Marine Chemistry

DOI: 10.1002/anie.201003311

Electrical Current Generation across a Black Smoker Chimney**

Ryuhei Nakamura,* Toshihiro Takashima, Souichiro Kato, Ken Takai, Masahiro Yamamoto, and Kazuhito Hashimoto

In environments isolated from solar radiation, diverse microbial populations and ecosystems are sustained by the chemical energy supplied from Earth's interior.[1] The most outstanding example is a deep-sea hydrothermal vent, which discharges enormous amounts of reductive energy in the form of reduced sulfur compounds, H_2, CH_4, and reduced metals during magma degassing and hydrothermal reactions with hot rocks.[2,3] Hydrothermal vent chimneys are generated by mineralization in the mixing zone between hot, reduced hydrothermal fluid and cold, oxygenated seawater and provide an ideal habitat for chemolithotrophic microbial communities.[3–5] As the chimney structures serve as an interface between the Earth's reductive interior and oxidative exterior, sustained microbial redox metabolism is very feasible. Simultaneously, the energy potential mediated by the chimney structure leads to many hypotheses concerning chemical evolution in the prebiotic ocean and the early evolution of energy metabolisms and cellular functions in the ancient Earth.[6–15]

Black smokers are a type of hydrothermal vent with sulfide-rich emissions that precipitate to form sulfide mineral chimneys consisting mainly of chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). The mineralogical and structural characteristics of black smoker chimneys have been extensively studied;[10–17] however, electrical conduction and electrocatalysis of black smoker chimneys have never been examined. Although bulk crystals of $CuFeS_2$ and FeS_2 are typically considered poor conductors, it is predicted that a chimney structure composed of nano- and microsized crystalline particles would have quite a large surface area with the potential of mediating the efficient electron transport.[18] Herein we therefore examine the electrochemical characteristics of the black smoker chimney and seek to estimate the redox potential between the hydrothermal fluid conduit and ambient seawater across the chimney wall. For the analysis, a black smoker sulfide chimney obtained from the Mariner hydrothermal field in the southern Lau Basin was characterized (Figure 1). The observed electrical conduction potential points to a possible new type of energy transport from hydrothermal fluid to seawater by electrical current generation in the sulfide chimney wall.

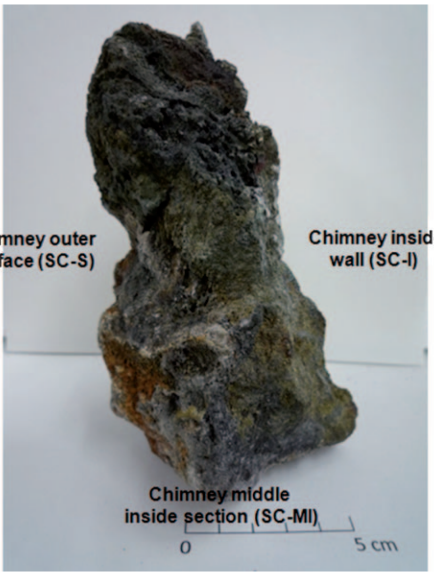

Figure 1. A cross-sectional image of a portion of the black smoker chimney structure obtained from Snow Chimney in the Lau Basin.

A portion of chimney structure was obtained from a hydrothermal vent site named Snow Chimney (SC; 22°10.825′S, 176°36.095′W, 1908 m) at the Mariner field in the Lau Basin.[19] The morphology and mineral composition of the chimney, effluent hydrothermal fluid chemistry, and microbial communities present in the chimney habitats were previously characterized.[19] The Snow Chimney structure was predominantly composed of $CuFeS_2$, FeS_2, and anhydrite ($CaSO_4$), although sphalerite (ZnS) and ferric oxides were also identified in the outer surfaces.[19] The specimens were collected from different zones of the SC sample (Figure 1), which consisted of the chimney inside wall (SC-I), chimney middle inside section (SC-MI), and chimney outer surface

---

[*] Dr. R. Nakamura
Department of Applied Chemistry, The University of Tokyo
4-6-1 Komaba, meguro-ku, Tokyo 153-8904 (Japan)
Fax: (+81) 3-5452-5748
E-mail: nakamura@light.t.u-tokyo.ac.jp

Dr. S. Kato
ERATO/JST, HASHIMOTO Light-Energy Conversion Project
4-6-1 Komaba, meguro-ku, Tokyo 153-8904 (Japan)

Dr. K. Takai, Dr. M. Yamamoto
Japan Agency for Marine-Earth Science and Technology (JAMSTEC)
Yokosuka (Japan)

T. Takashima, Prof. Dr. K. Hashimoto
Department of Applied Chemistry, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
and
ERATO/JST, HASHIMOTO Light Energy Conversion Project

[**] This work was financially supported by the Exploratory Research for Advanced Technology (ERATO) program of the Japan Science and Technology Agency (JST).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003311.

(SC-S), and were used for electrical conduction and electrocatalysis experiments. These specimens were comprised of micrometer and sub-micrometer crystalline particles that formed a densely interconnected structure (Figure 2A). The current–voltage (*I*–*V*) characteristics for the dried specimens over a 2 mm distance are shown in Figure 2B. As expected, clear electrical conduction was observed for all samples (SC-I, SC-MI, and SC-S), although the electrical conduction of SC-S varied considerably with the measuring position (Figure 2B-3), likely owing to the presence of insulating layers of ferric oxides or sphalerite. The observed linear increase in current with voltage verified the metallike electrical conduction of the chimney specimens, suggesting the existence of electron transport conduits comprised of the heavily doped chalcopyrite and pyrite precipitates. Not only was electrical conduction over a 2 mm distance in each chimney specimen observed, but a considerable long-distant conduit longer than 10 cm was also found when the bulk chimney structure (shown in Figure 1) was examined; the resistance was less than 100 Ω over a 10 cm distance at various positions across the chimney wall.

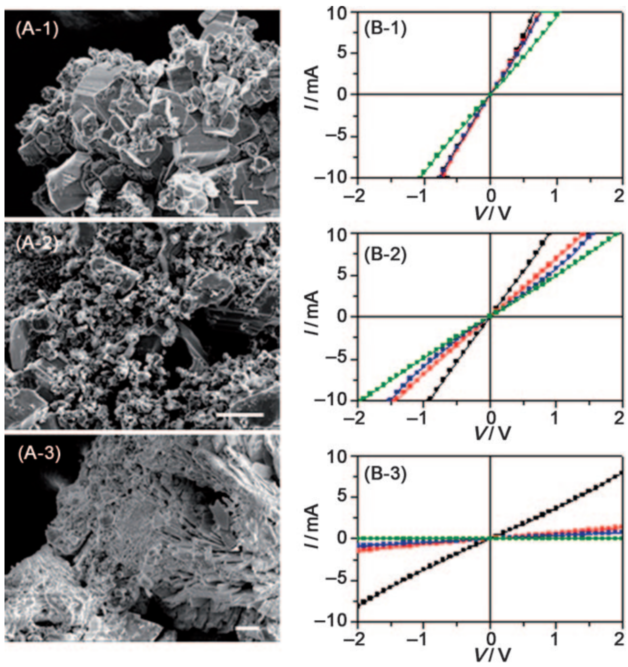

Figure 2. A) SEM images of the chimney inside wall (A-1: SC-I), chimney middle inside section (A-2: SC-MI), and chimney outer surface (A-3: SC-S). Scale bars: 20 μm. B) *I*–*V* characteristics of the chimney specimens measured at a 2 mm distance at room temperature. (B-1): SC-I, (B-2): SC-MI, and (B-3): SC-S. *I*–*V* curves were recorded at four different measuring positions for each specimen, as indicated by the different colors (green, blue, red, and black).

To examine catalysis of the SC sample, the chimney specimens were subjected to electrochemical experiments. SC-I and SC-S chimney specimens with a size of approximately 3 cm^3 were used as working electrodes. A copper wire was fixed to each chimney specimen using an adhesive silver paste, and the contacted specimen was protected by epoxy glue (Figure S1 in the Supporting Information). Current versus potential curves were measured with a potentiostat and a potential programmer, using a platinum wire as the counter electrode and a Ag/AgCl electrode as the reference electrode. We examined the catalytic activity using the SC-I electrode for oxidation of sulfide and the SC-S electrode for reduction of O_2, at 30 °C in aqueous sodium chloride (0.17 M). In the presence of concentrated sulfide ions (0.1 M Na_2S, pH 12), the SC-I electrode generated an anodic current at a potential of approximately −400 mV vs. SHE (Figure 2A, trace 1). X-ray photoelectron spectroscopy (XPS) analysis of the SC-I electrode showed the formation of a sulfur 2p peak at 163.5 eV, assignable to S^0 (Figure S2 in the Supporting Information). No significant anodic current was observed in the absence of sulfide ions (Figure 2A, trace 2). These results indicate that sulfide can be oxidized to elemental sulfur by the catalytic activity of the inner chimney wall. Meanwhile, in an oxygenated environment without sulfide, the SC-S electrode displayed the generation of a cathodic current (Figure 2B, trace 2) that was larger in current than that observed under anaerobic conditions (Figure 2B, trace 1). This cathodic current was generated at an onset potential of approximately 300 mV, which corresponds to the two-electron reduction of O_2.[20] The O_2 reduction on the SC-S electrode was greatly enhanced by the addition of either Mo^{VI} or Ni^{II} ions, which are typical trace minerals in the hydrothermal environment,[15,16] as co-catalysts in the electrolyte solution (Figure 2B, traces 3 and 4).

From these results, it was indicated that 700 mV represents the maximum potential gradient that could be generated across the chimney wall under the present experimental condition. In the bulk chimney structure, the chimney interior and exterior surfaces were electrically bridged by the metallike sulfide minerals. Therefore, the large potential gradient could be harnessed to generate electrical currents across the chimney wall and implies the occurrence of energy transport within sulfide chimneys by the redox reaction of sulfide and O_2 present in the hydrothermal fluid and ambient seawater, respectively (Figure 4). It is interesting to note that the equilibrium potential of the S^0/S^{2-} redox couple is located at −450 mV, as this value is consistent with the onset potential of the sulfide oxidation on the SC-I electrode (Figure 3A, trace 1). This observation is striking, as the inner chimney wall, which is mainly composed of microsized chalcopyrite and pyrite crystals (see the SEM image in Figure 2A-1), catalyzes the two-electron oxidation of sulfide to elemental sulfur without any thermodynamic loss of energy. Thus, the chimney wall facilitates the highly efficient conversion of the spatially discrete redox potential to electrical current (Figure 4).

On deep-sea hydrothermal vents, the redox potential across the chimney wall is likely bridged by the diffusion and convection of fluids and the mixing between reductive and oxidative chemicals.[12] It is believed that all physiologically and phylogenetically diverse extremophiles are fostered by the primary production on the basis of the redox reactions of existing reductive chemicals such as H_2S and H_2 at the hydrothermal mixing interface.[3–5] Our findings indicate that

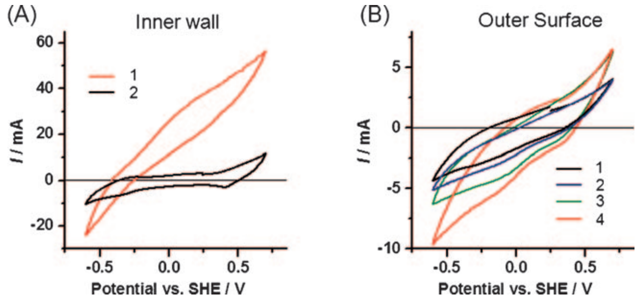

Figure 3. A) Cyclic voltammograms of SC-I electrodes in an argon-purged aqueous solution of NaCl (0.17 M) with (trace 1) and without (trace 2) the addition of sulfide ions (0.1 M Na_2S, pH 12). B) Cyclic voltammograms of SC-S electrodes in argon-purged (trace 1) and O_2-purged (trace 2) solutions (0.17 M NaCl, pH 7). The effects of adding Na_2MoO_4 (trace 3) or $NiCl_2$ (0.1 M, trace 4) on the catalytic activity of oxygen reduction at the SC-S electrodes were also examined. The scan rate was 10 $mV s^{-1}$.

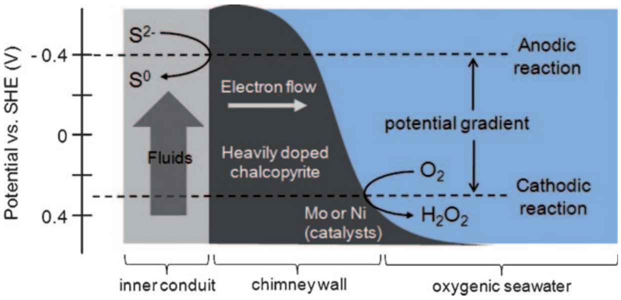

Figure 4. Schematic illustration of an energy diagram for the anodic and cathodic reactions occurring at the inner and outer surfaces, respectively, of the chimney. The potential gradient across the chimney serves as a driving force for electrical current generation.

hydrothermal vent chimneys can generate an electron flow by exploiting the electrical conduction and electrocatalysis of the microsized sulfide crystal network. This implies that at least a portion of the chemolithotrophic microbial components living in chimney habitats may directly utilize the electrons transported from the hydrothermal fluids through the sulfide crystal network as an energy source for carbon fixation, but not the reductive chemicals.[21–24] Moreover, the potential electron transport may be associated with the prebiotic synthesis of organic compounds in ancient deep-sea hydrothermal environments.[4–7] Further investigation will shed light on the impact of electrical and electrocatalytic function of the hydrothermal sulfide chimneys and deposits on microbial and chemical processes in the present and ancient deep ocean.

Experimental Section

Current–voltage measurements: The electrical characteristics of the chimney specimens were measured using Keithley 2400 and 6430 source/measurement units at room temperature at a distance of 2 mm.

Electrochemical measurements: The chimney specimens obtained from the Mariner hydrothermal field in the southern Lau Basin were stored at 4 °C in an argon-purged aqueous solution containing Na_2S until needed for electrochemical experiments. A copper wire was fixed to each chimney specimen (with a size of ca. 3 cm^3) using an adhesive silver paste, and the contacted specimen was protected by epoxy glue. Current versus potential curves for chimney specimens were measured at 30 °C with a commercial potentiostat and a potential programmer (HZ-5000, HOKUTO DENKO Automatic Polarization System) using a platinum wire as the counter electrode and a Ag/AgCl/sat.KCl electrode as the reference electrode. An Ar- or O_2-purged aqueous solution of NaCl (0.17 M) was used as the electrolyte solution.

Received: June 1, 2010

Keywords: electrochemistry · microbiology · mineralogy · nanostructures · sustainable chemistry

[1] A.-L. Reysenbach, E. Shock, *Science* **2002**, *296*, 1077.
[2] K. Takai, K. Horikoshi, *Genetics* **1999**, *152*, 1285.
[3] K. Takai, S. Nakagawa, A.-L. Reysenbach, J. Hoek, *Geophys. Monogr.* **2006**, *166*, 185.
[4] W. Martin, J. Baross, D. Kelley, M. J. Russell, *Nat. Rev. Microbiol.* **2008**, *6*, 805.
[5] K. Takai, K. Nakamura, K. Suzuki, F. Inagaki, K. H. Nealson, H. Kumagai, *Paleontol. Res.* **2006**, *10*, 269.
[6] U. J. Meierhenrich, J.J. Filippi, C. Meinert, P. Vierling, J. P. Dworkin, *Angew. Chem.* **2010**, *122*, 3826; *Angew. Chem. Int. Ed.* **2010**, *49*, 3738.
[7] O. Dannenmuller, K. Arakawa, T. Eguchi, K. Kakinuma, S. Blanc, A. M. Albrecht, M. Schmutz, Y. Nakatani, G. Ourisson, *Chem. Eur. J.* **2000**, *6*, 645.
[8] E. V. Koonin, W. Martin, *Trends Genet.* **2005**, *21*, 647.
[9] J. A. Huber, G. Wächtershäuser, *Science* **1997**, *276*, 245.
[10] D. Rickard, G. W. Luther III, *Chem. Rev.* **2007**, *107*, 514.
[11] M. Pósfai, R. E. Dunin-Borkowski, *Rev. Mineral. Geochem.* **2006**, *61*, 679.
[12] P. Baaske, F. M. Weinert, S. Duhr, K. H. Lemke, M. J. Russell, D. Braun, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 9346.
[13] M. A. A. Schoonen, Y. Xu, J. Bebie, *Origins Life Evol. Biosphere* **1999**, *29*, 5.
[14] T. M. McCollom, J. S. Seewald, *Chem. Rev.* **2007**, *107*, 382.
[15] M. J. Russell, *Acta. Biotheor.* **2007**, *55*, 133.
[16] G. D. Cody, N. Z. Boctor, R. M. Hazen, R. M. J. A. Brandes, H. J. Morowitz, H. S. Yoder, *Geochim. Cosmochim. Acta* **2001**, *65*, 3557.
[17] C. C. Thornburg, T. M. Zabriskie, K. L. McPhail, *J. Nat. Prod.* **2010**, *73*, 489.
[18] A high surface-to-volume ratio of nano- and microsized particles facilitates effective carrier doping. Thus, the efficient long-distance electron transport is predicted to occur for the chimney structures composed of nano- and microsized $CuFeS_2$ and FeS_2.
[19] K. Takai, T. Nunoura, J. Ishibashi, J. Lupton, R. Suzuki, H. Hamasaki, Y. Ueno, S. Kawagucci, T. Gamo, Y. Suzuki, H. Hirayama, K. Horikoshi, *J. Geophys. Res.* **2008**, *113*, G02031.
[20] The cathodic current observed under anaerobic conditions (trace 1, Figure 2B) is mostly derived from the self-reduction reaction (Fe^{3+} to Fe^{2+} and/or S^- to S^{2-}) of chalcopyrite and pyrite.
[21] C. E. Reimers, L. M. Tender, S. Fertig, W. Wang, *Environ. Sci. Technol.* **2001**, *35*, 192.
[22] R. Nakamura, F. Kai, A. Okamoto, G. J. Newton, K. Hashimoto, *Angew. Chem.* **2009**, *121*, 516; *Angew. Chem. Int. Ed.* **2009**, *48*, 508.
[23] L. P. Nielsen, N. Risgaard-Petersen, H. Fossing, P. B. Christensen, M. Sayama, *Nature* **2010**, *463*, 1071.
[24] R. Nakamura, A. Okamoto, N. Tajima, G. N. Netwon, F, Kai, T, Takashima, K. Hashimoto, *ChemBioChem* **2010**, *11*, 643.