

Electrochemistry

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Spontaneous and Widespread Electricity Generation in Natural Deep-Sea Hydrothermal Fields

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Abstract: Deep-sea hydrothermal vents discharge abundant reductive energy into oxidative seawater. Herein, we demonstrated that in situ measurements of redox potentials on the surfaces of active hydrothermal mineral deposits were more negative than the surrounding seawater potential, driving electrical current generation. We also demonstrated that negative potentials in the surface of minerals were widespread in the hydrothermal fields, regardless of the proximity to hydrothermal fluid discharges. Lab experiments verified that the negative potential of the mineral surface was induced by a distant electron transfer from the hydrothermal fluid through the metallic and catalytic properties of minerals. These results indicate that electric current is spontaneously and widely generated in natural mineral deposits in deep-sea hydrothermal fields. Our discovery provides important insights into the microbial communities that are supported by extracellular electron transfer and the prebiotic chemical and metabolic evolution of the ocean hydrothermal systems.

Submarine hydrothermal vents are spouts on the seafloor that discharge geothermally heated water, referred to as hydrothermal fluid.^[1] Hydrothermal fluids contain abundant metal ions (for example, Fe^{2+} , Cu^{2+} , and Zn^{2+}) and reduced gases (for example, H_2S , H_2 , and CH_4) produced by magma degassing and high-temperature hydrothermal reactions with rocks in the Earth's crust.^[1a] The metal- and sulfide-rich fluids are rapidly cooled and mixed with seawater near the seafloor and precipitate minerals, thus forming sub-seafloor hydrothermal mineral deposits and seafloor structures, such as chimneys, flanges, and mounds.^[2] The reduced gases in the fluids diffuse into the surrounding environment and sustain deep-sea vent chemolithotrophic microbial communities by acting as the predominant electron donors.^[1b]

We have previously demonstrated that vent minerals enriched in metal sulfides are highly electrically conductive.^[3] Moreover, it has become evident that the vent sulfide minerals exhibit the catalytic ability to oxidize hydrogen sulfide and reduce molecular oxygen and a thermoelectric effect, which converts a temperature gradient to electricity.^[3–4] By means of an in situ electrochemical experiment, we have also demonstrated that the potential difference between a hydrothermal fluid and the surrounding seawater can generate electricity through noble metal electrodes.^[4a] These results have indicated that hydrothermal sulfide mineral deposits are able to generate electrical currents between the two exposed fluids, that is, the hydrothermal fluid and seawater. Redox reactions in deep-sea hydrothermal systems have long been believed to occur only in the spatially limited mixing zones between hydrothermal fluids and seawater. Therefore, identifying spontaneously generated and widespread electricity generation associated with natural hydrothermal mineral deposits would greatly improve our understanding of the spatial extent and functional effects of chemical and biological redox reactions on the biogeochemical interactions and microbial community development in deep-sea hydrothermal environments.

To identify the spontaneous and widespread electricity generation in natural deep-sea hydrothermal fields, we conducted deep-sea in situ redox potential measurements over a wide area of hydrothermal fields along with laboratory experiments to simulate the redox potential gradient across hydrothermal mineral deposits.

We attempted to directly measure the redox potentials of deep-sea hydrothermal mineral deposits. A large hydrothermal mound, named the Yarigatake mound, was found in the Iheya North Natsu field (Supporting Information, Figure S1) and has a horizontally expanded flange that is approximately 6 m in width at the top. High-temperature hydrothermal fluid is discharged both from conduits in the center of the roof, from the edges of the flange, and in pools in the space under the flange. Many squat crabs reside on the roof surface of the flange near the diffusing hydrothermal discharges at the edges, thus indicating that the roof surface is subject to mixing between the hydrothermal fluid and the ambient seawater because the squat crab populations are supported by their chemolithotrophic (thiotrophic and methanotrophic) epibiotic symbionts.^[5] The redox potential of seawater in the mixing zone above the flange roof was $+466 \pm 7$ mV with reference to a standard hydrogen electrode. This value was approximately 100 mV more negative than that of the seawater distal to the vent ($+568 \pm 1$ mV; Figure 1). When a platinum probe was held against the

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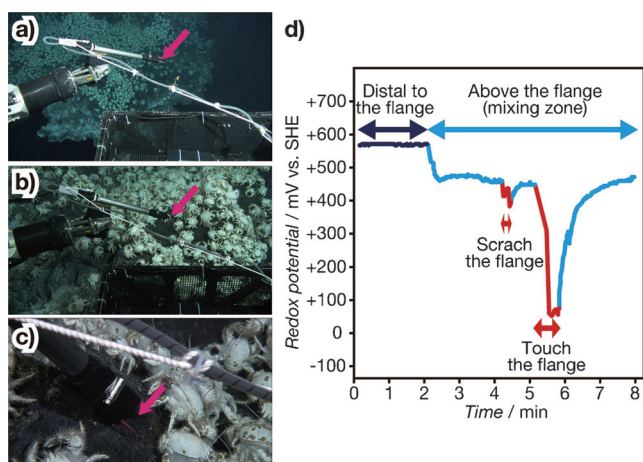


Figure 1. In situ measurements of redox potentials on the surface of the Yariyatake flange. a–c) Measuring redox potential by touching a platinum probe to minerals on the surface of the flange. The arrow indicates the point of measurement. d) Time vs. redox potential plot for the area surrounding the flange. Dark blue, distal to the flange (reference seawater); light blue, above the cap of the flange (that is, the mixing zone of hydrothermal fluid and seawater); red, sulfide minerals on the surface of the flange. Redox potentials are shown as values versus the standard hydrogen electrode (SHE).

mineral surfaces of the flange roof, the redox potential abruptly decreased to the minimal value of +49 mV (Figure 1). The sharp drop in potential after the probe touched the mineral surface was repeatedly observed at different measurement points, and we confirmed that this effect was not caused by direct exposure to hydrothermal fluid discharges (Movie 1 in the Supporting Information).

The redox potentials of the hydrothermal mineral-deposit surfaces were measured at a different hydrothermal vent site (the HDSK chimney) in another hydrothermal field (the Iheya North Aki field) in the Okinawa Trough (Supporting Information, Figure S2). This chimney structure is approximately 6 m in height, and vigorous hydrothermal fluid discharge was observed only at the top conduit of the chimney. The probe was allowed to touch the mineral surfaces at the bottom, middle, and top of the chimney (Figure 2). Sharp drops in potential were observed at all three points shortly after the probe touched the mineral surface. The potentials of the mineral surfaces were $+138 \pm 1$ mV, $+32 \pm 47$ mV, and -22 ± 33 mV at the bottom, middle, and top of the chimney, respectively. Finally, the probe was inserted into the high-temperature hydrothermal fluid through the fragile chimney wall at the top of the chimney, where it recorded the lowest redox potential of -96 ± 14 mV. This value was close to the in situ redox potential (-39 mV) of the high-temperature hydrothermal fluid at another Okinawa Trough hydrothermal field, the Iheya North Original field, observed in our previous work.^[4a] These results indicate that the redox potentials of the hydrothermal mineral surfaces exposed to seawater are highly negative. In addition, the negative potential appears to be primarily controlled by the redox potential of the hydrothermal fluid flowing through the mineral, and the magnitude of the value, is likely associated with the thickness of intervening mineral wall, that is, the

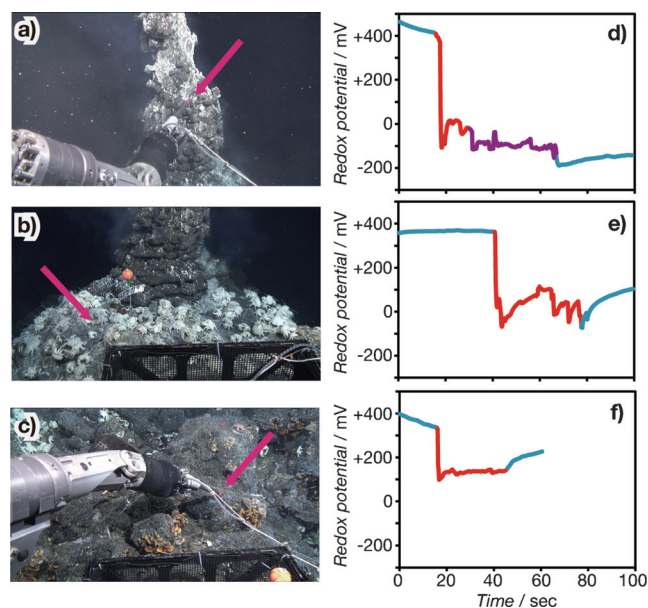


Figure 2. a–c) In situ measurements of redox potentials on the surface of the HDSK chimney. Measurement points are indicated by arrows and d–f) time vs. redox potential plots at the top (a, d), middle (b, e), and bottom (c, f) of the chimney. The redox potential colors correspond to surrounding seawater (light blue), the surface of the sulfide minerals (red), and the hydrothermal fluid (purple).

conductive distance between the hydrothermal fluid (reductant) and the seawater (oxidant).

In situ measurements of the redox potential on the seafloor were carried out over a wide area (approximately $150 \text{ m} \times 150 \text{ m}$) around the HDSK chimney site (Figure 3). At the HDSK chimney site, and at other focused vent and diffusing fluid flow sites, the hydrothermal mineral deposit surfaces showed highly negative potentials (approximately $+0.1$ V). In addition, there were a number of outcrops with negative potentials (approximately $+0.15$ to $+0.30$ V) that were distant from apparent seafloor hydrothermal fluid discharges. It has been shown that sulfide minerals catalyze the reduction of molecular oxygen at more negative potentials than $+0.30$ V.^[3] These results indicate widespread and distant electron transfer from the sub-seafloor hydrothermal fluid flows to the seawater above the seabed through the electrically conductive massive hydrothermal mineral deposits.

In a previous study, the sulfide minerals obtained from deep-sea hydrothermal vents were shown to exhibit electrical conductivity and behave as metallic conductors and electrodes.^[3] However, sulfide minerals can also behave as redox agents. To confirm that the negative potentials during the in situ measurements were derived from the hydrothermal fluid potentials rather than the redox reactions of mineral components, we performed laboratory experiments using a natural hydrothermal mineral deposit obtained from the HDSK chimney (Figure 4). The redox potential in a piece of sulfide chimney mineral dipped into an artificial seawater solution (0.6 M NaCl) was similar to the redox potential of the solution. However, when this piece was connected by a conducting wire to another sulfide chimney piece dipped in an

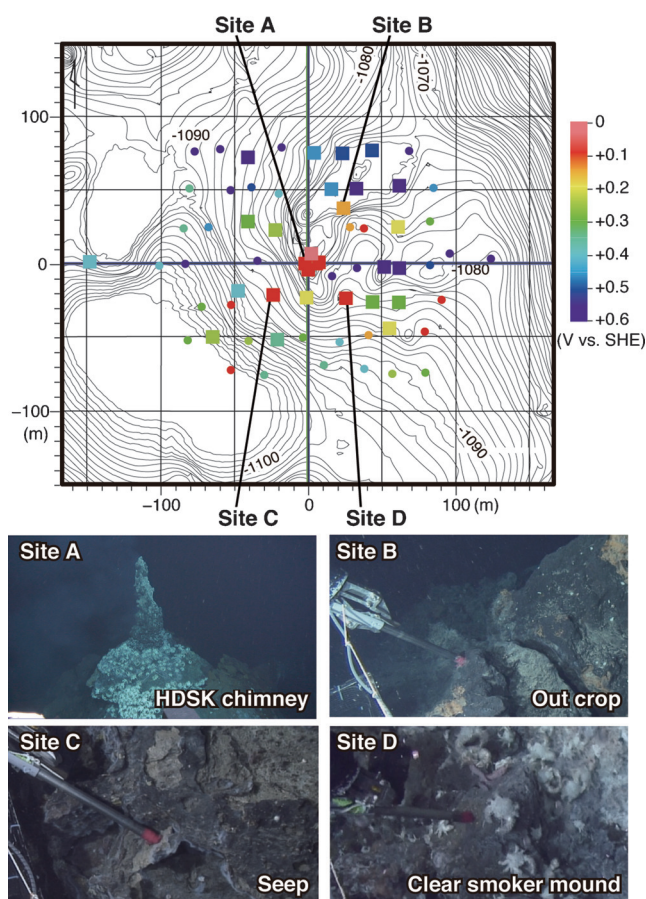


Figure 3. Redox potential mapping of the seafloor in a deep-sea hydrothermal field. The redox potential values are represented by the colors of the squares (rock sites) and circles (sediment sites). Contours indicate water depth (m) of the seafloor. The photographs show representative measurement points for rock sites. At the sediment sites, the electrode was inserted into the sediment, and the measured values do not indicate the redox potential of the surface of the seafloor.

artificial hydrothermal fluid solution (0.6 M NaCl, 0.1 M Na₂S), the redox potential of the piece in the artificial seawater showed a very negative value close to that of the artificial hydrothermal fluid. This result demonstrated that the redox potentials on sulfide mineral surfaces are derived from the exposed hydrothermal fluids rather than from the redox reactions of minerals themselves. Furthermore, the redox potentials on mineral surfaces are more strongly influenced by the redox potential of the hydrothermal fluid rather than that of the seawater. This result suggests that the oxidation of hydrogen sulfide at the interface between the hydrothermal fluid and the sulfide mineral surface (anodic reaction) proceeds faster than the reduction of molecular oxygen at the interface between the seawater and the sulfide mineral surface (cathodic reaction). In addition, it is reported that almost no current is generated by the self-reaction of a sulfide mineral electrode during voltammetry analysis from -0.3 to $+0.3$ V.^[3,4a] Thus, it appears very likely that the hydrothermal sulfide deposits behave as conductors rather than redox agents and that the massive sulfide deposits can propagate the

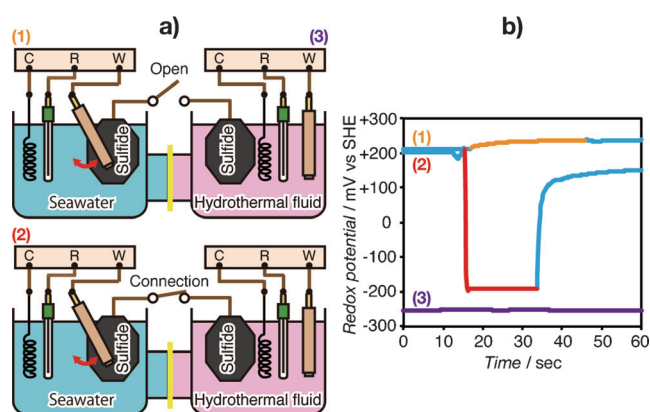


Figure 4. Redox potential on sulfide minerals in artificial fluids. a) Illustration of the redox potential measurement. Pieces of sulfide (dark grey octagon) were connected to conducting wires (brown line) and placed into solutions in the electrochemical cell, in which a proton-exchange membrane (yellow line) separated the two types of artificial fluids, seawater (left: 0.6 M NaCl, light blue) and hydrothermal fluid (right: 0.6 M NaCl with 0.1 M Na₂S, pink). C, R, and W indicate counter (Pt), reference (Ag/AgCl), and working (Pt) electrodes, respectively. b) Redox potential of the seawater, light blue line, and a piece of sulfide, orange line, (1). Redox potential of the seawater, light blue line, and a piece of sulfide connected to another piece in the hydrothermal fluid, red line, (2). Redox potential in hydrothermal fluid, purple line, (3).

redox potentials of the sub-seafloor hydrothermal fluids to the seafloor exposed to seawater.^[3,6]

In this work, we demonstrated widespread and distant electron transfer from the sub-seafloor hydrothermal fluid flows to the seafloor through the electrically conductive massive hydrothermal mineral deposits. Generation of electricity in deep-sea hydrothermal systems undoubtedly affects the surrounding biogeochemical processes and microbial community development.^[7] Laboratory and environmental experiments have identified an increasing number of microorganisms capable of directly utilizing electrons for their energy metabolism^[8] and even for biomass production and growth.^[9] Although no deep-sea vent microorganisms capable of directly utilizing electrons have been reported, it seems likely that some of the chemolithotrophic microbial populations in deep-sea hydrothermal environments may utilize the electrons available on the hydrothermal mineral deposit surfaces as an alternative energy source instead of other electron-donor molecules, such as molecular hydrogen, hydrogen sulfide, and methane. Thus, some of the chemolithotrophic microbial communities in the deep-sea hydrothermal environments, particularly some of the adhesive microbial populations on the hydrothermal sulfide mineral surfaces, may be sustained by the spontaneous and widespread generation of electricity between hydrothermal fluids and seawater through hydrothermal mineral deposits. The possible occurrence of such electron-utilizing (electrotrophic) microbial populations in natural deep-sea hydrothermal environments would shed light on a new type of ecosystem, the electrotrophic ecosystem, in addition to the chemotrophic and phototrophic ecosystems on this planet. In addition, deep-sea hydrothermal systems, forming sulfide mineral

deposits, are one of the most plausible locations for the origin of life.^[10] It is well known that electrochemical reactions can drive the generation and conversion of various inorganic and organic compounds, such as metabolic substrates, products, and intermediates, thus leading to the configuration of possible proto-metabolisms during the prebiotic chemical evolution.^[11] The spontaneous and widespread generation of electricity in ancient deep-sea hydrothermal systems might have served as a significant energetic driving force and might have provided the spatially extensive reaction beds for the prebiotic synthesis of the organic building blocks of life and the configuration of a proto-metabolism. To date, this system has merely been considered in the previous scenarios of the origin of life on this planet.^[10b,11b,c,12]

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Conflict of interest

The authors declare no conflict of interest.

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