

EXPRESS LETTER

H₂ generation by experimental hydrothermal alteration of komatiitic glass at 300°C and 500 bars: A preliminary result from on-going experiment

MOTOKO YOSHIKAZAKI,^{1,2*} TAKAZO SHIBUYA,² KATSUHIKO SUZUKI,^{2,3} KENJI SHIMIZU,^{2,3} KENTARO NAKAMURA,² KEN TAKAI,^{2,4} SOICHI OMORI¹ and SHIGENORI MARUYAMA¹

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan

²Precambrian Ecosystem Laboratory, Japan Agency for Marine-Earth Science and Technology (JAMSTEC),
2-15 Natsushima-cho, Yokosuka 237-0061, Japan

³Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC),
2-15 Natsushima-cho, Yokosuka 237-0061, Japan

⁴Subsurface Geobiology Advanced Research (SUGAR) project, Japan Agency for Marine-Earth Science and Technology (JAMSTEC),
2-15 Natsushima-cho, Yokosuka 237-0061, Japan

(Received April 7, 2009; Accepted August 28, 2009; Online published September 10, 2009)

Hydration of komatiite can be a source of significant amount of hydrogen in the Hadean and early Archean ocean floor. We report the first direct evidence for this process based on the results of our hydrothermal alteration experiments on the synthetic komatiitic glass at 300°C and 500 bars. Komatiitic glass was synthesized by dehydration and remelting of serpentinized Al-depleted komatiite collected from the early Archean Komati Formation, the Barberton Greenstone Belt, South Africa. Though the run is still continuing in our lab, the observed accumulation of hydrogen (2.4 mmol/kg) over 2,600 hours is truly significant and is comparable to those observed by hydration of peridotitic rocks. Our results suggest that hydrothermal alteration of komatiites may have provided the source of H₂ in the vicinity of hydrothermal vents that fueled the early evolution of living ecosystems in the Hadean and early Archean.

Keywords: hydrothermal alteration, komatiitic glass, laboratory experiment, early Earth, ultramafic rock

INTRODUCTION

Since their discovery in the late 1970s (Corliss *et al.*, 1979; Edmond *et al.*, 1979), deep-sea hydrothermal vents have been considered a possible environment for the origin and early evolution of life on Earth (e.g., Yanagawa and Kojima, 1985; Russell and Hall, 1997). Multidisciplinary studies suggest that the most ancient microbial ecosystems were sheltered in habitable environments in the vicinity of H₂-rich hydrothermal fluids that may have been sustained by chemolithoautotrophic primary producers such as hyperthermophilic hydrogenotrophic methanogens (Russell and Hall, 1997; Sleep *et al.*, 2004; Kelley *et al.*, 2005; Takai *et al.*, 2006; Canfield *et al.*, 2006).

In the modern ocean, H₂-enriched hydrothermal fluids are commonly associated with slow-spreading mid-ocean ridge (MOR) setting dominated by peridotite (Kelley *et al.*, 2001; Früh-Green *et al.*, 2004). The

serpentinization of abyssal peridotite has been well investigated both experimentally and theoretically. The investigations indicate that the peridotite-water reaction strongly affects the chemical compositions of hydrothermal fluids and provides an extraordinarily high concentration of H₂ in the fluids (e.g., Seyfried *et al.*, 1979; Allen and Seyfried, 2003; McCollom, 2007; McCollom and Bach, 2009). On the other hand, a possible modern analog of the most ancient microbial ecosystems was identified in the Kaurei hydrothermal field in the Central Indian Ridge and Lost City hydrothermal field in the Mid Atlantic Ridge (MAR), where the hydrothermal fluids were highly enriched with H₂ and microbially produced CH₄ (Takai *et al.*, 2004; Kelley *et al.*, 2005). Based on these observations, it was hypothesized that methanogenic ecosystems could exist in the sub-seafloor environments of deep-sea hydrothermal activities hosted by or associated with ultramafic rocks such as peridotite (Kelley *et al.*, 2005; Takai *et al.*, 2006; Sleep and Bird, 2007). This hypothesis suggests a linkage between ultramafic rocks, hydrothermal activity, and sufficient H₂ generation (hydrogenogenesis).

*Corresponding author (e-mail: yoshizaki.m.aa@m.titech.ac.jp)

Table 1. The chemical composition of high Mg[#] Al-depleted komatiite collected from the Barberton Greenstone Belt, South Africa used in this study. Komatiitic glasses were prepared by dehydration and remelting of this komatiite sample.

Sample	BB-262	Green <i>et al.</i> (1975)	After Smith <i>et al.</i> (1980)
SiO ₂	46.5	46.5	47.5
TiO ₂	0.30	0.19	0.36
Al ₂ O ₃	4.74	3.58	3.94
FeO*	11.9	10.4	11.2
MnO	0.21	0.21	0.19
MgO	29.3	33.0	29.0
CaO	6.32	5.10	7.14
Na ₂ O	0.35	0.49	0.14
K ₂ O	0.11	0.18	0.03
P ₂ O ₅	0.06	0.01	0.02
NiO	0.19	0.25	0.19
Mg ^{#(1)}	81.4	85.0	82.1

These data are 100% normalized. Loss on ignition is 6.5%.

⁽¹⁾Mg[#] = Mg/(Mg + Fe) × 100.

In the Hadean and early Archean ocean, however, it is believed that peridotite would be scarce in the ocean floor because the overlying oceanic crust at the time is thought to have been approximately two to three times thicker than the modern equivalent (Ohta *et al.*, 1996; Moores, 2002; Takai *et al.*, 2006). If this is true, what kind of ultramafic rock(s) drove the H₂-dominant hydrothermal activities? Komatiite is the most likely candidate and is also hypothesized to sustain the occurrence and propagation of ancient methanogenic ecosystems through its reaction with hydrothermal fluids (Kelley *et al.*, 2005; Takai *et al.*, 2006). Komatiite is a distinctive ultramafic volcanic rock common in Archean greenstone successions, less common in the Proterozoic and quite rare in the Phanerozoic (Condie, 2005). Very little is known about the potential H₂ production from hydrothermal alteration of komatiites. Therefore, we are conducting the first laboratory experiment to assess H₂ generation during hydrothermal alteration of komatiites. It will be shown in this paper that we observed unequivocal H₂ production during our experiment. Although the experiment is still ongoing in our laboratory, the observed H₂ production would, by itself, shed a new light on discussions about the establishment of the early ecosystem.

EXPERIMENT

High Mg[#] Al-depleted komatiite collected from the early Archean Komati Formation, Onverwacht Group, Barberton Greenstone Belt, South Africa (BB-262) was used in this study (Table 1) as representative of less-differentiated primary komatiitic magma. As with all komatiites, the sample was also highly serpentinized and

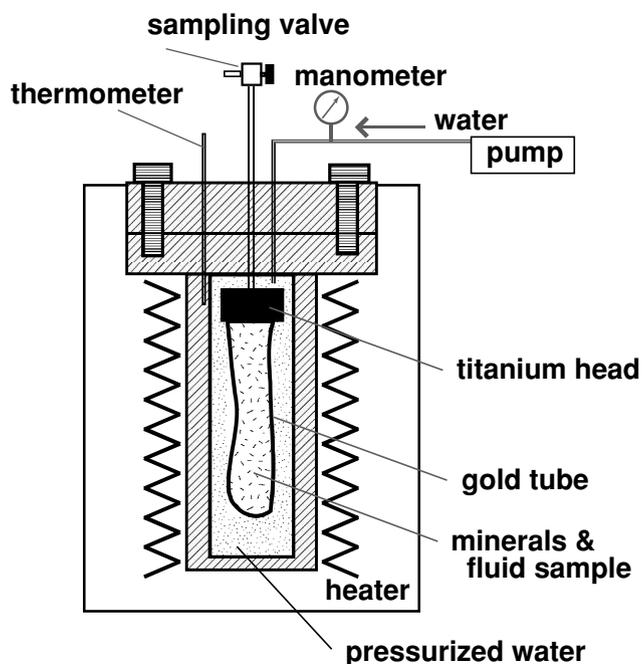


Fig. 1. Schematic diagram of the Inconel-alloy autoclave and flexible-cell hydrothermal apparatus used in this laboratory experiment.

contains secondary minerals such as serpentine, chlorite, magnetite, and pyrite, indicating previous secondary alteration and/or metamorphism. However, the sample does not show severe deformation, and the igneous orthocumulate texture is well preserved. Olivine is replaced by serpentine, chlorite, and magnetite. Orthopyroxene is partially replaced by serpentine and magnetite and interstitial glass is replaced by chlorite. Loss on ignition is 6.5%. To avoid the effect of hydrated and carbonated materials the sample was dehydrated and decarbonated: approximately 30 g of sample powder was placed in an alumina crucible and heated at 1050°C for 12 hours. Subsequently, the sample was fused using a Siliconit furnace at 1600°C for 30 minutes while regulating oxygen fugacity at QFM (quartz–fayalite–magnetite) buffer under an H₂–CO₂ mixed gas atmosphere to reproduce the oxidation state of komatiites that erupted in the early Archean (Canil, 1997). The sample was finally quenched to room temperature. The synthesized komatiitic glass with minor quench crystals (olivine and orthopyroxene) was crushed in an alumina mortar and sieved to obtain the <90-μm fraction. To remove possible contamination by organic matter during sample preparation, grains of komatiitic glass were ultrasonically washed with acetone and pure water and then dried at 50°C for 12 hours just before the experiment.

The steel-alloy autoclave used for the hydrothermal alteration experiment in this study is based on Seyfried

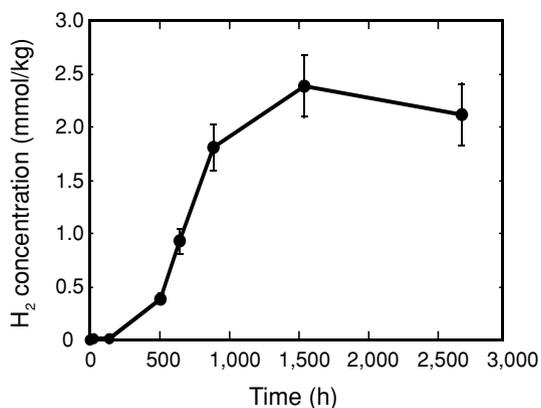


Fig. 2. Change in the dissolved H₂ concentrations with time for the komatiitic glass-water reaction experiment. The experiments were performed at 300°C, 500 bars and initial water-rock ratio of four.

(1987) (Fig. 1). The autoclave is made of Inconel-alloy, which is corrosion resistant and possesses adequate strength at elevated temperatures and pressures (up to 600°C and 600 bars). The reaction cell is made of a gold tube with a titanium head because these materials are inert to high-temperature water. In addition, gold being flexible, allows water inside the reaction cell to be pressurized by water around it. Although the Ti head is corrosion resistant, it is known that metal Ti can react with water to produce hydrogen. The surface of the Ti head was, therefore, oxidized prior to use. The flexible gold reaction cell allows on-line sampling of the aqueous fluid at almost constant temperature and pressure simply by adding a small amount of water under high pressure to the autoclave surrounding the cell. Thus, internally filtered fluid samples can be obtained from the reaction cell through a gold-lined sampling tube at any time during an ongoing experiment. All materials that came in contact with the reaction fluid in the experiment were baked in a muffle furnace at 500°C for 3 hours before use to eliminate organic matter that may produce H₂ and CH₄ under the high temperature range conditions of the experiment.

Komatiitic glass powder was reacted with pure water in the reaction cell at 300°C and 500 bars. The water/rock ratio was adjusted to four at the beginning of the experiment based on the results of Wetzal and Shock (2000) that the water/rock ratio in submarine hydrothermal system was limited to a value less than five. The hydrothermal fluid was directly sampled by a gas-tight syringe through a gold-lined tube connected to the reaction cell. The sampled fluid was immediately injected into a GC-TCD system (GC-2014 SHIMADZU) that was developed to directly analyze gas concentrations in an aqueous sample (Suzuki *et al.*, 2007). The detection limit and precision of H₂ concentration were 0.5 μmol/kg and 5%,

Table 2. The dissolved H₂ concentrations for the komatiitic glass-water reaction experiment conducted at 300°C, 500 bars and initial water-rock ratio of four. Blank data performed using pure water at 350°C and 500 bar are also presented.

Time (h)	H ₂ (mmol/kg) komatiite	Time (h)	H ₂ (mmol/kg) blank
0	n.d.	0	0.00099
24	0.0079	24	n.d.
139	0.0085	144	n.d.
504	0.39	338	0.008
644	0.93	838	0.0019
883	1.8	1320	0.00042
1536	2.4	1825	0.00072
2662	2.1	3843	0.00051

respectively. To estimate the background level of hydrogen production in the apparatus, a blank experiment without a rock sample was also conducted at 350°C and 500 bars for more than 3,800 hours. The uncertainty in gas concentration including sampling and instrumental errors, as determined by duplicate analysis, was less than 12% (1σ).

RESULTS AND DISCUSSION

The H₂ concentration throughout the blank experiment was lower than 0.008 mmol/kg although the experiment was done at higher temperature and longer reaction time. This blank level is negligible compared to the observed H₂ amounts in the komatiitic glass-water reaction. The experiment demonstrated that a significant amount of H₂ was produced as a result of komatiitic glass-water hydrothermal reaction.

During the komatiitic glass-water reaction experiment, the H₂ concentration in the hydrothermal fluid increased with the reaction time (Fig. 2 and Table 2). The change in the H₂ generation rate can be broadly divided into three stages. In the first stage, within the first few hundred hours of the experiment, the concentration of dissolved H₂ was close to the detection limit. Similar observation was reported by Seyfried *et al.* (2007) from their experiments on peridotites. In the case of peridotite-water reaction experiment, Seyfried *et al.* (2007) suggested that Fe substitution for Mg in serpentine and brucite limits the availability of Fe for magnetite formation. This mechanism in turn prohibits a significant release of hydrogen because the reduction of water by ferrous iron in olivine and pyroxene is considered to be a primary mechanism for the simultaneous formation of magnetite and hydrogen (Bach *et al.*, 2006). The same mechanism might also control the komatiite-water reaction because of essentially similar bulk composition with the peridotite-water reac-

tion experiment. Alternative explanation for insignificant H_2 generation in the first stage might be smectite formation. The presence of Al in the komatiite system which favors smectite over serpentine as secondary silicate mineral (Seyfried and Bischoff, 1981) is different from olivine-water system. In this case, ferrous iron in the komatiitic glass is directly incorporated into smectite without magnetite formation. This reaction might be dominant until most of the Al is consumed. After the first few hundred hours of insignificant hydrogen release, there was a stage of sudden and significant increase in hydrogen concentration over 500 to 900 hours of experimental time. In this second stage, serpentinization with magnetite formation might be the dominant reaction (e.g., Berndt *et al.*, 1996; Allen and Seyfried, 2003; Bach *et al.*, 2006). In our experiment, we suspect that reduction of water associated with oxidation of ferrous iron in komatiitic glass is the most likely mechanism for H_2 generation in the reacted fluid. In the last stage, after 900 hours, the hydrogen concentration was elevated up to 2.4 mmol/kg and remained rather constant within analytical errors. The decrease in the H_2 generation after 900 hours probably reflects equilibrium between alteration products and the hydrothermal fluid. The observed significant release of hydrogen during our experiments was possibly caused by serpentinization along with magnetite formation. Note that we are planning to continue this komatiitic glass-water experiments until over 5,000 hours. Thus, at this stage it is impossible to examine reacted materials which would surely be helpful to fully understand the mechanism of hydrogen generation observed in our experiments. The details of this subsequent experimental results will be presented elsewhere. At this stage, we believe it is very much worthwhile to report our observation because this is the first equivocal experimental evidence that shows significant release of hydrogen by komatiite-water interaction. Hereafter, we will explore the significance of this observation by comparing our results with natural deep-sea hydrothermal vent fluid compositions.

Because our komatiitic glass-water experiment is still ongoing, data on the nature of synthesized secondary minerals have not been obtained thus far. In this section, we discuss the significance of H_2 production during komatiite-water interaction by comparison with natural deep-sea hydrothermal vent fluids. The H_2 concentration in hydrothermal fluid is known to differ among hydrothermal systems with different host rocks (Fig. 3). Peridotite-hosted hydrothermal systems have higher H_2 concentration (~16 mmol/kg; Charlou *et al.*, 2002) than the typical basalt-hosted hydrothermal systems (<1 mmol/kg; Charlou *et al.*, 1996; Ding *et al.*, 2001; Gallant and Von Damm, 2006). The H_2 concentrations of the hydrothermal fluids in the Kairei field (2.5–8.5 mmol/kg) are comparable to those of fluids derived from peridotite-hosted systems (Fig. 3) (Takai *et al.*, 2004; Gallant and

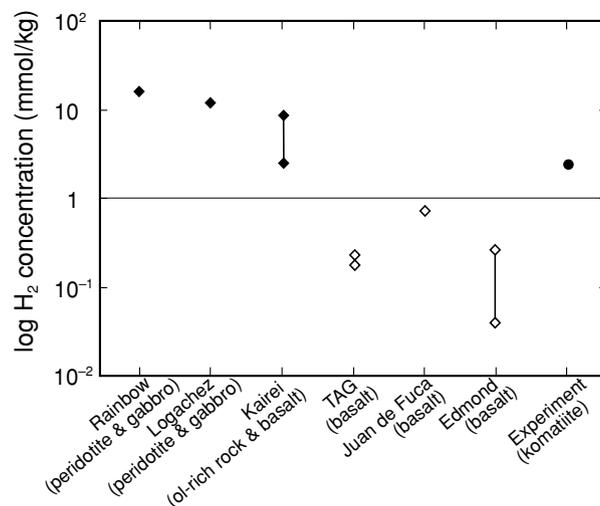


Fig. 3. Comparison of the H_2 concentration in the komatiitic glass-water reaction experiment obtained in this study (closed circle) with those in the deep-sea hydrothermal vent fluids (closed and open diamonds for ultramafic rock-hosted and basalt-hosted, respectively). The hydrothermal reaction in komatiitic glass with water enriches H_2 as much as in the serpentinization-influenced hydrothermal fluids of the Kairei field. Data sources for Rainbow and Logachev are from Charlou *et al.* (2002), Kairei from Gallant and Von Damm (2006); Takai *et al.* (2004); Kumagai *et al.* (2008), TAG (Trans-Atlantic Geotraverse) from Charlou *et al.* (1996), Juan de Fuca from Ding *et al.* (2001), and Edmond from Gallant and Von Damm (2006).

Von Damm, 2006; Kumagai *et al.*, 2008). Due to its location in a basaltic volcanic structure (Hakuho Knoll) located in the first segment of the Central Indian Ridge (Van Dover *et al.*, 2001), the Kairei field has been identified as a basalt-hosted system. However, it has also been predicted that the extraordinary H_2 concentrations in hydrothermal fluids can be significantly influenced by serpentinization somewhere in the hydrothermal circulation (Takai *et al.*, 2004, 2006). Recently, Nakamura *et al.* (2009) suggested that the generation of highly H_2 -enriched fluids was due to the serpentinization of olivine-rich rocks (plagioclase dunite, troctolite, and olivine gabbro) dominating the potential hydrothermal recharge zones in the oceanic crust near the Kairei hydrothermal field. Thus, the Kairei hydrothermal activity is now recognized as a system hosted by ultramafic rocks rather than by peridotitic rocks.

Recently, an increasing number of ultramafic-rock-associated hydrothermal activities have been discovered along slow-spreading MORs such as MAR (Douville *et al.*, 2002). In addition, we expect that serpentinization-influenced systems such as the Kairei field, which are not simply hosted by peridotite but are considerably influenced by ultramafic or related rocks, will be found in

the future. Nevertheless, ultramafic-rock-associated hydrothermal activities are restricted to specific tectonic settings in the modern Earth (Cannat *et al.*, 1997). In the Hadean and early Archean oceanic crust, komatiite was widely distributed and may be predominant in numerous large oceanic plateaus. Many of these ancient hydrothermal activities would have been, to some extent, influenced by the hydrothermal alteration of komatiite.

The experimental water-komatiitic glass hydrothermal reaction enriches H₂ as much as that observed in the serpentinization-influenced hydrothermal fluids of the Kairei field (Fig. 3). Our results clearly demonstrate that komatiite has the potential to enrich H₂ in hydrothermal fluids to a similar level as that of modern mantle peridotite. We suggest that ancient komatiite-associated hydrothermal circulations are capable of producing H₂-rich hydrothermal fluids from discharge zones and in the mixing zones with ambient deep seawater in the vicinity of hydrothermal vents, where the early evolution of living ecosystems may have been energized by large quantities of H₂ and CO₂ from the Hadean and early Archean crust and atmosphere (Takai *et al.*, 2006).

CONCLUSIONS

We report here the first experimental H₂ generation by hydrothermal alteration of komatiitic glass at 300°C and 500 bars, resulting in 2.4 mmol/kg of H₂ in the fluid after 2,662 hours. Although the experiment is still in progress, the H₂ concentration produced in the early part of the experiment is comparable to that observed in natural hydrothermal fluids derived from ultramafic-rock-associated systems such as the Kairei field, where methanogen is sustained by H₂-rich hydrothermal fluids. Our results imply that hydrothermal reaction between seawater and komatiite has a great potential to enrich hydrothermal fluids in H₂ in the same level as that observed from fluids derived from modern peridotite- or ultramafic rock-hosted systems. Hydrothermal alteration of komatiites may have provided the source of H₂ in the vicinity of hydrothermal vents that fueled the early evolution of living ecosystems in the Hadean and early Archean.

Acknowledgments—We thank F. Yanagisawa (Yamagata University) for offering practical knowledge of hydrothermal experiment. We thank T. Komiya (Tokyo Institute of Technology) and M. Cloete (Council for Geoscience, South Africa) for providing a komatiite rock sample. We want to express our thankfulness to M. L. G. Tejada for her valuable comments on our manuscript. We thank T. Tsujimori and an anonymous reviewer for their thoughtful comments that greatly improved the manuscript. We thank T. Matsumoto for his assistance as associate editor. This study was partially supported by the scientific research fund of the Trans-crustal Advection and In-situ reaction of Global sub-seafloor Aquifer (TAIGA) project.

REFERENCES

- Allen, D. E. and Seyfried, W. E., Jr. (2003) Compositional controls on vent fluids from ultramafic-hosted hydrothermal systems at mid-ocean ridges: An experimental study at 400°C, 500 bars. *Geochim. Cosmochim. Acta* **67**, 1531–1542.
- Bach, W., Paulick, H., Garrido, C. J., Ildefonse, B., Meurer, W. P. and Humphris, S. E. (2006) Unraveling the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). *Geophys. Res. Lett.* **33**, L13306.
- Berndt, E. M., Allen, E. D. and Seyfried, W. E., Jr. (1996) Reduction of CO₂ during serpentinization of olivine at 300°C and 500 bar. *Geology* **24**, 351–354.
- Canfield, D. E., Rosing, M. T. and Bjerrum, C. (2006) Early anaerobic metabolisms. *Phil. Trans. R. Soc. B* **361**, 1819–1836.
- Canil, D. (1997) Vanadium partitioning and the oxidation state of Archean komatiite magmas. *Nature* **389**, 842–845.
- Cannat, M., Lagabrielle, Y., Bougault, H., Casey, J., de Coutures, N., Dmitriev, L. and Fouquet, Y. (1997) Ultramafic and gabbroic exposures at the Mid-Atlantic Ridge: geological mapping in the 15°N region. *Tectonophysics* **279**, 193–213.
- Charlou, J. L., Donval, J. P., Jean-Baptiste, P., Dapoigny, A. and Rona, P. A. (1996) Gases and helium isotopes in high temperature solutions sampled before and after ODP Leg 158 Drilling at TAG Hydrothermal Field (26°N, MAR). *Geophys. Res. Lett.* **23**, 3491–3494.
- Charlou, J. L., Donval, J. P., Fouquet, Y., Jean-Baptiste, P. and Holm, N. (2002) Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14' N, MAR). *Chem. Geol.* **191**, 345–359.
- Condie, K. C. (2005) *Earth as an Evolving Planetary System*. Elsevier, 350 pp.
- Corliss, J. B., Dymond, J., Gordon, L. I., Edmond, J. M., Von Herzen, R. P., Ballard, R. D., Green, K., Williams, D. A. B., Crane, K. and Van Andel, T. H. (1979) Submarine thermal springs on the Galapagos Rift. *Science* **203**, 1073–1083.
- Ding, K., Seyfried, W. E., Jr., Tivey, M. K. and Bradley, A. M. (2001) *In situ* measurement of dissolved H₂ and H₂S in high-temperature hydrothermal vent fluids at the Main Endeavour Field, Juan de Fuca Ridge. *Earth Planet. Sci. Lett.* **186**, 417–425.
- Douville, E., Charlou, J. L., Oelkers, E. H., Bienvenu, P., Jove Colon, C. F., Donval, J. P., Fouquet, Y., Prieur, D. and Appriou, P. (2002) The rainbow vent fluids (36°14' N, MAR): the influence of ultramafic rocks and phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids. *Chem. Geol.* **184**, 37–48.
- Edmond, J. M., Measures, C., McDuff, R. E., Chan, L. H., Collier, R., Grant, B., Gordon, L. I. and Corliss, J. B. (1979) Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: The Galapagos data. *Earth Planet. Sci. Lett.* **46**, 1–18.
- Früh-Green, G. L., James, A. D., Plas, A., Kelley, D. S. and Geobety, B. (2004) Serpentinization of oceanic peridotites: Implications for geochemical cycles and biological activity. *The Subseafloor Biosphere at Mid-Ocean Ridges* **144**,

- 119–136.
- Gallant, R. M. and Von Damm, K. L. (2006) Geochemical controls on hydrothermal fluids from the Kairei and Edmond Vent Fields, 23°–25°S, Central Indian Ridge. *Geochem. Geophys. Geosys.* **7**, Q06018.
- Green, D. H., Nicholls, I. A., Viljoen, M. and Viljoen, R. (1975) Experimental demonstration of the existence of peridotitic liquids in earliest archaean magmatism. *Geol. Soc. America* **3**, 11–14.
- Kelley, D. S., Karson, J. A., Blackman, D. K., Früh-Green, G. L., Butterfield, D. A., Lilley, M. D., Olson, E. J., Schrenk, M. O., Roe, K. K., Lebon, G. T., Rivizzigno, P. and the AT3-60 Shipboard Party (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30° N. *Nature* **412**, 145–149.
- Kelley, D. S., Karson, J. A., Früh-Green, G. L., Yoerger, D. R., Shank, T. M., Butterfield, D. A., Hayes, J. M., Schrenk, M. O., Olson, E. J., Proskurowski, G., Jakuba, M., Bradley, A., Larson, B., Ludwig, K., Glickson, D., Buckman, K., Bradley, A. S., Brazelton, W. J., Roe, K., Elend, M. J., Delacour, A., Bernasconi, S. M., Lilley, M. D., Baross, J. A., Summons, R. E. and Sylva, S. P. (2005) A serpentinite-hosted ecosystem: The Lost City hydrothermal field. *Science* **307**, 1428–1434.
- Kumagai, H., Nakamura, K., Toki, T., Morishita, T., Okino, K., Ishibashi, J.-i., Tsunogai, U., Kawagucci, S., Gamo, T., Shibuya, T., Sawaguchi, T., Neo, N., Joshima, M., Sato, T. and Takai, K. (2008) Geological background of the Kairei and Edmond hydrothermal fields along the Central Indian Ridge: Implications of their vent fluids' distinct chemistry. *Geofluids* **8**, 1–13.
- McCollom, T. M. (2007) Geochemical constraints on sources of metabolic energy for chemolithoautotrophy in ultramafic-hosted deep-sea hydrothermal systems. *Astrobiology* **7**, 933–950.
- McCollom, T. M. and Bach, W. (2009) Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochim. Cosmochim. Acta* **73**, 856–875.
- Moores, E. M. (2002) Pre-1 Ga (pre-Rodinian) ophiolites: Their tectonic and environmental implications. *Geol. Soc. America Bull.* **114**, 80–95.
- Nakamura, K., Morishita, T., Bach, W., Klein, F., Hara, K., Okino, K., Takai, K. and Kumagai, H. (2009) Serpentinized troctolites exposed near the Kairei Hydrothermal Field, Central Indian Ridge: Insights into the origin of the Kairei hydrothermal fluid supporting a unique microbial ecosystem. *Earth Planet. Sci. Lett.* **280**, 128–136.
- Ohta, H., Maruyama, S., Takahashi, E., Watanabe, Y. and Kato, Y. (1996) Field occurrence, geochemistry and petrogenesis of the Archean Mid-Oceanic Ridge Basalts (AMORBs) of the Cleaverville area, Pilbara Craton, Western Australia. *Lithos* **37**, 199–221.
- Russell, M. J. and Hall, A. J. (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *J. Geol. Soc.* **154**, 377–402.
- Seyfried, W. E., Jr. (1987) Experimental and theoretical constraints on hydrothermal alteration processes at Mid-Ocean Ridges. *Ann. Rev. Earth Planet. Sci.* **15**, 317–335.
- Seyfried, W. E., Jr. and Bischoff, J. L. (1981) Experimental seawater-basalt interaction at 300°C, 500 bars, chemical exchange, secondary mineral formation and implications for the transport of heavy metals. *Geochim. Cosmochim. Acta* **45**, 135–147.
- Seyfried, W. E., Jr., Gordon, P. C. and Dickson, F. W. (1979) A new reaction cell for hydrothermal solution equipment. *Amer. Mineral.* **64**, 646–649.
- Seyfried, W. E., Jr., Foustoukos, D. I. and Fu, Q. (2007) Redox evolution and mass transfer during serpentinization: An experimental and theoretical study at 200°C, 500 bar with implications for ultramafic-hosted hydrothermal systems at Mid-Ocean Ridges. *Geochim. Cosmochim. Acta* **71**, 3872–3886.
- Sleep, N. H. and Bird, D. K. (2007) Niches of the pre-photosynthetic biosphere and geologic preservation of Earth's earliest ecology. *Geobiology* **5**, 101–117.
- Sleep, N. H., Meibom, A., Fridriksson, T., Coleman, R. G. and Bird, D. K. (2004) H₂-rich fluids from serpentinization: Geochemical and biotic implications. *Proc. Natl. Acad. Sci.* **101**, 12818–12823.
- Smith, H. S., Erlank, A. J. and Duncan, A. R. (1980) Geochemistry of some ultramafic komatiite lava flows from the Berberfontein Mountain Land, South Africa. *Precam. Res.* **11**, 399–415.
- Suzuki, K., Nakamura, K., Yasui, S. and Takai, K. (2007) Direct determination of hydrogen, methane and carbon dioxide gasses in solutions using gas chromatography equipped with gas-liquid separation tube (abstract). InterRidge Theoretical Institute: Biogeochemical Interaction at deep-sea vents. Woods Hole, MA.
- Takai, K., Gamo, T., Tsunogai, U., Nakayama, N., Hirayama, H., Nealson, K. H. and Horikoshi, K. (2004) Geochemical and microbiological evidence for a hydrogen-based, hyperthermophilic subsurface lithoautotrophic microbial ecosystem (HyperSLiME) beneath an active deep-sea hydrothermal field. *Extremophiles* **8**, 269–282.
- Takai, K., Nakamura, K., Suzuki, K., Inagaki, F., Nealson, K. H. and Kumagai, H. (2006) Ultramafics-Hydrothermalism-Hydrogenesis-HyperSLiME (UltraH3) linkage: a key insight into early microbial ecosystem in the Archean deep-sea hydrothermal systems. *Palaeontol. Res.* **10**, 269–282.
- Van Dover, C. L., Humphris, S. E., Fornari, D., Cavanaugh, C. M., Collier, R., Goffredi, S. K., Hashimoto, J., Lilley, M. D., Reysenbach, A. L., Shank, T. M., Damm, K. L. V., Banta, A., Gallant, R. M., Dötz, G., Green, D., Hall, J., Harmer, T. L., Hurtado, L. A., Johnson, P., McKiness, Z. P., Meredith, C., Olson, E., Pan, I. L., Turnipseed, M., Won, Y. C. R. Y., III and Vrijenhoek, R. C. (2001) Biogeography and ecological setting of Indian Ocean hydrothermal vents. *Science* **294**, 818–823.
- Wetzel, L. R. and Shock, E. L. (2000) Distinguishing ultramafic—from basalt-hosted submarine hydrothermal systems by comparing calculated vent fluid compositions. *J. Geophys. Res.* **105**, 8319–8340.
- Yanagawa, H. and Kojima, K. (1985) Thermophilic microspheres of peptide-like polymers and silicates formed at 250°C. *J. Biochem.* **97**, 1521–1524.