Mechanoradical H_2 generation during simulated faulting: Implications for an earthquake-driven subsurface biosphere

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[1] Molecular hydrogen, H_2, is the key component to link the inorganic lithosphere with the subsurface biosphere. Geochemical and microbiological characterizations of natural hydrothermal fields strongly suggested that H_2 is an important energy source in subsurface microbial ecosystems because of its metabolic versatility. One of the possible sources of H_2 has been considered as earthquakes: mechanoradical reactions on fault surfaces generate H_2 during earthquake faulting. However it is unclear whether faulting can generate abundant H_2 to sustain subsurface chemolithoautotrophic microorganisms, such as methanogens. Here we present the result of high velocity friction experiments aimed to estimate the amount of H_2 generated during earthquakes. Our results show that H_2 generation increases with frictional work (i.e., earthquake magnitude) and that a H_2 concentration of more than 1.1 mol/kg of fluid can be achieved in a fault zone after earthquakes of even small magnitudes. The estimated earthquake-derived H_2 concentration is sufficiently high to sustain a H_2-based subsurface lithoautotrophic microbial ecosystem. Furthermore, earthquakes have initiated on the Earth at least since tectonic plate movement began ~3.8 Ga, implying the possible existence of ancient earthquake-driven ecosystems. Seismic H_2 based subsurface ecosystems might exist not only over the Earth but also other planets.
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1. Introduction

[2] There has been increasing attention given to chemolithoautotrophic microorganisms and their role in the deep subsurface biosphere, in Earth's earliest microbial ecosystems and as potential analogues for life on other planets. For such subsurface ecosystems, H_2 is an important energy source owing to its metabolic versatility [e.g., *McCollom and Shock*, 1997; *Kelley et al.*, 2005]. In particular, hydrogenotrophic methanogens that can grow on CO_2 and H_2 as their sole energy source is thought of as one of the most probable players for completely photosynthesis-independent ecosystems in the modern and even ancient Earth or other planets [*McCollom*, 1999; *Ueno et al.*, 2006]. Although CO_2 has been universally abundant, H_2 has been much lower concentration than CO_2 throughout the Earth's history [*Kasting and Howard*, 2006]. How and when abiotic H_2 appeared in abundance in the inorganic ancient earth are therefore fundamental questions related to the early evolution of life on Earth.

[3] In the last few decades, three different abiotic H_2 generation processes have been proposed: (1) water–rock redox reactions, mostly under hydrothermal conditions [*Janecky and Seyfried*, 1986; *Coveney et al.*, 1987], (2) radiolytic reactions of H_2O [*Savary and Pagel*, 1997], and (3) mechanoradical formation on wet fault surfaces during earthquakes [*Wakita et al.*, 1980]. In the modern ocean, hydrogenotrophic methanogens most likely metabolize H_2 produced by hydrothermal ultramafic rock–water reactions (e.g., serpentinization) [*Kelley et al.*, 2005; *Takai et al.*, 2006]. H_2 production by peridotite-water and komatiite-water hydrothermal reactions, as modern and ancient analogs, respectively, has been quantitatively estimated in laboratory experiments [*Seyfried et al.*, 2007; *Yoshizaki et al.*, 2009]. Radiogenic production of H_2 is supported by the analysis of H_2-bearing fluid inclusions in quartz containing U-bearing minerals [*Dubessy et al.*, 1988], and has been quantitatively estimated in a laboratory γ-irradiation experiment [*Lin et al.*, 2005]. The H_2 flux per unit of surface area from redox reactions has been estimated to be 3×10^{-4} mol/m^{2}yr from a 1 km column of mafic/ultramafic rock with 10 wt% FeO [*Sleep and Zoback*, 2007], and the estimated flux from water radiolysis in the Witwatersrand basin, South Africa, is 8×10^{-6} mol/m^{2}yr [*Lin et al.*, 2005]. In contrast, the H_2 flux associated with earthquakes and its significance in subsurface ecosystems has not yet been explored in either the field or laboratory.

[4] The earthquake-associated H_2 generation has been first found by the gas monitoring along the surface trace of the active Yamasaki fault, southwestern Japan [*Wakita et al.*, 1980] and more recently, in the drilling cores obtained near hypocenters of microearthquakes along the San Andreas fault, California [*Wiersberg and Erzinger*, 2008]. *Kita et al.* [1982] considered that the following reaction, expressed in terms of mechanoradicals on the fresh surfaces of silicate minerals and water molecules, is a possible mechanism for H_2 generation during faulting:

$$2(\equiv \mathrm{Si}\,\cdot) + 2\mathrm{H_2O} \rightarrow 2(\equiv \mathrm{SiOH}) + \mathrm{H_2} \quad (1)$$

Experiments using a ball mill to crush rocks have verified the possibility of the mechanoradical reactions during faulting [*Kita et al.*, 1982; *Kameda et al.*, 2004]. However, it has been difficult to estimate the H_2 flux associated with natural earthquakes from such experiments. We thus performed high-velocity sliding experiments, which can reproduce slip velocities and displacements typical of natural earthquakes,

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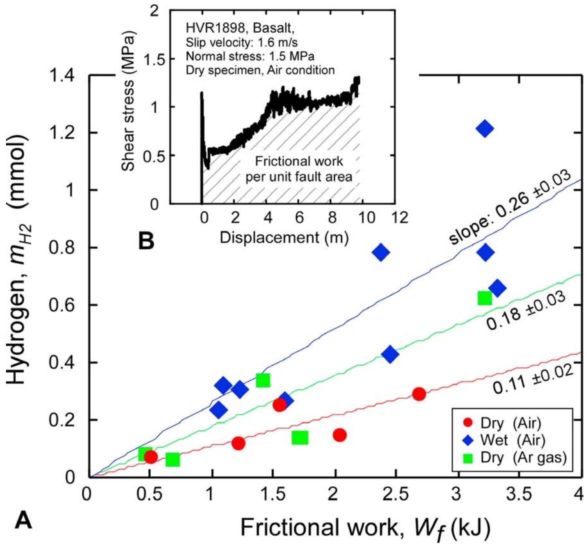

Figure 1. (a) Hydrogen generation (in mmol) as a function of frictional work (in kJ) during high-velocity friction experiments on dry and wet basalt specimens at a slip velocity of 1.6 m/s and a displacement of 10 m under air or argon gas atmospheres. The amount of hydrogen generated tended to increase 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 is 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.

in order to estimate the earthquake-derived H_2 flux in nature by establishing the correlation between H_2 production and earthquake magnitude.

2. Experimental Methods

[5] The experiments were conducted on representative rock types of Earth's crust, namely, basalt, dunite, granites, marble, and sandstones at a constant slip velocity of 1.6 m/s, normal stress of 0.5–2.5 MPa and a displacement of 10 m using a rotary-shear friction testing apparatus [e.g., *Hirose and Shimamoto*, 2005] (auxiliary material).[1] Most of experiments were conducted in air, but some were conducted under oxygen-free conditions to simulate the anoxic conditions where earthquakes typically occur at depth. Slip on an artificial fault under normal stress was obtained by pressing together a pair of hollow and solid cylindrical specimens with an outer diameter of 25 mm, and keeping one specimen stationary while rotating the other one at high speed. The sliding surfaces were ground and roughened with 100 grit SiC powder. The specimens were either dried in an oven at 100°C for more than two weeks or saturated with distilled water in a vacuum chamber (referred to as dry and wet specimens, respectively, hereafter). Rapid sliding was reproduced within a pressure vessel, and the H_2 released during the experiments was measured by a vessel-mounted gas chromatograph with a thermal conductivity detector. The H_2O used to wet the specimens and the H_2 released from the wet-basalt specimen were also sampled for stable isotope analyses. In this study, H_2 production during simulated faulting was scaled by frictional work (Figure 1a) as it can be estimated for natural earthquakes under few assumptions.

3. Results

[6] The findings of the experiments on basalt specimens are summarized into three points. First, the amount of H_2 (m_{H2}, mmol) increased almost linearly with frictional work (W_f, kJ) for both dry and wet specimens, and the resulting slopes were 0.11 and 0.26, respectively (Figure 1a). These linear relationships held at least over the range of experimentally producible frictional work. As frictional work increases, abrasive wearing processes become more effective. In addition, a rapid temperature rise to more than ~400°C due to frictional heating (auxiliary material) causes thermal fracturing of the sliding surfaces, leading to the breakage of covalent bonds in the rock specimens and eventually to the formation of very fine grained reactive materials (as small as ~80 nm; Figure 2). The generation of fine-grained materials with fresh mineral surfaces can enhance free-radical reactions and thus

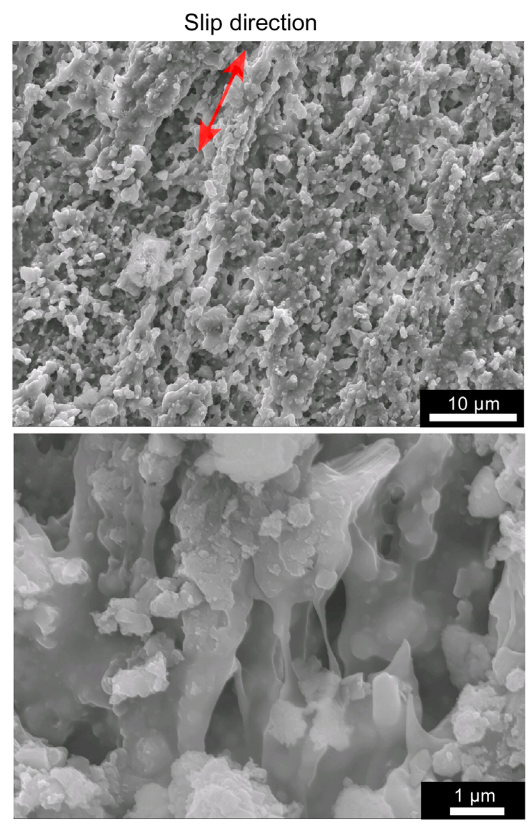

Figure 2. Representative microstructures on the sliding surface of a wet basalt specimen sheared at a slip velocity of 1.6 m/s under a normal stress of 1.0 MPa. Abrasive wear processes along with frictional heating due to rapid sliding break micron-size asperities on sliding surfaces into reactive nanoparticles. Free radicals on the fresh surfaces of the fine-grained particles react with H_2O, leading to the generation of H_2.

[1] Auxiliary materials are available in the HTML. doi:10.1029/2011GL048850.

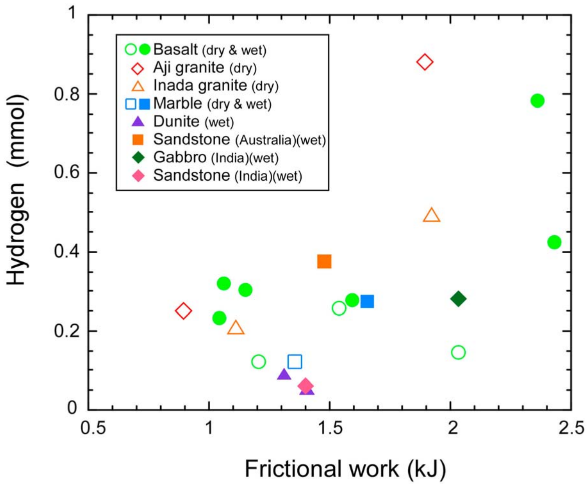

Figure 3. Hydrogen generation as a function of frictional work during high-velocity friction experiments for various types of rock specimens at a slip velocity of 1.6 m/s and a displacement of 10 m. Open and solid symbols indicate dry and wet specimens, respectively. H_2 was generated from all rock types, even from non-silicates, implying that H_2 can form during earthquakes in any tectonic setting.

H_2 generation. In fact, the amount of H_2 generated by grinding has been shown to be linearly related to the surface area of the ground sample [*Kameda et al.*, 2004]. Such fine grained materials could bond together by the formation of chemical bonds through fluid-rock interactions during an interseismic period. The bonds eventually will break at subsequent seismic slip, resulting in H_2 generation by radical reactions.

[7] Second, the H_2 production of wet specimens is a few times larger than that of dry specimens (Figure 1a), suggesting that H_2 generation is enhanced by the presence of H_2O, in agreement with the reaction kinetics (1). The generation of H_2 even under dry conditions could be because H_2O molecules that escaped from fluid inclusions in mineral grains and fluids along grain boundaries during faulting subsequently participate in mechanoradical reactions. In addition to H_2O in fluid inclusions, hydroxyls within crystal structures can be a source of H for H_2 generation. Third, there is no significant difference in H_2 production between air and argon gas atmospheres (Figure 1a), indicating that H_2 can be generated mechanoradically in the deep, oxygen-free crust where most earthquakes occur.

[8] We also performed the experiments on other rock types representative of the various tectonic settings. Although the amount of H_2 generation varied by a few times depending on the rock type, H_2 was generated during all experiments irrespective of rock type, even with marble, a non-silicate rock (Figure 3). Thus, any highly reactive radicals formed through the rupture of chemical bonds, not only Si–O· bonds, can generate H_2 during faulting. Therefore, the production of H_2 may depend more on the production of fine-grained materials with fresh reactive surfaces than on the rock or mineral type or the specific molecular bond. Although the detailed mechanism of mechanoradical H_2 generation remains uncertain, the experimental data strongly indicate that mechanoradical H_2 generation can occur in many different tectonic settings by fault activity.

4. Discussion and Conclusion

4.1. Estimation of Global Earthquake-Derived H_2 Flux

[9] We extrapolated the experimentally-determined m_{H2}–W_f relationship to natural conditions in order to estimate the amount of H_2 generation during earthquakes with different magnitudes. Frictional work by natural earthquakes can be calculated by

$$W_f(M) = S(M) \cdot D(M) \cdot \sigma_{eff} \cdot \mu_d \tag{2}$$

where S is fault surface area (in meter squared), D is average displacement (in meter), σ_{eff} is effective pressure acting on the fault surface (S), and μ_d is the average dynamic friction coefficient. S and D are related with earthquake magnitude, M, ($\log S = M + 2$ and $\log D = 0.5 \cdot M - 3.1$) [e.g., *Utsu*, 2001]. Consequently, the amount of H_2 generation as a function of earthquake magnitude can be calculated by

$$H_2(M) = \alpha \cdot W_f(M) = \alpha \cdot S(M) \cdot D(M) \cdot \sigma_{eff} \cdot \mu_d \tag{3}$$

where α is the slope of the m_{H2} versus W_f curve (Figure 1a). Thus, H_2 generation increases with earthquake magnitude following a power-law relation (Figure 4a). For example, an earthquake of magnitude M = 1.0, with σ_{eff} = 16 MPa (corresponding to a depth of about 1 km under hydrostatic conditions), μ_d = 0.25 (typical dynamic friction during seismic fault motion), and α = 0.26 mmol/kJ (experimental value for a wet basalt specimen) would thus generate 2.63 mol of H_2.

[10] Using the correlation between H_2 generation (m_{H2}) and frictional work (W_f), equation (4) and the Gutenberg and Richter (G-R) relationship (given below), we can estimate the average annual global H_2 flux associated with earthquakes:

$$H_{2\ \text{global flux}} = \int_{M_{min}}^{M_{max}} \frac{N(M) \cdot \alpha \cdot W_f(M)}{S(M)} dM \tag{4}$$

The G-R relationship is

$$\log N(M) = 7.47 - b \cdot M$$

where N is earthquake frequency and b is an empirically determined parameter. If earthquakes with magnitudes between 0 (M_{min}) to 4 (M_{max}) that occur for one year follow the G-R relationship shown above, we can calculate the cumulative H_2 flux associated with the earthquakes to be 2.3×10^5 mol/m^{2}yr using b = 1 and the same values for α, σ_{eff}, and μ_d as we used in the example above (Figure 4a). This estimated H_2 flux is about 10 orders of magnitude higher than H_2 fluxes due to other processes: water–rock redox reaction (3×10^{-4} mol/m^{2}yr) [*Sleep and Zoback*, 2007] and water radiolysis (8×10^{-6} mol/m^{2}yr) [*Lin et al.*, 2005]. Thus, if all abiotic H_2 is consumed by microbes, the earthquake-driven ecosystem might be the largest ecosystem fed by abiotic H_2 on modern Earth.

4.2. Estimation of Local H_2 Concentration Along Faults

[11] In addition to the global H_2 flux, the local H_2 concentration must be known to determine the contribution of

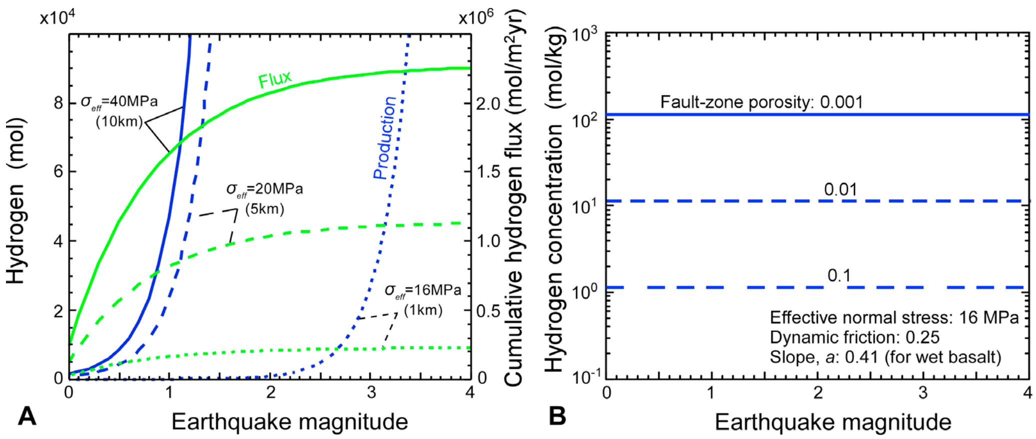

Figure 4. (a) Generated hydrogen (in blue) and cumulative hydrogen flux (in green) as a function of earthquake magnitude, based on equations (3) and (4), respectively, for effective normal stresses of 16, 20, 40 MPa (corresponding to a hypocenter depth of 1, 5, 10 km, respectively), a dynamic friction coefficient of 0.25, and a slope (a) of the W_f–m_{H2} curve of 0.41, experimentally determined using wet basalt specimens (Figure 1a). H_2 production increases with earthquake magnitude according to a power-law relation. (b) Hydrogen concentration in fluid within a fault zone with different porosities (0.001, 0.01 and 0.1) just after an earthquake as a function of earthquake magnitude, based on equation (7) for effective normal stress of 16 MPa and other parameters are the same as those in Figure 4a. Calculated H_2 concentrations in the fault zone are sufficiently high to sustain a H_2-based subsurface lithoautotrophic microbial ecosystem.

H_2 to a subsurface ecosystem around fault zones. The local H_2 concentration in fluids along faults can be estimated from the amount of H_2 generation and the potential fluid volume within a fault zone. If we assume negligible fluid flow within the fault zone over the recurrence interval of small-magnitude earthquakes, the local H_2 concentration within a fault zone can be calculated as

$$H_{2\,\mathrm{local}}(M) = \alpha \cdot W_f(M)/\phi \cdot H(M) \cdot S(M) \tag{5}$$

where ϕ is average porosity within the fault zone immediately after an earthquake and H is average width of the fault zone ($\phi{\cdot}H{\cdot}S$ gives the fluid volume within the fault zone, if all pores are filled with fluid). The width of the fault zone tends to be proportional to fault displacement in natural faults [e.g., *Scholz*, 1987] and is expressed by

$$H \cong 10^{-2} \cdot D \tag{6}$$

Then, equation (5) becomes

$$H_{2\,\mathrm{local}}(M) \cong \alpha \cdot \sigma_{\mathrm{eff}} \cdot \mu_d / 10^{-2} \cdot \phi \tag{7}$$

[12] Thus, the local H_2 concentration is mathematically independent of earthquake magnitude. In the case that ϕ is 0.1 and other parameters are the same as those used for global H_2 estimation, equation (7) yields a local H_2 concentration of ~1.1 mol/kg of fluid just after an earthquake (Figure 4b). This concentration is sufficiently high to sustain a H_2-based subsurface lithoautotrophic microbial ecosystem, as geochemical and microbiological observations from hydrothermal fields suggest that the concentration of the order of mmol/kg is required [*Takai et al.*, 2006]. Although the concentration depends strongly on the fluid flux in fault zones, an uncertain quantity, H_2-rich fluid may be present in fault zones at least for certain periods because H_2 would be continuously supplied by microseismicity in active tectonic regions such as mid-ocean ridges and subduction zones.

4.3. Implications for Subsurface Biosphere

[13] The stable isotope ratio of H_2 released during an experiment on a wet basalt specimen, dampened with water with $\delta D_{H2O} = -40‰$, was determined to be $\delta D_{H2} = -222‰$. While it could be due to kinetic isotope effect, the observed δD difference between H_2 and H_2O can be explained by temperature-dependent equilibrium isotope fractionation at 660°C [*Horibe and Craig*, 1995]. Such high temperatures can be achieved at small-area contacts on sliding surface by rapid frictional heating, whereas D-enriched H_2 is unlikely to be generated by hydrothermal reactions or water radiolysis [*Lin et al.*, 2005; *Kawagucci et al.*, 2010]. The δD_{H2} value of geofluids is controlled mainly by equilibrium isotope fractionation, leading to the use of the value as a geochemical thermometer [*Proskurowski et al.*, 2006]. In natural fault zones, measured δD_{H2} values range between −470‰ and −770‰ [*Kita et al.*, 1980; *Wiersberg and Erzinger*, 2008], corresponding to equilibrium values at temperatures between 255°C and 15°C. Although at high temperatures, abiotic isotope exchange reactions proceed rapidly to isotope equilibrium, at room temperature, the exchange occurs on a geological time scale without microbial H_2 metabolic activity, which dramatically promotes the rate of isotope exchange to reach equilibrium [*Campbell et al.*, 2009]. Thus, even though D-enriched H_2 is initially produced by earthquake faulting, the D-depleted H_2 observed in natural faults may imply the presence of H_2-metabolizing organisms around natural fault zones. Moreover, if D enrichment of mechanoradically produced H_2 is transferred during microbial H_2 consumption into metabolites such as methane and lipids, then δD values of these molecules obtained from rocks and fluid in natural fault zones might indicate the presence of a mechanoradical H_2-based microbial ecosystem.

[14] We now ask whether earthquakes contributed to early Earth ecosystems. In other words, when did earthquakes first produce H_2 on Earth? The oldest known accretionary orogens are the Isua supracrustal belt (~3.8 Ga) [*Furnes et al.*, 2007] and the Acasta gneiss complex (~4.4 Ga) [*Wilde et al.*, 2001] in southwestern Greenland and northwestern Canada, respectively. These orogens are strong geological evidence that plate tectonic activity has most likely occurred at least since ~3.8 Ga. Because plate motion would have generated seismic activity at mid-ocean ridges and in subduction zones, H_2 was presumably generated by earthquakes before the oldest known timing of active hydrogenotrophic methanogenesis (~3.5 Ga) [*Ueno et al.*, 2006]. Thus, seismic activity and the consequent release of H_2 might have sustained subsurface microbial communities as long ago as 3.8 Ga. Moreover, mechanoradical H_2 generation can be induced by meteorite impacts as well as by earthquakes, and thus might play an important role in the evolution of subsurface biosphere not only on Earth but also on other planets.

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