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# 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 $\gamma$-irradiation experiment [*Lin et al.*, 2005]. The $H_2$ flux per unit of surface area from redox reactions has been estimated to be $3 \times 10^{-4}$ 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 $8 \times 10^{-6}$ 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:

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

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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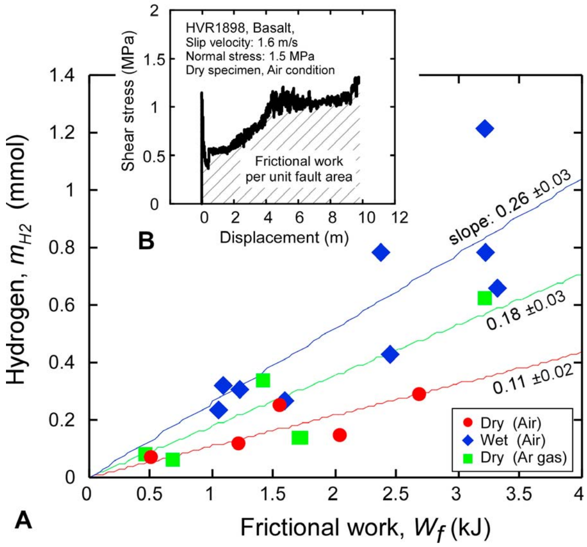


**Figure 1.** (a) Hydrogen generation (in mmol) as a function of frictional work (in kJ) during high-velocity friction experiments on dry and wet basalt specimens at a slip velocity of 1.6 m/s and a displacement of 10 m under air or argon gas atmospheres. The amount of hydrogen generated tended to increase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

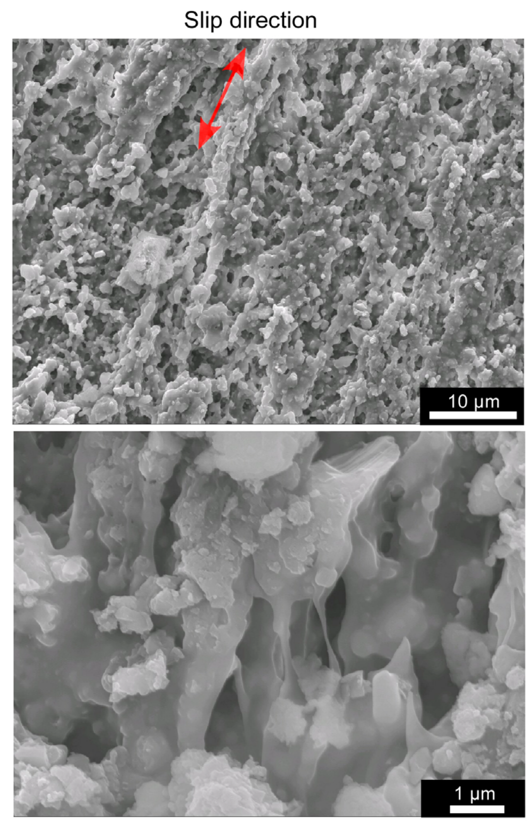


**Figure 2.** Representative microstructures on the sliding surface of a wet basalt specimen sheared at a slip velocity of 1.6 m/s under a normal stress of 1.0 MPa. Abrasive wear processes along with frictional heating due to rapid sliding break micron-size asperities on sliding surfaces into reactive 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.

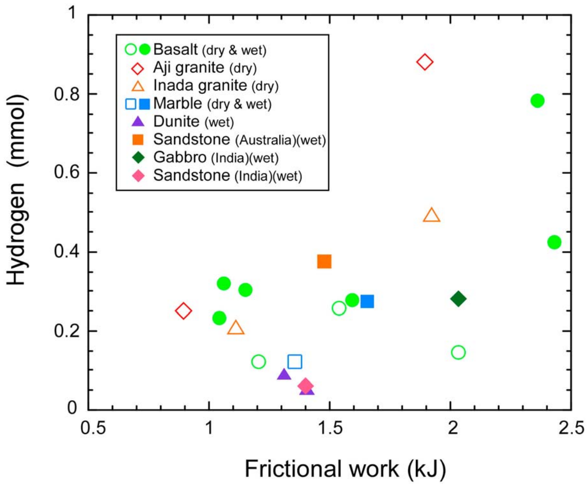


**Figure 3.** Hydrogen generation as a function of frictional work during high-velocity friction experiments for various types of rock specimens at a slip velocity of 1.6 m/s and a displacement of 10 m. Open and solid symbols indicate dry and wet specimens, respectively. $H_2$ was generated from all 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

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

where $S$ is fault surface area (in meter squared), $D$ is average displacement (in meter), $\sigma_{eff}$ is effective pressure acting on the fault surface ($S$), and $\mu_d$ 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

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

where $\alpha$ 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 $\sigma_{eff}$ = 16 MPa (corresponding to a depth of about 1 km under hydrostatic conditions), $\mu_d$ = 0.25 (typical dynamic friction during seismic fault motion), and $\alpha$ = 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:

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

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 $2.3 \times 10^5$ mol/m$^2$yr using $b$ = 1 and the same values for $\alpha$, $\sigma_{eff}$, and $\mu_d$ 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 ($3 \times 10^{-4}$ mol/m$^2$yr) [*Sleep and Zoback*, 2007] and water radiolysis ($8 \times 10^{-6}$ 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

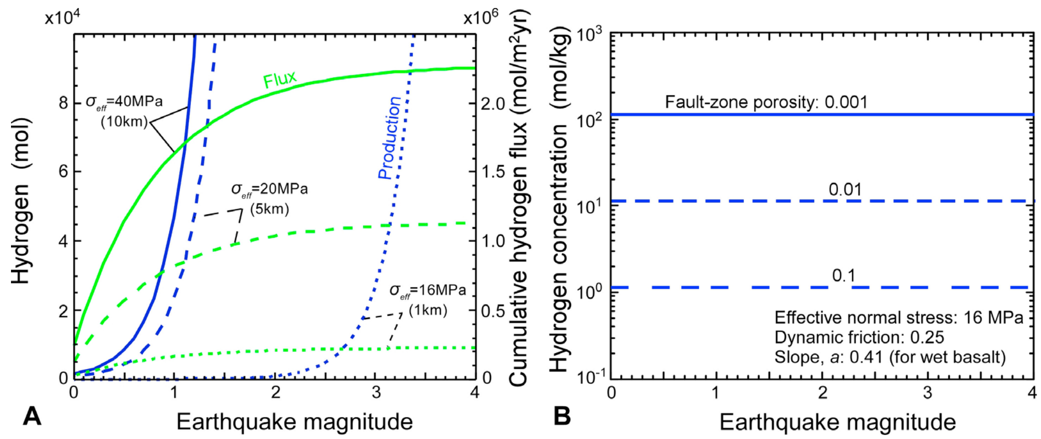


**Figure 4.** (a) Generated hydrogen (in blue) and cumulative hydrogen flux (in green) as a function of earthquake magnitude, based on equations (3) and (4), respectively, for effective normal stresses of 16, 20, 40 MPa (corresponding to a hypocenter depth of 1, 5, 10 km, respectively), a dynamic friction 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 $\phi$ 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 $\phi$ 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 $\delta D$ 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 $\delta D_{H2}$ 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 $\delta D_{H2}$ 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 $\delta D$ 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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