\text{HS}^-$  concentrations are predicted to be 90–120 mM in total, equilibrium  $\text{H}_2\text{S}$  distribution being assumed in the gas and liquid phases without the surface adsorption.

### Sample analysis

Inorganic gases including  $\text{H}_2$ , CO, and  $\text{CH}_4$  were quantified by a Shimadzu GC system equipped with a BID-2010 Plus detector (Tracera). A MICROPACKED-ST column (Shinwa) was attached. He ( $>99.99995\%$ ) was used as the carrier gas at a column flow rate of  $7\text{ ml min}^{-1}$ . The column temperature was initially kept at  $35^\circ\text{C}$  for 2.5 min, raised to  $250^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$ , and then raised to  $265^\circ\text{C}$  at a rate of  $4^\circ\text{C min}^{-1}$ . A chromatogram for a standard gas sample is shown in Supplementary Fig. 14 with obtained calibration curves.

Gas-phase sulfur compounds were analyzed by using a Shimadzu gas chromatograph-mass spectrometer (GCMS-QP2010 Ultra) equipped with a DB-SULFUR SCD column (60 m, 0.32 mm I.D, Agilent). He ( $>99.99995\%$ ) was used as the carrier gas at a column flow rate of  $33.2\text{ cm sec}^{-1}$ . The column temperature was initially kept at  $35^\circ\text{C}$  for 5 min, raised to  $155^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ , and then raised to  $235^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$ . The scan range was set to  $m/z$  5–200 Da. Compounds were identified by comparing the observed retention times and mass spectra with those of respective standards prepared from commercial reagents, and were quantified based on calibration curves (Supplementary Fig. 15). Several gas samples were also analyzed by the Tracera GC system with a DB-SULFUR SCD column at the measurement condition described in this paragraph (Supplementary Fig. 16).

Aqueous-phase products were characterized, after filtration with a polytetrafluoroethylene membrane filter (pore size,  $0.2\text{ }\mu\text{m}$ ), by using a Shimadzu HPLC system equipped with an electric conductivity detector and an anion exchange column (Shim-pack SCR-102H, Shimadzu) set at  $40^\circ\text{C}$ . The *p*-toluenesulfonic acid aqueous solution (5 mM) was used as the eluent at a rate of  $1.6\text{ ml min}^{-1}$ . A chromatogram for several organic acids is shown in Supplementary Fig. 17 with the obtained calibration curves.

Note that basified aqueous samples stored in non-airtight containers over several days occasionally showed 1–10  $\mu\text{M}$  of acetate and pyruvate signals (data not shown) because basification facilitates absorption of organic acids from ambient air. To avoid crucial contaminations such as pyruvate, we set our detection cutoff at 0.01 mM and analyzed all aqueous samples as soon as they were prepared.



### Quantification of organosulfur products

The four organosulfur compounds observed in the present study (methanethiol, MTA, dimethyl sulfide, and dimethyl disulfide) distribute both the gas- and aqueous-phases with significant fractions. Thus, aqueous-phase concentrations of methanethiol, dimethyl sulfide, and dimethyl disulfide were calculated from the partial pressures of respective compounds quantified by GC with the Henry's law constants reported in the literature (0.38, 0.56, and 0.58 mol l<sup>-1</sup> atm<sup>-1</sup>, respectively)<sup>43</sup>. The constant for MTA was determined experimentally to be 5.8 ± 1.0 mol l<sup>-1</sup> atm<sup>-1</sup> from three independent measurements of the water-gas partitioning of MTA in a closed glass vial containing a certain volume of 100 mM phosphate buffer solution (pH 6.7). The constants for methanethiol, dimethyl sulfide, and dimethyl disulfide determined by this method were in agreement with the literature values with the percentage errors less than 15%.

The organosulfur compounds may also be present on the sulfide surfaces. Actually, when 1 M phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) was added after the 7-day interaction of methanethiol with the NiS<sub>2</sub>PERM formed at -1.0 V<sub>SHE</sub>, the gas-phase concentrations of MTA and methanethiol increased by 30 and 70%, respectively, while that of dimethyl sulfide decreased by 50%. Nevertheless, because such chemical processes may cause undesirable reactions that consume MTA, we did not take account of the surface adsorption in the yield determination of organosulfur compounds. For the same reason, in the nonenzymatic thioester synthesis experiment, we report the amounts of inorganic gases (H<sub>2</sub>, CO, and CH<sub>4</sub>) quantified from the gas-phase analysis alone (Supplementary Figs. 19b, 22 and 23, Supplementary Table 3 and 4).

Dimethyl disulfide was always observed in the presence of methanethiol with the amount typically less than a few percent of the initial amount of methanethiol (Supplementary Figs. 19a and 20). A probable cause of the dimethyl disulfide formation is methanethiol oxidation by atmospheric O<sub>2</sub> (2 CH<sub>3</sub>SH + 0.5 O<sub>2</sub> → CH<sub>3</sub>SSCH<sub>3</sub> + H<sub>2</sub>O) at the timing of sample injections into the GC system owing to air intrusion (Supplementary Fig. 19b). Except for dimethyl disulfide, no oxidative organosulfur compound was detected (Supplementary Fig. 20). It was also confirmed that MTA, dimethyl sulfide, and dimethyl disulfide were stable in air.

### Thermodynamic calculation

Redox potentials ( $E_h$ ) of the H<sup>+</sup>/H<sub>2</sub> and the CO<sub>2</sub>/CO couples as functions of temperature and pH (Supplementary Fig. S1) were calculated with the following equations

$$E_h = \frac{1}{2F} (2RT \ln \alpha_{H^+} - RT \alpha_{H_2} - \Delta_f G^\circ(H_2)) \quad (2)$$

$$E_h = \frac{1}{2F} \left( 2RT \ln \alpha_{H^+} + RT \ln \alpha_{CO_2} - RT \ln \alpha_{CO} \right) \quad (3)$$

In these equations, T, R, and F stand for temperature in kelvins, the gas constant (8.31447 J mol<sup>-1</sup> K<sup>-1</sup>), and the Faraday constant (96485 J mol<sup>-1</sup> V<sup>-1</sup>), respectively.  $\alpha_i$  represents the activity of the species i that was calculated either using the extended Debye-Hückel equation<sup>44</sup> for aqueous ionic species (H<sup>+</sup>) or setting the activity coefficient to unity for aqueous neutral species (H<sub>2</sub>, CO<sub>2</sub> and CO).  $\Delta_f G^\circ(i)$  signifies the standard Gibbs energy of formation of the species i at the temperature and pressure of interest, which were calculated according to the revised HKF equations of state<sup>45</sup> together with the thermodynamic data and the revised HKF parameters reported in ref. 46 for H<sub>2</sub> and CO<sub>2</sub> and in ref. 47 for CO.  $\Delta_f G^\circ$  of H<sub>2</sub>O was taken from Helgeson and Kirkham<sup>48</sup>.

In Supplementary Fig. 1, 1 mmol kg<sup>-1</sup> H<sub>2</sub> was considered because it is a typical H<sub>2</sub> concentration in fluids from the present-day serpentine-hosted hydrothermal systems<sup>29,49</sup>. The CO<sub>2</sub>/CO activity ratio was set to one. Equilibrium calculation with this ratio gives the potential conditions where CO<sub>2</sub> and CO are equally stable. A ten-fold change in the activity ratio changes the redox potential by ± ~30 mV at 25°C and by ± ~40 mV at 150°C.

The potential/pH diagrams of the sulfide-metal systems (Fig. 1b and Supplementary Fig. 4) were computed with the Act2 program in Geochemist's Workbench version 10.0.5 by using the thermodynamic dataset for aqueous species calculated by the above procedures, those for sulfide minerals listed in Supplementary Table 3 presented by Kitadai et al.<sup>1</sup>, and those for pure metals compiled in Robie and Hemingway<sup>50</sup>.

### References

1. Adam, P. S., Borrel, G. & Gribaldo, S. Evolutionary history of carbon monoxide dehydrogenase/acetyl-CoA synthase, one of the oldest enzymatic complexes. *Proc. Natl. Acad. Sci. USA* **115**, E1166–E1173 (2018).
2. Russell, M. J. & Martin, W. The rocky roots of the acetyl-CoA pathway, *TRENDS Biochem. Sci.* **29**, 358–363 (2004).
3. Sousa, F. L. et al. Early bioenergetic evolution. *Phil. Trans. R. Soc. B.* **368**, 20130088 (2013).
4. Schuchmann, K. & Müller, V. Autotrophy at the thermodynamic limit of life: a model for energy conservation in acetogenic bacteria. *Nature Rev. Microbiol.* **12**, 809–821 (2014).
5. Can, M., Giles, L. J., Ragsdale, S. W. & Sarangi, R. X-ray absorption spectroscopy reveals an organometallic Ni–C bond in the CO-treated form of acetyl-CoA synthase, *Biochem.* **56**, 1248–1260 (2017).

6. Huber, C. & Wächtershäuser, G. Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions. *Science* **276**, 245–247 (1997).
7. Yamamoto, M. et al. Spontaneous and widespread electricity generation in natural deep-sea hydrothermal fields. *Angew. Chem. Int. Ed.* **56**, 5725–5728 (2017).
8. Ang, R. et al. Thermoelectricity generation and electron–magnon scattering in a natural chalcopyrite mineral from a deep-sea hydrothermal vent. *Angew. Chem. Int. Ed.* **54**, 12909–12913 (2015).
9. Krissansen-Totton, J., Arney, G. N. & Catling, D. C. Constraining the climate and ocean pH of the early Earth with a geological carbon cycle model. *Proc. Natl. Acad. Sci. USA* **115**, 4105–4110 (2018).
10. Yamaguchi, A. et al. Electrochemical CO<sub>2</sub> reduction by Ni-containing iron sulfides: How is CO<sub>2</sub> electrochemically reduced at bisulfide-bearing deep-sea hydrothermal precipitates? *Electrochim. Acta* **141**, 311–318 (2014).
11. Ooka, H., McGlynn, S. E. & Nakamura, R. Electrochemistry at deep-sea hydrothermal vents: utilization of the thermodynamic driving force towards the autotrophic origin of life. *ChemElectroChem* **6**, 1316–1323 (2019).
12. Kitadai, N. et al. Geoelectrochemical CO production: Implications of the autotrophic origin of life. *Sci. Adv.* **4**, ea07265 (2018).
13. Kitadai, N. et al. Metals likely promoted protometabolism in early ocean alkaline hydrothermal systems. *Sci. Adv.* **5**, ea07848 (2019).
14. Zhu, W. et al. Nickel sulfide microsphere film on Ni foam as an efficient bifunctional electrocatalyst for overall water splitting. *Chem. Commun.* **52**, 1486–1489 (2016).
15. Xiao, H., Goddard III, W. A., Cheng, T. & Liu, Y. Cu metal embedded in oxidized matrix catalyst to promote CO<sub>2</sub> activation and CO dimerization for electrochemical reduction of CO<sub>2</sub>. *Proc. Natl. Acad. Sci.* **114**, 6685–6688 (2017).
16. Hori, Y. & Murata, A. Electrochemical evidence of intermediate formation of adsorbed CO in cathodic reduction of CO<sub>2</sub> at a nickel electrode. *Electrochim. Acta* **35**, 1777–1780 (1990).
17. Hansen, H. A., Varley, J. B., Peterson, A. A. & Norskov, J. K. Understanding trends in the electrocatalytic activity of metals and enzymes for CO<sub>2</sub> reduction to CO. *J. Phys. Chem. Lett.* **4**, 388–392 (2013).
18. Kondo, T. & Mitsudo, T. Metal-catalyzed carbon–sulfur bond formation. *Chem. Rev.* **100**, 3205–3220 (2000).
19. Hirschbeck, V., Gehrtz, P. H. & Fleisher, I. Metal-catalyzed synthesis and use of thioesters: recent developments. *Chem. Eur. J.* **24**, 7092–7107 (2018).
20. Pietrocola, F., Galluzzi, L., Pedro, J. M. B., Madeo, F. & Kroemer, G. Acetyl coenzyme A: A central metabolite and second messenger. *Cell Metabolism* **21**, 805–821 (2015).
21. Satanowski A. & Bar-Even, A. A one-carbon path for fixing CO<sub>2</sub>. *EMBO reports* **21**, e50273 (2020).
22. Erley, W. & Wagner, H. Sulfur poisoning of carbon monoxide adsorption on Ni(111). *J. Catal.* **53**, 287–294 (1978).
23. Ma, S. H., Jiao, Z. Y., Wang, T. X. & Zu, X. T. Effect of preadsorbed S on the adsorption of CO on Co(0001). *J. Phys. Chem.* **113**, 16210–16215 (2009).
24. Chandru, K., Gilbert, A., Butch, C., Aono, M. & Cleaves II, H. J. The abiotic chemistry of thiolated acetate derivatives and the origin of life. *Sci. Rep.* **6**, 29883 (2016).
25. Lindahl, P. A. Acetyl-coenzyme A synthase: the case for a Ni<sup>0</sup><sub>p</sub>-based mechanism of catalysis. *J. Biol. Inorg. Chem.* **9**, 516–524 (2004).
26. Horn, B., Limberg, C., Herwig, C. & Mebs, S. (2011) The conversion of nickel-bound CO into an acetyl thioester: organometallic chemistry relevant to the acetyl coenzyme A synthase active site. *Angew. Chem. Int. Ed.* **50**, 12621–12625 (2011).
27. Bekker, A. et al. Atmospheric sulfur in Archean komatiite-hosted nickel deposits. *Science* **326**, 1086–1089 (2009).
28. Morrill, P. L. et al. Geochemistry and geobiology of a present-day serpentinization site in California: The Cedars. *Geochim. Cosmochim. Acta* **109**, 222–240 (2013).
29. Tivey, M. K. Generation of seafloor hydrothermal vent fluids and associated mineral deposits. *Oceanography* **20**, 50–65 (2007).
30. Heinen, W. & Lauwers, A. M. Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an anaerobic aqueous environment. *Orig. Life Evol. Biosph.* **26**, 131–150 (1996).
31. Schulte, M. D. & Rogers, K. L. Thiols in hydrothermal solution: standard partial molal properties and their role in the organic geochemistry of hydrothermal environments. *Geochim. Cosmochim. Acta* **68**, 1087–1097 (2004).
32. Baaske, P. et al. Extreme accumulation of nucleotides in simulated hydrothermal pore systems. *Proc. Natl. Acad. Sci.* **104**, 9346–9351 (2007).
33. Benner, S. A. et al. When did life likely emerge on Earth in an RNA-first process? *ChemSystemsChem* **1**, e1900035 (2019).

34. Weber, A. L. Nonenzymatic formation of “energy-rich” lactoyl and glyceroyl thioesters from glyceraldehyde and a thiol. *J. Mol. Evol.* **20**, 157–166 (1984).
35. Chevallot-Beroux, E., Gorges, J. & Moran, J. Energy conservation via thioesters in a non-enzymatic metabolism-like reaction network. *ChemRxiv* (2019) DOI:10.26434/chemrxiv.8832425.
36. Ragsdale, S. W. Life with carbon monoxide, *Crit. Rev. Biochem. Mol. Biol.* **39**, 165–195 (2004).
37. Aono, M., Kitadai, N. & Oono, Y. A principled approach to the origin problem. *Orig. Life. Evol. Biopsh.* **45**, 327–338 (2015).
38. Amend, J. P. & McCollom, T. M. Energetics of biomolecule synthesis on early Earth, in *Chemical Evolution II: From the Origins of Life to Modern Society*, Zaikowski, L., Fredrich, J. M. & Seidel, S. R. Eds. (American Chemical Society, 2009), pp. 63–94.
39. Shibuya, T., Russell, M. J. & Takai, K. Free energy distribution and hydrothermal mineral precipitation in Hadean submarine alkaline vent systems: Importance of iron redox reactions under anoxic conditions. *Geochim. Cosmochim. Acta* **175**, 1–19 (2016).
40. Bridge, M. E., Comrie, C. M. & Lambert, R. M. Chemisorption studies on cobalt single crystal surfaces I. carbon monoxide on Co(0001). *Surf. Sci.* **67**, 393–404 (1977).
41. Gonzalez, L., Miranda, R. & Ferrer, S. A thermal desorption study of the adsorption of CO on Fe(110); enhancement of dissociation by surface defects. *Sur. Sci.* **119**, 61–70 (1982).
42. Abild-Pedersen, F. & Andersson, M. P. CO adsorption energies on metals with correction for high coordination adsorption sites – A density functional study. *Surf. Sci.* **601**, 1747–1753 (2007).
43. Sander, R. Compilation of Henry’s law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.* **15**, 4399–4981 (2015).
44. Helgeson, H. C., Kirkham, D. H. & Flowers, G. C. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 KB. *Am. J. Sci.* **281**, 1249–1516 (1981).
45. Shock, E. L., Oelkers, E. H., Johnson, J. W., Sverjensky, D. A. & Helgeson, H. C. Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures. *J. Chem. Soc. Faraday Trans.* **88**, 803–826 (1992).
46. Shock, E. L., Helgeson, H. C. & Sverjensky, D. A. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* **53**, 2157–2183 (1989).
47. Shock, E. L. & McKinnon, W. B. Hydrothermal processing of cometary volatiles—applications to triton. *Icarus* **106**, 464–477 (1993).
48. Helgeson, H. C. & Kirkham, D. H. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: I. summary of the thermodynamic/electrostatic properties of the solvent. *Am. J. Sci.* **274**, 1089–1198 (1974).
49. Schrenk, M. O., Brazelton, W. J. & Lang, S. Q. Serpentinization, carbon, and deep life. *Rev. Mineral. Geochem.* **75**, 575–606 (2013).
50. Robie, R. A., Hemingway, B. S. “*Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10<sup>5</sup> Pascals) Pressure and at Higher Temperatures*” (U.S. Geological Survey Bulletin 2131, U.S. Geological Survey, 1995).

**Acknowledgments:** We thank Reiko Nagano and Atsuko Fujishima for their help in laboratory experiments. **Funding:** This research was supported by JSPS KAKENHI (Grant Number; 18H04456) and the Astrobiology Center Program of NINS (Grant Number; AB292004). **Author contributions:** N.K and Y.O. conceived the whole project based on the principled approach (31) and N.K. realized nonenzymatic thioester synthesis. Y.T. measured XANES spectra of the sulfide samples. S.O. performed SEM-EDX analysis, and W.T. prepared figures for the SEM-EDX data. N.K. performed all experiments except for the XANES and SEM-EDX measurements with technical support of Y.N., and prepared all figures and tables for the obtained results. S.O. considered possible intermediate steps in the MTA formation. All authors contributed to writing the paper. **Competing interests:** Authors declare no competing interests. **Data and materials availability:** All data is available in the main text or the supplementary materials.