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Experimental Hydrogen Production in Hydrothermal and Fault Systems: Significance for Habitability of Subseafloor H_2 Chemoautotroph Microbial Ecosystems

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Abstract

Hydrogen generated in hydrothermal and fault systems has recently received considerable attention as a potential energy source for hydrogen-based microbial activity such as methanogenesis. Laboratory experiments that have reproduced conditions for the serpentinization of ultramafic rocks such as peridotite and komatiite have clarified the chemical and petrological processes of H_2 production. In a frictional experimental study, we recently showed that abundant H_2 can also be generated in a simulated fault system. This result suggests that microbial ecosystems might exist in subseafloor fault systems. Here we review the experimental constraints on hydrogen production in hydrothermal and fault systems.

Keywords

Friction experiment • Hydrogen generation • Hydrothermal experiment • Simulated fault system • Ultramafic rocks

8.1 Introduction

The discovery of chemolithoautotrophic microbial ecosystems in the modern ocean has suggested that hydrothermal fluids enriched in H_2 fuel H_2-driven primary producers such as hyperthermophilic hydrogenotrophic methanogens (Cannat et al. 1997; Takai et al. 2004; Kelley et al. 2005) . Moreover, multidisciplinary studies have indicated that an H_2-driven chemolithoautotrophic ecosystem may have supported the earliest life on Earth (Russell and Hall 1997; Sleep et al. 2004; Kelley et al. 2005; Canfield et al. 2006; Takai et al. 2006). H_2-rich hydrothermal fluids are generated by the serpentinization of Mg- and Fe-rich ultramafic rocks, which are igneous and meta-igneous

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rocks consisting mainly (>90 %) of mafic minerals with high magnesium and iron contents. These rocks have a very low silica content (<45 %), MgO generally more than 18 %, high FeO, and low potassium. The Earth's mantle is composed of ultramafic rocks. The production of hydrogen by the serpentinization of ultramafic rocks is a central tenet of the hypothesis that life first emerged on Earth in an H_2-rich hydrothermal environment (Russell et al. 2010).

In the modern ocean, the basement rocks of the oceanic crust are generally composed of mid-ocean ridge basalt (MORB). Along slow-spreading ridges such as the North Atlantic Ridge and the Southwest Indian Ridge, volcanic activity is low and severely serpentinized peridotites (peridotite: ultramafic rocks composed of olivine and pyroxene) are exposed along transform faults (e.g., Miyashiro et al. 1969; Aumento and Loubat 1971; Cannat 1993). Hydrogen-enriched hydrothermal fluids are common in such peridotite-dominated slow-spreading ridge settings (Kelley et al. 2001; Früh-Green et al. 2004). Since the first discovery of natural peridotite-hosted hydrothermal vents with abundant H_2 at Logachev field on the Mid-Atlantic Ridge in 1995 (Krasnov et al. 1995), other peridotite-hosted and -associated hydrothermal vents have been found, namely, the Rainbow, Nibelungen, Lost City, and Achaze fields on the Mid-Atlantic Ridge (Charlou et al. 1998, 2002, 2008; Douville et al. 2002; Kelley et al. 2005; Melchert et al. 2008) and the Kairei field on the Central Indian Ridge (Van Dover et al. 2001). A pronounced feature of peridotite-hosted systems is the presence of hydrothermal solutions enriched not only in H_2 but also in CH_4 and other hydrocarbons (Charlou et al. 2002). Measured H_2 concentrations in these fluids range from 2.5 to 16 mmol/kg, with the highest concentrations reported at steady-state, unsedimented mid-ocean ridge hydrothermal vents. The generated H_2 supports ecosystems, including hyperthermophilic subsurface lithoautotrophic ecosystems (HyperSLiME) (Takai et al. 2004; Nealson et al. 2005), in which methanogens utilize H_2 and CO_2 and produce methane as a metabolic product.

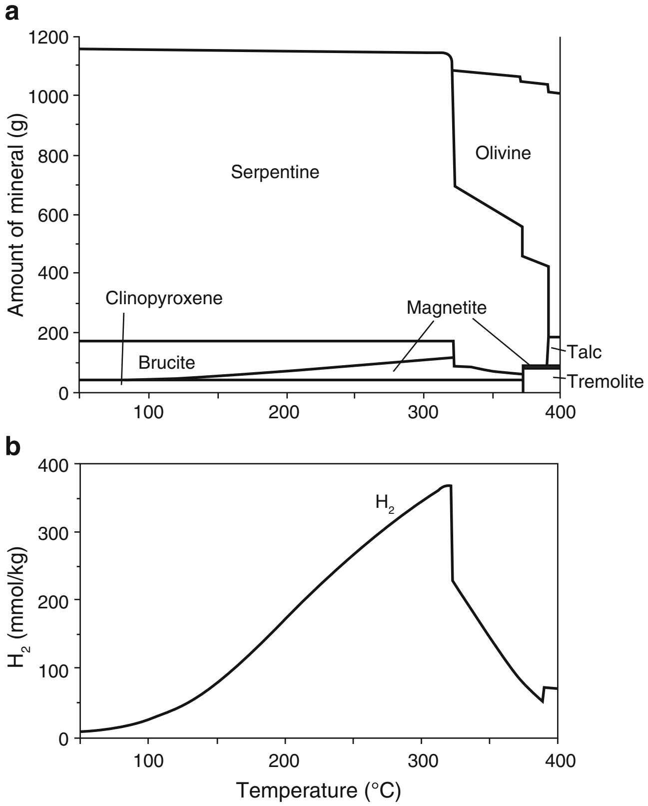

Fig. 8.1 Predicted alteration mineralogy and fluid composition during hydrothermal alteration of harzburgite over a range of temperatures at a 1:1 water:rock ratio, modified from McCollom and Bach (2009). (**a**) Equilibrium mineral composition: amount of each mineral per kilogram of harzburgite reacted. (**b**) H_2 concentration in the fluid

Several petrographical (Cressey 1979) and theoretical (Wetzel and Shock 2000; Sleep et al. 2004) studies have examined the H_2-generating geochemical and mineralogical reactions associated with the serpentinization of ocean-floor ultramafic rocks, and experimental investigations (Berndt et al. 1996; Allen and Seyfried 2003; Seyfried et al. 2007) have significantly increased our understanding of the mechanisms of H_2 production during serpentinization. In the present paper, we focus on these experimental results, because it is generally difficult to directly observe chemical processes in subseafloor environments. Thermodynamic modeling of seawater–peridotite reactions is also an important tool, both for understanding the experimental results and for inferring the natural serpentinization processes (Klein et al. 2009; McCollom and Bach 2009). McCollom and Bach (2009) examined the effect of temperature on the mineral assemblage and fluid composition produced by serpentinization of harzburgite (a peridotite consisting mainly of olivine and orthopyroxene) (Fig. 8.1). They reported that at temperatures below 315 °C, the serpentinized rock was composed of typical serpentinite minerals, such as serpentine, brucite, magnetite, and minor secondary clinopyroxene. With increasing temperature, the amount of magnetite increased, and consequently, the concentration of H_2 generated by serpentinization also increased with temperature up to ~360 mmol/kg. Above 315 °C, however, olivine became stable and coexisted in equilibrium with other secondary minerals and fluid, and above 390 °C it remained almost completely unaltered. Therefore, the amount of Fe converted to magnetite decreased as the temperature increased above 315 °C, with the result that the H_2 concentration in the fluid was lower at these higher temperatures. Contrary to expectation, theoretical modeling of these water–rock interactions does not always produce results that are quantitatively consistent with the experimental results. Therefore, further investigation is needed to clarify the reasons for the discrepancy between theoretical and experimental results.

Another extreme environment where H_2 may be abundant is found in natural fault systems. Wakita et al. (1980) first reported high concentrations of H_2 (up to 3 % v/v) in soil gas from sites in the Yamasaki fault zone, southwestern Japan, and Wiersberg and Erzinger (2008) reported high concentrations of H_2 in drilling cores obtained near micro-earthquake hypocenters along the San Andreas fault in California. These observations led to the hypothesis that methanogenic ecosystems might also be found in deep fault systems below the seafloor. To examine whether fault-driven H_2 generation can produce enough H_2 to maintain a chemolithoautotrophic microbial ecosystem, we conducted high-velocity sliding experiments using velocities and displacements typical of natural earthquakes (Hirose et al. 2011, 2012).

Thus, both hydrothermal and frictional experimental systems can be effectively used to elucidate physicochemical processes in natural systems. In this chapter, we review experiments, performed both as part of Project TAIGA (Trans-crustal Advection and In-situ bio-geochemical processes of Global sub-seafloor Aquifer) and by other groups, examining the generation of hydrogen by water/rock interactions at high temperature and pressure, including both reactions between water and komatiite, an Archean volcanic ultramafic rock, and those in frictional fault systems.

8.2 Constraints on H_2 Production During Experimental Hydrothermal Alteration of Ultramafic Rocks

Peridotite exposed on slow-spreading ridge systems is often severely serpentinized as a result of hydration due to long-term reaction with seawater (Ildefonse et al. 2007; Morishita et al. 2009; Nakamura et al. 2009). Isotopic investigations have shown that such serpentinized peridotites, similar to altered MORB, are the products of high-temperature and -pressure reactions between peridotite and seawater (Wenner and Taylor 1971, 1973; Sakai and Tsutsumi 1978). Hydrothermal alteration of peridotite was studied experimentally (Seyfried and Dibble 1980; Hajash and Chandler 1981; Janecky and Seyfried 1986) even before the discovery of natural peridotite-hosted hydrothermal vents at Logachev field (Krasnov et al. 1995). Reactions between peridotite and seawater under high temperature and pressure have also been examined in batch-type experiments (see Chap. 7). Under high temperature and pressure, the oxidation of ferrous ion [Fe(II)] in primary minerals such as olivine and pyroxene to Fe(III) in secondary minerals such as magnetite reduces water and releases H_2 gas:

$$2(\mathrm{FeO})_{\mathrm{mineral}} + \mathrm{H_2O} \rightarrow (\mathrm{Fe_2O_3})_{\mathrm{mineral}} + \mathrm{H_2} \tag{8.1}$$

where $(\mathrm{FeO})_{\mathrm{rock}}$ denotes the ferrous constituent of a primary silicate mineral such as olivine and $(\mathrm{Fe_2O_3})_{\mathrm{rock}}$ denotes the ferric constituent of an secondary alteration mineral such as magnetite. The serpentinization of olivine ($\mathrm{Fo_{90}}$) generates H_2 as follows:

$$\begin{aligned} &\underset{\text{Olivine (Fo}_{90})}{\mathrm{Mg_{1.8}Fe_{0.2}SiO_4}} + 1.37\mathrm{H_2O} \rightarrow \underset{\text{Serpentine}}{0.5\mathrm{Mg_3Si_2O_5(OH)_4}} \\ &\quad + \underset{\text{Brucite}}{0.3\mathrm{Mg(OH)_2}} + \underset{\text{Magnetite}}{0.067\mathrm{Fe_3O_4}} + 0.067\mathrm{H_2} \end{aligned} \tag{8.2}$$

In this reaction, olivine supplies Fe(II), and hydrogen and magnetite, which contains Fe(II) and Fe(III) in equal amounts, are produced. Note that Eq. (8.2) is a simplified formula provided to illustrate the generation of H_2 by serpentinization; in natural systems, the produced serpentine and brucite commonly contain Fe as well.

Janeckey and Seyfried (1986) experimentally investigated the serpentinization of harzburgite at 300 °C and 50 MPa, but they did not measure hydrogen continuously during their experiment. Instead, they collected samples for hydrogen measurement only twice, after 10 months and 2 years. In both samples, they found high concentrations of H_2 (0.1 and 0.33 mmol/kg), but because they did not measure H_2 in other fluid samples collected during the experiment, the H_2 generation reaction cannot be unambiguously interpreted. Using a similar experimental apparatus, McCollom and Seewald (2001) assessed the potential of olivine serpentinization to reduce CO_2 and produce hydrocarbons. In their experiments, they reacted powdered olivine with a 0.5 M NaCl solution at 300 °C and 35 MPa and obtained abundant H_2 (concentration > 70 mmol/kg, Fig. 8.2) after 700 h.

Allen and Seyfried (2003) reacted olivine, orthopyroxene, and clinopyroxene, the major constituent minerals in peridotite, with a NaCl–$\mathrm{MgCl_2}$ solution at 400 °C and 50 MPa to assess the potential of these minerals to produce H_2. They used olivine ($\mathrm{Fo_{89}}$), orthopyroxene ($\mathrm{En_{85}}$), and clinopyroxene ($\mathrm{Di_{89}}$) both individually and in combination to constrain the chemical processes of ultramafic-hosted hydrothermal systems in mid-ocean ridges. The olivine alteration rate was slow, as indicated by the absence of hydrous alteration products, whereas reactions including pyroxenes were rapid, resulting in significant increases in dissolved H_2 as well as in Ca, $\mathrm{SiO_2}$, and Fe (Fig. 8.3), and in the formation of $\mathrm{SiO_2}$-rich secondary minerals such as talc, tremolite, and magnetite (Fig. 8.3; McCollom and Bach 2009). High pH and low Fe concentrations are theoretically predicted under the assumption of full equilibrium at 400 °C and 50 MPa in the MgO-CaO-FeO-Fe_2O_3-SiO_2-Na_2O-H_2O-HCl system (Allen and Seyfried 2003). In their laboratory experiments, however, Allen and Seyfried (2003) reported that when the initial olivine:pyroxene ratio was 3:1 (the typical mineral composition of abyssal peridotite), pH remained low and Fe concentrations remained high. Moreover, the pH also remained relatively low in their experiments that included orthopyroxene and clinopyroxene, a result that may have been caused by talc–fluid and talc–tremolite–fluid equilibria, respectively.

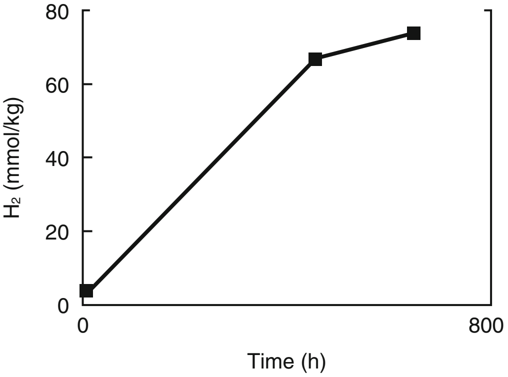

Fig. 8.2 Measured concentrations of dissolved H_2 during a hydrothermal reaction in the presence of olivine at 300 °C and 35 MPa as a function of reaction time. Modified from McCollom and Seewald (2001)

Allen and Seyfried (2003) suggested that the reactions occurring in ultramafic rock-hosted hydrothermal systems such as the Rainbow system on the Mid-Atlantic Ridge may be very similar to those observed in these experiments, because of the similarity of the experimental conditions to the temperature and chemistry conditions of the vent fluid, in which concentrations of SiO_2, Ca, H_2, and Fe are relatively high (Charlou et al. 1998, 2002). In fact, Fe concentrations in the Rainbow system, which are the highest of any vent system yet discovered, imply a relatively low pH in the subseafloor reaction zone. The findings of Allen and Seyfried (2003) are very important because the experimental results together with the observed Rainbow fluid chemistry suggest that pyroxene dissolution is the dominant reaction in the Rainbow hydrothermal system, even though abundant olivine is present in the reaction zone. To better constrain the temporal evolution of the hydrothermal alteration of ultramafic rocks in subseafloor reaction zones, experimental data

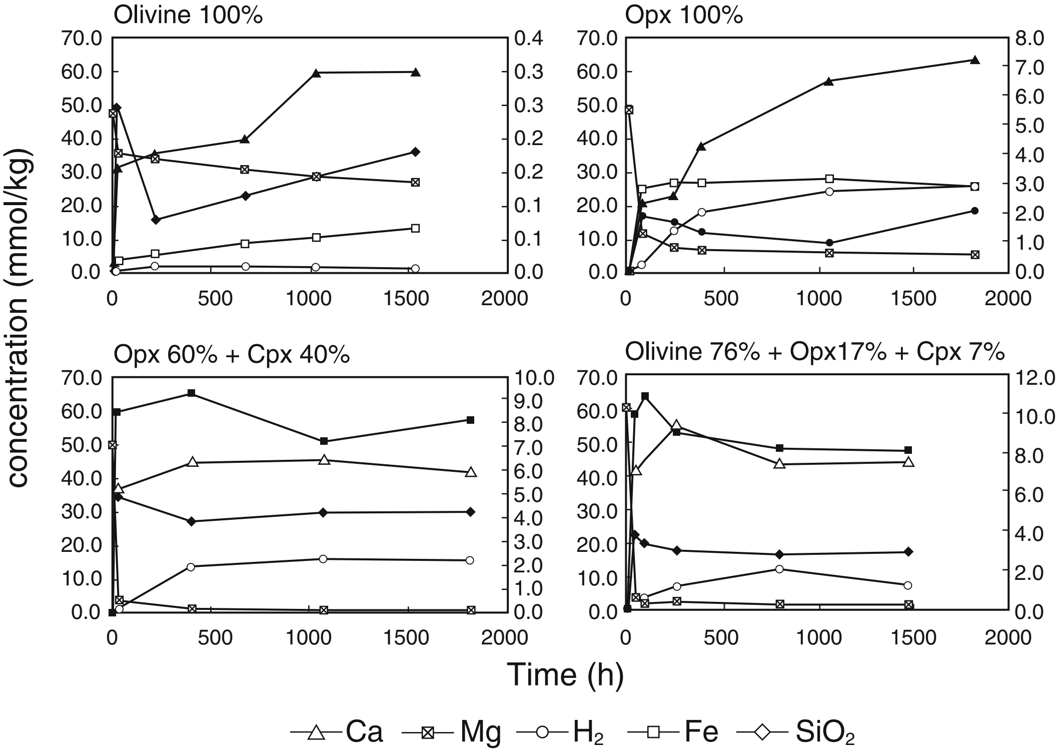

Fig. 8.3 Changes in the dissolved concentrations of selected species with time during four experiments, modified from Allen and Seyfried (2003). All experiments were performed at 400 °C, 50 MPa and with mineral:fluid ratios from 2 to 4. Values on the left vertical axis apply to species represented by *open symbols* and to Mg, and those on the right axis apply to species represented by *closed symbols*. *Cpx* clinopyroxene, *Opx* orthopyroxene

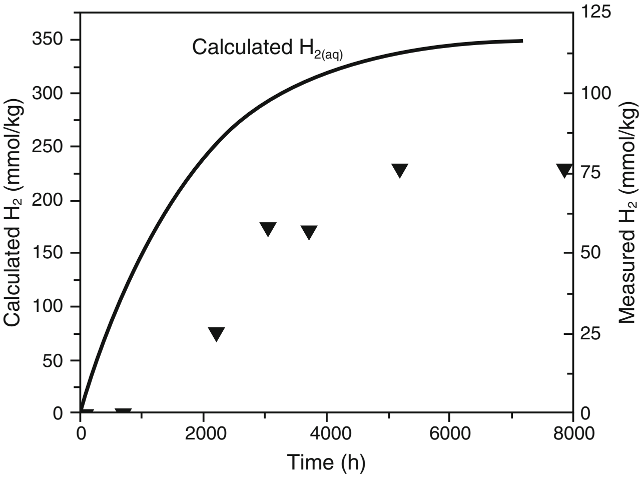

Fig. 8.4 Calculated (*line*) and measured (*inverted triangles*) time-series changes in dissolved hydrogen in fluid coexisting with lherzolite and alteration products (Seyfried et al. 2007). The difference between measured and predicted dissolved H_2 concentrations may reflect (in part) the lack of thermodynamic data for Fe-rich alteration minerals in the database used for the theoretical model

obtained under various conditions should be compared with thermodynamic simulation results.

The experiments just described were conducted at high temperatures (300 °C or higher), but actual reaction zone temperatures in ultramafic rocks are likely to be variable. For example, in the Lost City hydrothermal field on the Mid-Atlantic Ridge, H_2 is abundant, the pH is high, and the reactions occur at moderately low temperature. When Seyfried et al. (2007) experimentally constrained hydrogen production at the low temperature of 200 °C and 50 MPa, they found that changes in the concentrations of Ca, Mg, and Si in the reacted fluid agreed quantitatively with those predicted theoretically by a reaction pathway model of seawater–lherzolite interaction (fluid:rock mass ratio, 1:1) at 200 °C and 50 MPa. However, the time variations of pH, dissolved chloride, and H_2 monitored during their experiment did not agree with the theoretically predicted results (Fig. 8.4). Dissolved H_2 increased in a series of abrupt steps, and reached a maximum concentration that was only about 20 % of the theoretically predicted concentration. Interestingly, serpentine, the most abundant alteration mineral, contained both ferric and ferrous iron, and magnetite was present only in trace amounts. They therefore inferred that the low rate of H_2 generation, which was lower than that estimated on the basis of predicted serpentinization rates, was due to the production of diverse Fe-bearing alteration minerals.

In a recent experiment, Mayhew et al. (2013) reacted ultramafic and mafic rocks such as peridotite and minerals such as pyroxene, olivine, and magnetite with an anoxic fluid at 55 °C and 100 °C, temperatures that are habitable for (hyper)thermophilic microbes. Their synchrotron-based X-ray analysis results showed that the amount of H_2 produced was strongly dependent on whether spinel phases such as magnetite were present, and they observed Fe(III)-oxide products on the surface of the spinels. They proposed, therefore, that Fe(II) and water adsorbed on the surface of spinels reacted together under kinetic control to produce H_2 at low temperatures.

8.3 Experimental H_2 Generation During Komatiite Alteration: Simulation of an Archean Hydrothermal System

The experiments described in Sect. 8.2 showed by simulating peridotite–seawater systems that abundant H_2 is generated in a modern slow-spreading ridge by the serpentinization of peridotite. Sufficiently high concentrations of H_2 occur in the vent fluids of these systems to sustain an ecosystem based on H_2-driven chemolithoautotrophic primary producers such as methanogens. Moreover, an H_2-driven ecosystem is the most probable candidate habitat for the earliest life on Earth (Russell and Hall 1997; Sleep et al. 2004; Kelley et al. 2005; Takai et al. 2006; Canfield et al. 2006). On this basis, it has been hypothesized that hydrothermal fluids with H_2, sufficiently abundant to sustain methanogens, existed in the early Earth (Takai et al. 2006).

In contrast to the modern ocean, in the Hadean and early Archean ocean, peridotite was probably scarce beneath the crust of the ocean floor, because at that time the oceanic crust may have been two to three times the thickness of the modern oceanic crust (Ohta et al. 1996; Moores 2002; Takai et al. 2006). In this tectonic setting, komatiite, a distinctive ultramafic volcanic rock, was most likely the main component of ultramafic rocks on the floor of Hadean and Archean oceans. In fact, komatiite is common in Archean greenstone belts, whereas it is less common in Proterozoic successions and quite rare in Phanerozoic strata (Condie 2005). We therefore hypothesized that komatiite was the dominant ultramafic rock in the early history of the Earth (Yoshizaki et al. 2009) and that the interaction of komatiite with fluid at high temperature produced abundant H_2. To test this hypothesis, we examined whether we could reproduce a hydrothermal environment habitable for early life by experimentally reacting komatiite with water.

Modern komatiite in exposed Archean rocks has already been severely altered, so komatiite in its present form could not be used for our experiments. Therefore, we synthesized komatiite glass by dehydrating and remelting serpentinized komatiite collected from the Komati Formation, Barberton Greenstone Belt, South Africa, and then reacted the synthesized komatiitic glass with an NaCl solution at 300 °C and 50 MPa (Yoshizaki et al. 2009).

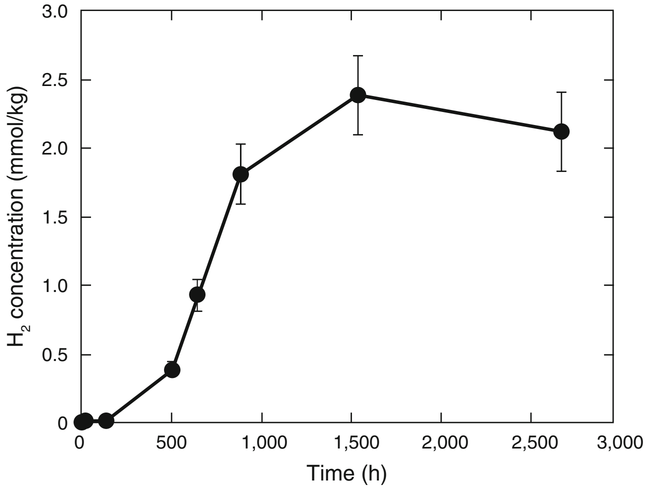

Fig. 8.5 Changes in the dissolved H_2 concentration with time during a komatiitic glass–water reaction experiment (Yoshizaki et al. 2009). The experiment was performed at 300 °C and 50 MPa with an initial water: rock ratio of 4:1

The concentration of produced H_2 reached 2.4 mmol/kg after 1500 h (Fig. 8.5) (Yoshizaki et al. 2009). This concentration is comparable to concentrations obtained by hydration of peridotitic rocks (see Sect. 8.2). These results suggest that hydrothermal alteration of komatiite in the Hadean and early Archean may have provided sufficient H_2 to fuel microbial ecosystems in the vicinity of hydrothermal vents.

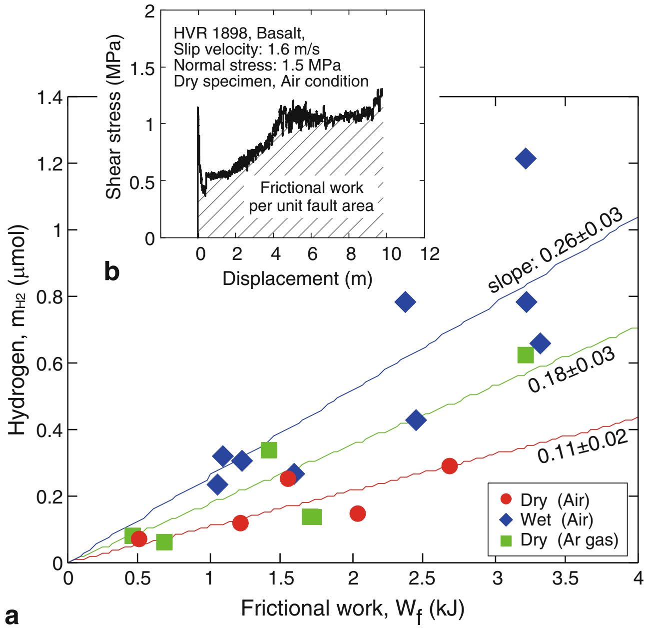

Fig. 8.6 (**a**) Hydrogen generation (μmol) as a function of frictional work (kJ) during high-velocity friction experiments with dry and wet basalt specimens at a slip velocity of 1.6 m/s and a displacement of 10 m under an air or argon gas atmosphere (Hirose et al. 2011). The amount of hydrogen generated tended to increase linearly with frictional work (correlation coefficient of 0.814, 0.899, and 0.777 for wet-air, dry-Ar gas, and dry-air conditions, respectively). (**b**) A typical shear stress versus displacement curve obtained during a friction experiment. Frictional work was calculated by integrating shear stress over the displacement (area under the shear stress versus displacement curve) and then multiplying the result by the fault surface area

8.4 Mechanoradical H_2 Generation During Simulated Faulting

As we have described, hydrothermal alteration of peridotites and komatiites can produce abundant H_2 in subseafloor settings. Other potential sites of H_2 generation are active fault systems. Earthquake or fault-related H_2 generation was first found by gas monitoring along the active Yamasaki fault, southwestern Japan (Wakita et al. 1980), and more recently H_2 generation has been inferred from drill cores obtained near microearthquake hypocenters along the San Andreas fault in California (Wiersberg and Erzinger 2008). Kita et al. (1982) suggested that H_2 may be generated in fault systems by the following reaction, expressed in terms of mechanoradicals on fresh surfaces of silicate minerals and water molecules:

$$2(\equiv \mathrm{Si})^{\cdot} + 2\mathrm{H_2O} \rightarrow 2(\equiv \mathrm{SiOH}) + \mathrm{H_2} \tag{8.3}$$

Experiments in which a ball mill was used to crush rocks had previously reproduced possible mechanoradical reactions during faulting (Kita et al. 1982; Kameda et al. 2004), but no quantitative investigations of the generation of H_2 in an active fault system have been carried out. To examine whether a natural fault system can produce enough H_2 to sustain a microbial methanogen-based ecosystem, we performed high-velocity sliding experiments that reproduced slip velocities and displacements typical of natural earthquakes and then quantitatively estimated the concentrations of H_2 produced (Hirose et al. 2011). To collect the generated gas samples, we placed a reaction cell around the rock specimen in a high-velocity frictional experiment system (see Chap. 7 in this volume). The results showed that H_2 generation increases with frictional work (i.e., earthquake magnitude) (Fig. 8.6). Therefore, the earthquake-derived H_2 flux in nature can be estimated by establishing the correlation between H_2 production and earthquake magnitude (Hirose et al. 2011, 2012). Moreover, an H_2 fluid concentration higher than 1.1 mmol/kg can be achieved in a fault zone after even a small-magnitude earthquake (Hirose et al. 2011, 2012). This concentration of H_2 is potentially high enough to sustain a methanogen-based ecosystem, we can expect to find diverse microbial ecosystems in deep fault systems. Thus, such fault systems may also have provided habitable zones for early life on Earth.

8.5 Concluding Remarks and Future Perspectives

In modern oceans, H_2-rich hydrothermal fluids (i.e., H_2 concentrations from a few to a few tens mmol/kg) have been observed in ultramafic rock-hosted systems. Such concentrations are sufficiently high to sustain H_2-based lithoautotrophic microbial ecosystems, including phylogenetically ancient microbes (Takai et al. 2006). In this regard, the experiments simulating H_2 generation described here have improved our understanding of not only geochemical and biological interactions driven by serpentinization in modern oceans but also the potential habitability of Hadean/Archean komatiite hydrothermal systems, in which life might have originated. Additionally, the results of friction experiments suggest the intriguing idea that H_2 generated in a fault system might also sustain lithoautotrophic microbial ecosystems. Such fault system ecosystems may also have existed on the early Earth. To verify the fault zone model, we anticipate the results of microbial investigations of fault systems performed using fresh drill cores. It should be emphasized, however, that there are certain basic difficulties associated with the described hydrothermal experiments. For example, as described in Sect. 8.2, some results from experimental hydrothermal reactions conflict with both natural observations and theoretical calculations. The discrepancies may reflect mainly inappropriate initial experimental conditions or inaccurate thermodynamic data. Thus, future experiments must correct these problems.

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