Sources of Hydrogen as Food for Deep Microbial Communities

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To survive in deep subsurface environments autolithotrophic microbial communities require a sustainable food supply. One possible source is H_2 which forms when H_2O reacts with ferrous iron at rock surfaces or mineral grain boundaries to produce H_2 plus ferric iron. The amount of H_2 that can be supplied in this way, however, is relatively small and may not last for more than a few hundred or thousand years. A much larger reservoir of H_2 exists in the rocks, inside mineral grains, arising from an as yet little–known redox conversion that affects OH^- in nominally anhydrous minerals. These OH^- represent small amounts of "water" that become incorporated during crystallization in H_2O–laden environments. A corollary of the H_2 formation from OH^- is the formation of peroxy, an oxidized form of oxygen. While the peroxy become part of the mineral structure, the H_2 molecules are diffusively mobile and can escape from within the mineral grains, entering the intergranular space. Assuming cautiously realistic number densities of OH^- undergoing the *in situ* redox conversion to H_2 plus peroxy, a 10 km deep rock column is expected to contain enough H_2 to allow for a constant degassing rate of 50–100 nmole H_2 per day per cm^2 over 30 million years.

In their report on microbial communities in deep aquifers in the Columbia River basalt, Stevens and McKinley (1) suggest H_2 as a food source, assuming that it arises from an interaction between ground water and basalt according to the modal reaction $H_2O + 2\ Fe^{2+}O = H_2 + 2\ Fe_2^{3+}O_3$ and producing H_2 at a rate of about 10 nmole H_2 day^{-1} g^{-1} basalt (2). This view has been contested by Anderson et al. (3) who point out that such a high H_2 production rate could not have been sustained over the lifetime of the Columbia River basalts, >17 million years, and that remeasured rates of H_2 production between water and crushed basalt at pH 8, a more realistic pH value for pore water, were much lower than the values previously determined at pH 6 (1).

Bypassing the discussion whether dissolved organic carbon may be the most probable alternative food supply in basalt aquifers (3), I would like to draw attention to a different H_2 source from deep rocks which has not yet been fully recognized. On a tectonically active planet like the

Earth this H_2 source is potentially very large and nearly inexhaustible. To understand where this H_2 comes from, we have to look at the rocks themselves.

Thermodynamics and the phase rule (4) require that every mineral crystallizing in the presence of H_2O must incorporate a small amount of the H_2O component, just as it would pick up any other "impurity" from its environment. This law applies to minerals crystallizing from an H_2O–saturated magma or recrystallizing in a metamorphic H_2O–laden setting. It applies to all minerals that are nominally anhydrous but crystallize in the presence of H_2O. Thus the vast majority of rock–forming minerals in the crust and the upper mantle will contain traces of "impurity" H_2O.

A common feature of H_2O incorporation is that each H_2O molecule contributes two protons which attach to lattice O^{2-}, thereby forming two OH^- or $O_3X\text{-}OH$ with $X = Si^{4+}$, Al^{3+} etc. To balance the charge of the two protons brought in, a cation must be left out, say a divalent cation Me^{2+}. The result is an Me^{2+} vacancy in the mineral structure. Its double negative charge will preferentially be compensated by two OH^- nearby, taking the place of two O^{2-} next to the Me^{2+} vacancy: $[OH^- \lozenge HO^-]$ or $[O_3X/^{OH} \lozenge {}_{HO}/XO_3]$, where $\lozenge$ stands for the cation vacancy and the brackets indicate that we are considering only a section out of the 3-dimensional mineral structure.

In gas and liquid phases H_2O is stable and will not spontaneously decompose into H_2 plus O, unless physical energy is supplied in form of UV light (5) or chemical energy is supplied by a reductant, often a transition metal cation such as Fe^{2+}. In minerals which grow with OH^- as an integral part of their crystal structures, for example micas and clays, the OH^- are likewise stable. However, in nominally anhydrous mineral structures where OH^- are "impurities", the situation can be very different.

Relative to the ideal structure, a cation vacancy represents a negatively charged site. In its immediate vicinity the electric field gradients can be so high as to pull the protons of the adjacent OH^- together and to cause the oxygen to act as electron donor. Under certain circumstances, apparently quite common in mineral structures at cation vacancies neighbored by OH^- pairs (6), the hydroxyl oxygens transfer an electron each onto their respective protons, thereby oxidizing from the O^{2-} to the O^- state while reducing two H^+ to H_2. The H_2 molecule thus formed will first occupy the cation vacancy, while the two O^- form an O^-–O^- bond, giving rise to a peroxy anion, O_2^{2-}, or to a peroxy link, $O_3X/^{OO}\backslash XO_3$. The redox conversion can be written as $[OH^- \lozenge HO^-] = [H_2 + O_2^{2-}]$ or $[O_3X/^{OH} \lozenge {}_{HO}/XO_3] = [H_2 + O_3X/^{OO}\backslash XO_3]$.*

This redox conversion reminds us that oxygen has two oxidation states, O^- and O^{2-}, and that O^{2-} is endowed with a large negative electron affinity, 5.9 eV (8) which makes it effectively

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* One characterstic feature seems to be that the redox conversion just described is confined to the anion sublattice and does not interact with the other surrounding cations. The rodox conversion takes place even when there are reduced transition metal cations such as Fe^{2+}, Mn^{2+}, Cr^{3+} etc. nearby in the same structure (7).

unstable. In predominantly ionic oxides such as MgO, O^{2-} is prevalent because the Coulomb interaction between Mg^{2+} and O^{2-} overrides the negative electron affinity of the O^{2-} (6). As the cation radii grow larger from Mg^{2+} to its heavier homologues, the peroxides become more stable and, in the case of BaO_2, exceed the stability of the oxide BaO (9). Were it not for the fact that O^- is a radical (with 7 electrons in the valence shell), we would be much less accustomed to think of O^{2-} as the stable form of oxygen in the mineral world.

The redox conversion inside the mineral can be viewed as a "water splitting" reaction in which the oxygen becomes part of the mineral structure, namely as a peroxy anion or peroxy link replacing two O^{2-}, while the H_2 molecules are free to diffuse away.

First experimental evidence for this redox conversion was obtained during a study of OH^- and OD^-–doped MgO of otherwise ultrahigh purity (10). As shown in **Figure 1**, despite an extremely low transition metal content of «5 ppm, H_2 was observed to evolve. The H_2 evolution was accompanied and followed by release of atomic O conforming to the disproportionation of the peroxy anions, $O_2^{2-} = O + O^{2-}$.

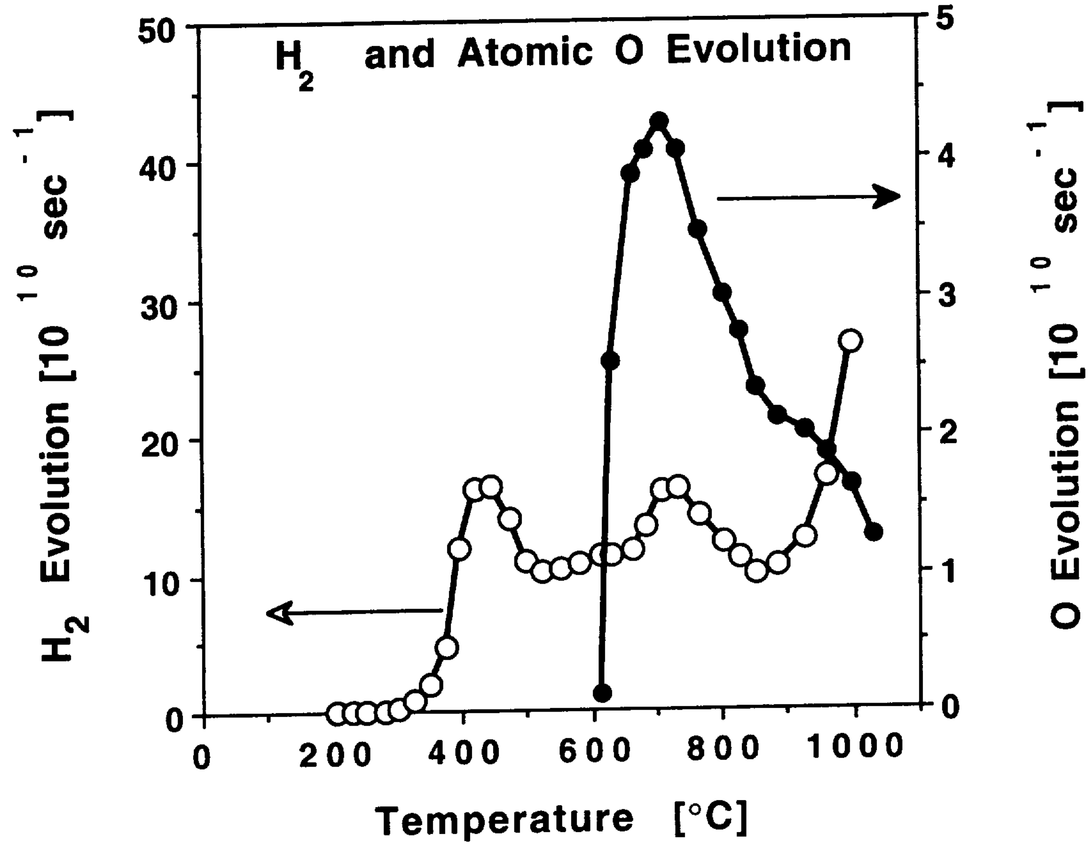

Figure 1: *Evolution of molecular H_2 and atomic O during the degassing of ultrapure, finely divided MgO (after (10))*

Quantitative measurement of the H_2 evolved indicated that 8,000 ppm OH^- in the MgO structure, nearly 1% in number, had converted to H_2 plus peroxy (10). Peroxy-type oxidants in even larger quantity were found in CaO, up to 20,000 (11). Shelby (12) observed that "dry" fused silica, made to have a very low Si–OH content of <5 ppm, reacted with H_2 to produce a total of 80 ppm Si–OH. This implied that the apparently "dry" silica contained about 75 ppm peroxy links, $O_3Si/^{OO}\backslash SiO_3$, a stable defect in the silica glass structure (13). The number density of peroxy and, by implication, of H_2 molecules in melt-grown MgO crystals was estimated to be of the order of 500–1000 ppm (14). This means that probably more than 90% of all OH^- in MgO had converted to $H_2 + O_2^{2-}$ (15, 16). Infrared spectroscopic studies of the residual OH^- in MgO crystals indicated that the redox conversion to H_2 plus O_2^{2-} takes place during cooling around 500°C (15).

The same apparent deficiency of Si–OH pairs holds for olivine, the predominant mineral in upper mantle rocks (16). Most crystals of olivine and other minerals reportedly have very low OH^- contents, from nil to about 50 ppm, and are thought by many to be nearly "water-free" (17–23). However, a new technique (24) which is sensitive to peroxy and has been extensively tested with MgO (24, 25), finds peroxy in olivine (26), volcanic glass and various minerals (27), including many that are replete with reduced transition metal cations, pointing at a very wide occurrence of the redox conversion of OH^- pairs.

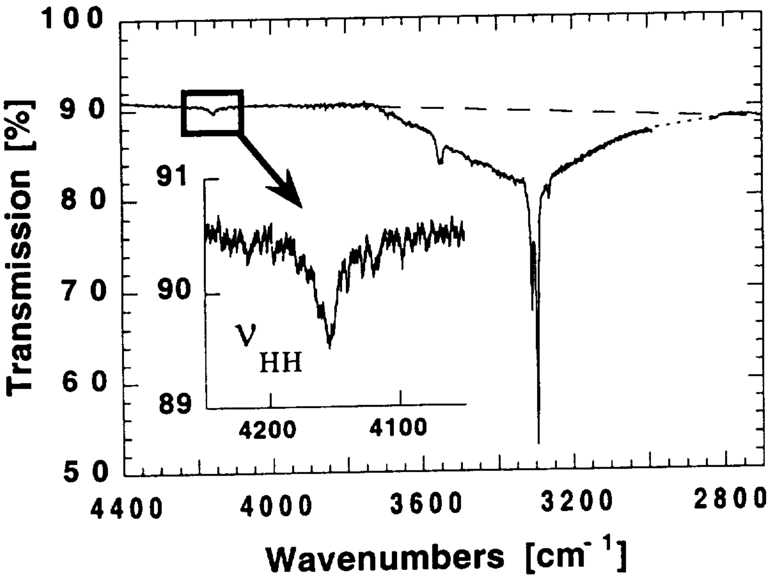

Figure 2: *IR spectrum of an MgO crystal from 2800-4400 cm^{-1} which includes both the O–H stretching and the H–H stretching regions. In addition to three O–H stretching features, arising from OH^- at different defect sites, the weak band near 4150 cm^{-1} is due to the H–H stretching mode of molecular H_2 made IR–active by combining with a low frequency MgO lattice mode (15).*

In some cases the very weak infrared signal from the forbidden H–H stretching band around 4150 cm^{-1} (2.4 μm) can be seen (15) as depicted in **Figure 2** and in the spectrum of olivine (16). Without a very high concentration of H_2 molecules in the mineral matrix, outnumbering the residual OH^- by a factor of 10, the intrinsically very weak H–H signal would not be detectable.

Since there is evidence that peroxy is present in most, if not all rock-forming minerals (27), pointing a the ubiquity of the redox conversion of OH^- or X–OH pairs, large amounts of H_2 may be be present inside the minerals of common rocks and may therefore be released.

In principle, it should be straightforward to determine the amount of H_2 by crushing the minerals or rocks to a fine powder and measuring the volume of H_2 released either during crushing or during subsequent heating. In practice such experiments are not easy. The difficulties arise from the fact that peroxy in the mineral matrices coexist with the H_2 molecules.

Peroxy is the chemical designation for two O^- forming the very short O^-–O^- bond, only 1.5 Å (28) compared to the more typical O^{2-}–O^{2-} distances of 2.7-2.9 Å (9). From a physicist's perspective an O^- that occupies an O^{2-} site is a defect electron, a "positive hole" (29), a mobile charge that resides in and can travel along the O 2p-dominated valence band (6, 30). Two O^- bonded to a peroxy are a positive hole pair, existing in an electrically inactive, dormant state. An important aspect of the peroxy bond is the shortness of its O^-–O^- bond, about 1.5 Å (27). This leads to a strong Coulomb repulsion between the two oxygen nuclei which in turn weakens the O^-–O^- bond. This causes the O^-–O^- bond to break easily. Experimentally, to demonstrate our case, we can break the O^-–O^- bond by sending a small shockwave through a crystal. An acoustic wave produced by fracturing is strong enough. As it races through the crystal the shock generates highly mobile electronic charge carriers, e.g. the positive holes as described above. At first the positive holes are distributed throughout the volume. However, because they are all positively charged and highly mobile, they repel each other and are driven toward the surface (6). Upon arrival at the fracture surface the positive holes reveal their "second nature": they are also highly oxidizing O^- radicals. They oxidize anything reduced within their reach, for instance H_2 molecules that linger in the mineral structure and try to escape through the freshly formed fracture surface.

Figure 3 shows the results of a fracture experiment with an upper mantle olivine crystal which did not display any sharp absorption bands in the O–H stretching region of the infrared and should have therefore be considered free of dissolved H_2O (17, 18, 21). When a 1 mm slice of this crystal was fractured in front of a fast mass spectrometer which analyzes in direct line of sight the gases released from the fracture surface, H_2 and H_2O molecules are emitted in abundance with a peculiar time sequence evident from **Figure 3** (31). After brittle fracture (completed within 5 μsec) H_2 molecules escape through the fracture surface. As the number of H_2 increases, so does the number of H_2O molecules, but within 200 msec the H_2 signal goes through a maximum and decreases, reaching a minimum after ≈400 msec. Beyond 400 msec the number of H_2O decreases, while the number of H_2 goes up again, reaching a second maximum after ≈600 msec.

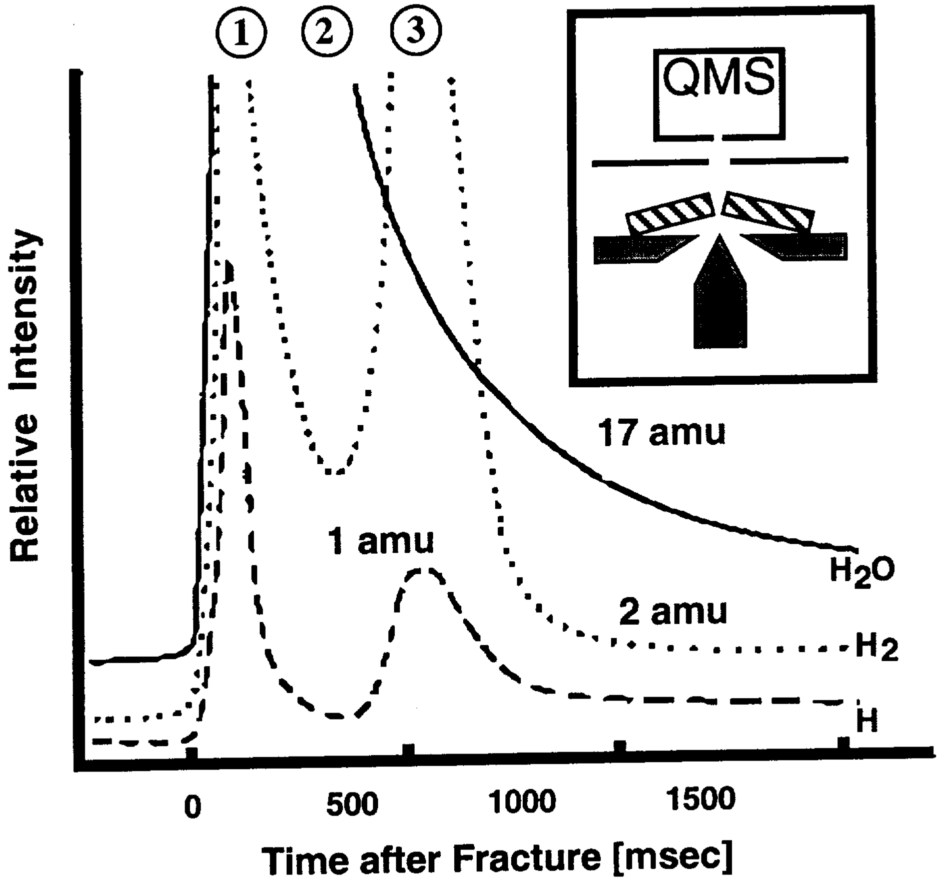

Figure 3: *H_2 and H_2O evolution after fracture of a San Carlos upper mantle–derived olivine crystal by mass spectroscopy (80 msec time resolution). Upon fracture, at t = 0, H_2 molecules (H^+: 1 amu, H_2^+: 2 amu) evolve together with H_2O molecules, (OH^+: 17 amu). After 400 ms, as the H_2O emission is highest, the H_2 emission goes through a minimum and resumes, reaching a second maximum about 600 msec after fracture. Inset: Experimental lay-out. QMS: quadrupole mass spectrometer; cross hatched: fractured crystal; stippled: support and advancing wedge.*

To understand this time sequence we need to understand the interaction of the H_2 molecules with the peroxy after fracture. As soon as the fracture surface is created, H_2 molecules begin to escape, obviously drawing from a reservoir of H_2 molecules beneath the surface in the olivine structure, probably on interstitial sites. However, the shockwave of brittle fracture carries enough energy to dissociate the $O_3Si/^{OO}\backslash SiO_3$ links in the olivine structure and release highly mobile positive holes into the valence band. These charges propagate at velocities of 100-300 m/sec (32), repel each other in the bulk and flood the fracture surface, carrying with them a positive charge. They oxidize the H_2 which try to escape through the surface by way of the reaction $2\ O^- + H_2 =$

$H_2O + O^{2-}$. For each H_2O molecule thus made which leaves the surface two positive charges are deposited. The rapid accumulation of positive charge prevents further positive holes from reaching the surface. Therefore, the "burning" of H_2 to H_2O ends and the number of H_2O molecules declines. Being neutral, however, the H_2 molecules are not impeded by the positive surface charge. They can resume diffusing through the fracture surface, escaping into the vacuum.

This fracture experiment demonstrates that an apparently "water-free" olivine crystal from the upper mantle contains H_2. Since the same crystal contains peroxy, it ascertains that the H_2 molecules are the product of the *in situ* redox conversion of OH^- which the olivine had incorporated during its crystallization in the H_2O–laden upper mantle environment.

The number of H_2 per unit volume of this olivine from the upper mantle and of other rock-forming minerals from crustal environments is still quite uncertain, because there is no systematic study yet on the amounts of H_2 that could be released from various typical magmatic or metamorphic rocks. Any attempt to determine such values will be beset with difficulties and will carry a large margin of error because we do not know how much of the H_2 formed inside the rock is still there. Being diffusively mobile, even in the densest mineral structures over geological time scales, the H_2 molecules will have slowly but surely diffused out. As the rocks cool, the thermodynamic driving force for outdiffusion becomes larger. Once H_2 molecules have made the transit from the mineral structure into the grain boundary space, they can percolate upwards without a need for open pores or fissures. If water-filled pores and fissures exist, additional H_2 can be generated through the conventional grain boundary reaction $H_2O + 2\ Fe^{2+}O = H_2 + 2\ Fe_2^{3+}O_3$ and mix with the H_2 that seeps out of the mineral grains. This reaction is expected to have the highest H_2 production rates in regions in the crust where elevated temperatures prevail. Steep geotherms exist in volcanically active regions where H_2O–laden fluids penetrate from below, bringing with them the possibility of extensive H_2O–Fe^{2+} reactions along grain boundaries. Most of the stable mid–crust, however, is believed to be essentially "dry", devoid of H_2O–laden fluids (33), and hence unlikely to produce H_2 on a large scale by the conventional H_2O–Fe^{2+} reaction.

Despite the current lack of a broader data base, it is possible to set boundaries as to the maximum and minimum number density of H_2 inside typical rock-forming minerals. A number density as large as 8,000 and 20,000 ppm H_2, as determined in very finely divided MgO and CaO (10, 11), is likely to represent an upper limit. 100 ppm as found in fused silica (12) probably represents a lower limit. Concentrations of OH^- in olivine crystals from different parts of the world as determined from infrared spectroscopy, reach 50 ppm (16) and tend to be higher in minerals from crustal rocks (17, 21). If the ratio of OH^- undergoing redox conversion to residual OH^- is 10:1 as suggested above, the number density of H_2 should be 500–1000 ppm or 3–6 x 10^{19} H_2 molecules per cm^3, within the same order of magnitude of the values determined for

MgO crystals (14). From this value we can estimate, by order of magnitude, the size of the H_2 reservoir in the rock column. Let's assume a rock column of 1 cm^2 cross section, 10 km deep. The total number of H_2 molecules in this volume is 3–6 x 10^{25}, equivalent to 50–100 moles. Assuming a constant rate of H_2 outgassing over a chosen time period, say 30 million years (10^9 days), the rock column could continuously release 50–100 nmole H_2 per day per cm^{-2} cross section. This is 5–10 times the amount of H_2 postulated by Stevens and McKinley (1) to be produced per g basalt per day through H_2O reacting with Fe^{2+}.

While the basic physical and chemical features of the *in situ* redox conversion are fairly well established, many questions are still open. The main purpose of this report is to draw attention to the fact that a large H_2 reservoir may exist in the deep underground due to the remarkable and apparently ubiquitous reaction by which traces of H_2O dissolved inside nominally anhydrous minerals change into H_2 plus peroxy.

If the H_2 reservoir in the rock column is as large as we have reason to assume, even a minute leakage of H_2 could conceivably provide an nearly inexhaustible, continuous supply of H_2 to microbial communities living in deep horizons. Such supply would be guarantied on an H_2O–laden and tectonically active planet like the Earth wherever large-scale vertical movements bring rocks to shallower depth and into cooler environments on a 10–100 million year time scale. A similar H_2 reservoir should exist on Mars where magmatic systems were and presumably still are H_2O–laden. However, on Mars, the lack to extensive tectonic activity should have caused this H_2 reservoir to become depleted over time.

In closing I should note that the facts and arguments presented here do not preclude any other sources of H_2, including that stemming from the reaction of water with Fe^{2+} (1, 2), or other reduced gases and dissolved organic carbon (3). However, I should also point out that the mechanism by which H_2 is generated under the conditions discussed here is fundamentally different from that envisioned by Gold (34) in his deep gas hypothesis.

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