H₂-rich fluids from serpentinization: Geochemical and biotic implications

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Metamorphic hydration and oxidation of ultramafic rocks produces serpentinites, composed of serpentine group minerals and varying amounts of brucite, magnetite, and/or FeNi alloys. These minerals buffer metamorphic fluids to extremely reducing conditions that are capable of producing hydrogen gas. Awaruite, FeNi₃, forms early in this process when the serpentine minerals are Fe-rich. Olivine with the current mantle Fe/Mg ratio was oxidized during serpentinization after the Moon-forming impact. This process formed some of the ferric iron in the Earth’s mantle. For the rest of Earth’s history, serpentinites covered only a small fraction of the Earth’s surface but were an important prebiotic and biotic environment. Extant methanogens react H₂ with CO₂ to form methane. This is a likely habitable environment on large silicate planets. The catalytic properties of FeNi₃ allow complex organic compounds to form within serpentinite and, when mixed with atmospherically produced complex organic matter and waters that circulated through basalts, constitutes an attractive prebiotic substrate. Conversely, inorganic catalysis of methane by FeNi₃ competes with nascent and extant life.

Ultramafic rocks, composed mainly of olivine and pyroxene (Mg and Fe²⁺ silicates), are a common feature in the lithospheres of early terrestrial planets. On early Earth these rocks formed by eruption as near total melts from the mantle, by solidification of cumulates from partial crystallization of mafic melts at shallow depths, and by exhumation from the mantle through impacts and tectonics. Tectonic exposure and cumulative formation of ultramafic rocks continue on modern Earth. The most common exposure today is along the axis of slow and very slow spreading ridges where the mantle is too cool to form significant basalts; ~10% of oceanic crust forms at such ridges (1).

Here, we consider thermodynamic constraints on the formation of H₂-rich fluids by reaction of H₂O with ultramafic rocks at moderate temperatures and pressures. At temperatures <300°C and low concentrations of aqueous silica, these rocks react with H₂O to form hydrous Mg and Fe²⁺ silicates and hydroxides (2, 3). The fluid oxidizes some of the Fe²⁺ to magnetic liberating gaseous and aqueous H₂ to the environment, a process that can be observed today where hydrogen seeps occur on land, sometimes producing natural flames (4). Geochemists report hydrogen-bearing gases trapped in spring waters issuing from serpentinizing peridotites and ancient serpentinites undergoing modern weathering from Oman (5, 6), the Zambales ophiolite in the Philippines (4–8), Kansas oil wells (9, 10), the Sakalin and Koryak Plateau in Russia (11, 12), and Milford Sound in New Zealand (13). More recently, marine geologists discovered low-temperature fluids from vents rich in methane and hydrogen in midocean ridge systems (3, 14). The Lost City vent field along the mid-Atlantic ridge system supports microbial colonies with anaerobic thermophiles (3). Robert Rye (personal communication) has found similar microbial colonies within highly alkaline springs at the Cedars ultramafic complex in California, within the Franciscan trench melange (15).

Buffering of solutions by serpentinite mineral assemblages and production of H₂, considered in this study, are of interest to early biotic, and perhaps prebiotic, evolution on the Earth and other rocky planets. In addition, we suggest a global geochemical implication of H₂ production in the formation of ferric oxide in the Earth’s mantle.

Biological Motivations

An important class of habitable environments supported by H₂ involves mixing of serpentinite-derived water with CO₂-rich water. The CO₂ reacts with H₂ to form methane by the reaction

\[ 4H_2 + CO_2 \rightarrow CH_4 + 2H_2O. \]  

This reaction occurs abiotically in hydrothermal systems in serpentine (3, 16) and lower-temperature environments beneath oceans (17) and continents (18). Over geological time, metamorphism of carbonates and the degassing of lavas continually recharge ocean and atmosphere with CO₂.

Reaction 1 supports extant biota and abiotic processes. Methanogens in rocks can thrive at H₂ concentrations of ~13 nM (19), orders of magnitude below the concentration in equilibrium with serpentinite presented below. Magnetite and awaruite (FeNi₃, a common trace mineral in serpentinite) both catalyze methane production in the laboratory at hydrothermal conditions (21, 22). Complex organic matter forms abiotically from this process both in the laboratory and nature (3, 16, 18, 21, 22).

The formation of abiotic methane and more complex organic compounds is a boon to certain modern microbes that react them with photosynthetically generated oxygen (16, 20). This niche did not exist before life. Rather, abiotic methanogenesis was a mixing blessing to nascent life forms. Abiotic formation of methane competes with life by removing the energy source in reaction 1. This is particularly true if awaruite or magnetite efficiently catalyzes the reaction (22). The reaction (along with the formation of MgCO₃) is also likely to occur when CO₂-rich water penetrates hot serpentine. This competition is evident in modern subsurface environments with a slow supply of the limiting reactant (either CO₂ or H₂) (18). Methanogens do exist there, but the abiotic consumption of their food reduces their productivity. There is a finite productivity below which abiotic processes outcompete life. At present, this limit is poorly constrained, but it could be fairly high for inept prebiotic autocatalysis and early life forms.

We continue with the positive aspects of serpentinization for life. Once life originated, methanogenesis was a continual subsurface niche on the Earth. This niche likely exists on Mars and Europa (16). The use of Ni, a common element in serpentinites and a rare element in other rocks, in the key enzyme of methanogens points to the great antiquity of this process on Earth and the probable origin of methanogenesis within fluids that reacted with serpentinite (23, 24).

The H₂-rich waters formed by low-CO₂ hydrothermal fluids circulating through ultramafic rocks generate a “Darwin soup” by mixing with other fluids and organic substrates. Mixing produced disequilibria and gathered the full repertoire of biological...
elements. First, the H₂ and the methane formed a very reduced atmosphere. Lightning is known to produce complex organic compounds in this situation (25). More transient reducing atmospheres from the oxidation of metallic Fe occurred after large asteroid impacts (26). In both cases, the presence of H₂ increases the yield of complex organic compounds (27). Similarly, complex organic compounds formed within the highly reducing subsurface environments in serpentinites (16).

Below, we provide examples of gathering of elements by flow through various serpentinite environments. Mixing may yield a solution enriched in several biologically important elements. For example, surface waters may contain amino acids formed from nitrogen, whereas ground waters in basalt may contain significant phosphorus. Finally, the strong catalytic properties of FeNi₃, with Fe⁺₃ in serpentines make them a potential site for prebiotic chemistry. We are aware of no extant or fossil organisms that put these surfaces to a useful purpose or that use FeNi₃ within their cells. We feel that a diligent search is warranted.

**Rock–Water Reaction**

To quantify our biological motivations, we compute concentrations of aqueous H₂ in fluids in equilibrium with serpentinites and the conditions where awaruite is stable. We use equilibrium thermodynamic relations to illustrate implications of a well known geologic process. We represent rocks as a mixture of minerals of limited compositional variation and the redox state in terms of the molality of aqueous H₂. In the case of ultramafic rocks, we consider the thermodynamic components H₂O, H₂, FeO, MgO, SiO₂, and NiO. We ignore sulfur and refer the reader to the work of Frost (28). Früh-Green et al. (3) discuss similar systems with significant carbon.

The mineralogy of ultramafic rocks is mostly olivine [(Mg,Fe)₂SiO₄] and pyroxene [both orthopyroxenes (Mg,Fe)₂SiO₃ and clinopyroxenes Ca(Mg,Fe)₂Si₂O₆], with atomic Mg/Fe ratios of ~9:1. Traditionally, the redox state of these geologic systems is controlled by the quartz-fayalite-magnetite (QFM) buffer, represented by equilibrium in the aqueous fluid for the reaction (29).

$$3\text{Fe}_2\text{Si}_2\text{O}_5 + 2\text{H}_2\text{O} \leftrightarrow 3\text{SiO}_2 + 2\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{(aq)};$$

fayalite + water ⇔ quartz + magnetite + hydrogen. \[2\]

This buffer is relevant to redox conditions of ultramafic rocks under igneous conditions and the more silicic mafic rocks (30) even to temperatures of hydrothermal processes (31). Redox conditions defined by reaction 2 are inappropriate at temperatures <~300°C for ultramafic rocks, as the stable phases are serpentine [(Mg,Fe)₃Si₂O₅(OH)₃], brucite [(Mg,Fe)OH]₂], and magnetite, where the activity of aqueous silica is far below that required to form quartz. Such hydrated metamorphic ultramafic rocks are called serpentinites (32).

During serpentinization of ultramafic rocks Mg and Fe₂⁺ partition between serpentine and brucite so that the chemical potentials of MgO and FeO are the same in both phases (33, 34). We represent appropriate redox reaction for serpentine by

$$2\text{Fe}_2\text{Si}_2\text{O}_5(\text{OH})_3 + 6\text{Mg}(\text{OH})_2 \leftrightarrow$$

$$2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{(aq)} + 4\text{H}_2\text{O},$$

Fe-chrysotile + Mg-brucite ⇔ chrysotile + magnetite + hydrogen + water. \[3\]

where the stoichiometry corresponding to the Fe-chrysotile [Fe₂Si₂O₅(OH)₃], chrysotile [Mg₂Si₂O₅(OH)₃] and Mg-brucite [Mg(OH)₂], and Fe-brucite [Fe(OH)₂] denotes components of Mg-Fe₂⁺ substitution in solid solution minerals of serpentine and brucite, respectively. We base our thermodynamic evaluation of Fe²⁺ substitution in serpentine and brucite on the mineral compositions of geologic serpentinites (see Appendix). This analysis demonstrates the importance of modest Fe²⁺ substitution in these minerals on H₂ generation in planetary crusts.

Reaction 3 applies when there is enough Mg plus Fe(II) to form brucite; that is, (Mg + Fe(II)) >1.5 Si, as occurs in dunites [nearly monomineralic olivine with (Mg + Fe(II)):Si = 2] and some harzburgites (rocks with olivine and minor orthopyroxene). These rock types occurred on the ancient Earth (35). With a lower ratio Mg + Fe(II)/Si than 1.5, the assemblage serpentine plus talc is more oxidized. We consider serpentine plus brucite as we are interested in the more reduced assemblage that equilibrates with a higher concentration of H₂. We recognize that the assemblage serpentine-brucite-magnetite (SBM) does form directly from olivine, and we restrict our analysis to equilibrium conditions near open fractures.

Metallic iron was present on the early Earth during accretion, just after the Moon-forming impact, and locally after major asteroid impacts. Awaruite, a Ni-rich alloy with compositions close to that of the ordered mineral Ni₃Fe, occurs within modern serpentinites (35, 36). The formation of awaruite in the presence of magnetite is of interest here because H₂ is produced during formation of magnetite from ferrous iron. We represent an additional set of redox reactions involving metallic Ni-Fe alloys as

$$\text{FeO} + \text{H}_2 \leftrightarrow \text{Fe} + \text{H}_2\text{O},$$

FeO + H₂ ⇔ Fe + H₂O, \[4a\]

and

$$\text{NiO} + \text{H}_2 \leftrightarrow \text{Ni} + \text{H}_2\text{O},$$

NiO + H₂ ⇔ Ni + H₂O, \[4b\]

where Fe and Ni oxides denote thermodynamic components in SBM (reaction 3), and Fe and Ni denote components in Ni-Fe alloy awaruite. Reaction 4a allows us to represent equilibria between SBM (reaction 3) and awaruite in terms of the activity of Fe in awaruite as:

$$4\text{Fe}_2\text{Si}_2\text{O}_5(\text{OH})_3 + 12\text{Mg}(\text{OH})_2 \leftrightarrow$$

$$4\text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{Fe}_2\text{O}_4 + 3\text{Fe} + 12\text{H}_2\text{O},$$

Fe-chrysotile + Mg-brucite ⇔ chrysotile + magnetite + Fe in awaruite + water, \[5a\]

and

$$3\text{Fe}(\text{OH})_2 + \text{Fe}_2\text{Si}_2\text{O}_5(\text{OH})_3 + 3\text{Mg}(\text{OH})_2 \leftrightarrow$$

$$2\text{Fe}_3\text{O}_4 + \text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{H}_2\text{O} + 2\text{H}_2\text{O}\text{(aq)},$$

Fe-brucite + Fe-chrysotile + Mg-brucite ⇔ magnetite + chrysotile + water + hydrogen. \[5b\]

These reactions provide compositional constraints among serpentine and brucite in equilibrium with magnetite as a function of the activity of Fe in awaruite and the molality of H₂ (see Appendix).

**Phase Equilibria**

We compute phase equilibria by using thermodynamic data, standard state conventions, and solid solution approximations defined in Appendix. Our intent is to illustrate basic features of aqueous H₂ concentrations and fluid saturation with H₂ consistent with the common serpentinite mineral assemblages: (Mg-Fe)-chrysotile, (Mg-Fe)-brucite, and magnetite, for reactions in
cannot simply apply reaction rated in serpentine and brucite that precipitate slowly. We rapidly dissolve in ground waters, making the water supersaturated. Olivine is commonly in contact with lizardite. Polymorph lizardite develops in the rock matrix, where relic olivine is commonly in contact with lizardite.

At Earth surface temperatures, olivine and orthopyroxene rapidly dissolve in ground waters, making the water saturated in serpentine and brucite that precipitate slowly. We cannot simply apply reaction because kinetically controlled supersaturated reactants occur on both sides. It has not escaped us that disequilibrium between dissolved Fe(II), water, and the products magnetite and H2 is a potential biotic reaction in this environment.

We present diagrams that help constrain mass balance of a biological or an industrial process based on aqueous H2. The concentration of H2 per mass of fluid stays constant as a fluid-dominated region heats or cools, unless the fluid becomes saturated with respect to H2 gas. This lets us represent a water-dominated part of fluid circulation, like a vein. We assume a fluid pressure of 500 bars, which is appropriate for primary ultramafic rocks, since the mode of serpentine is much enriched fluid then vents to the surface and is replaced at depth saturated with respect to H2(gas) at temperatures more than ~160°C. The buffer assemblage S0.1BM (Fig. 1) represents an extensively oxidized serpentine, where most of the Fe is in magnetite and XFe = 0.025 in serpentine and XFe = ~0.05 in brucite (S0.025B0.05M). Fluids in equilibrium with serpentine and brucite of these compositions are undersaturated with respect to H2(gas) at all temperatures shown in Fig. 1. The oxidation reaction still may proceed if the H2 concentration is undersaturated with H2(gas). We expect this situation when fluid vigorously circulates through the rock, removing dissolved hydrogen. The hydrogen-enriched fluid then vents to the surface and is replaced at depth with hydrogen-poor fluid from the ocean.

Equilibria for the buffer reactions QFM (reaction 2) and SBM (reaction 3) are shown in Fig. 1 as a function of temperature and the molality of aqueous H2. The isopleth labeled S0.1BM represents equilibrium for reaction 3, where the mole fraction XFe = Fe/(Mg + Fe) of Fe(II) in serpentine is 0.1 and XFe in the brucite is in equilibrium with the serpentinite (see Appendix). The S0.1BM isopleth represents a “high-Fe(II)” system. For comparison, the isopleth-labeled S0.025BM represents equilibrium with “low-Fe(II)” substitution in serpentine and brucite. Note the differences of aqueous hydrogen concentrations required by the mineral buffers QFM and SBM and the sensitivity of H2(aq) concentrations of SBM equilibria to Fe(II) substitution. The curve labeled H2 Saturation in Fig. 1 denotes saturation of the fluid with H2(gas) at 500 bars total fluid pressure (see Appendix); mineral reactions to the right of this saturation curve are metastable. If a more reduced phase is initially present (for example, metallic Fe), it is oxidized, producing hydrogen gas. Gas bubbles may build up in the fluid because the equilibrium does not depend on the amount of bubbles present. Reactions to the left of the solubility curve cannot saturate the fluid with H2(gas) at a total fluid pressure of 500 bars. Finally, the curve S0.1BM in Fig. 1 represents the initial stage of oxidation in the early Earth and that of modern alpine peridotite. The atomic fraction XFe is 0.1 in serpentine and ~0.18 in brucite (S0.1B0.18M), in total XFe being approximately the same as in primary ultramafic rocks, since the mode of serpentine is much larger than that of brucite.

S0.1BM is an effective buffer in serpentinites. The addition of hydrogen to a previously closed system equilibrium will result in reduction of magnetite, which consumes some of the added hydrogen and some of the magnetite. The new equilibrium has increased hydrogen pressure and increased XFe in serpentine and brucite.

Fluids buffered by the assemblage S0.1BM (Fig. 1) are supersaturated with respect to H2(gas) at temperatures more than ~160°C. The buffer assemblage S0.025BM (Fig. 1) represents an extensively oxidized serpentine, where most of the Fe is in magnetite and XFe = 0.025 in serpentine and XFe = ~0.05 in brucite (S0.025B0.05M). Fluids in equilibrium with serpentine and brucite of these compositions are undersaturated with respect to H2(gas) at all temperatures shown in Fig. 1. The oxidation reaction still may proceed if the H2 concentration is undersaturated with H2(gas). We expect this situation when fluid vigorously circulates through the rock, removing dissolved hydrogen. The hydrogen-enriched fluid then vents to the surface and is replaced at depth with hydrogen-poor fluid from the ocean.

Fig. 2 illustrates the SBM buffer equilibrium as a function of temperature and H2(aq) concentrations for serpentinite compositions ranging from XFe 0.025 to 0.1. The curve labeled 500 bars denotes fluid saturation with respect to H2(gas) and the curves

![Figure 1](https://www.pnas.org/cgi/doi/10.1073/pnas.0405289101)  
**Fig. 1.** Molality of H2(aq) for SBM buffer (reaction 3) as a function of temperature at 500 bars total fluid pressure. Isotherm S0.1BM represents high-Fe serpentinite, with XFe = 0.1 in crysotile and XFe = 0.07 in brucite, and S0.025BM represents low-Fe serpentinite, with XFe = 0.025 in crysotile and 0.0175 in brucite. QFM buffer and hydrogen solubility bars are shown.

![Figure 2](https://www.pnas.org/cgi/doi/10.1073/pnas.0405289101)  
**Fig. 2.** Phase diagram as in Fig. 1 showing isopleths of SBM buffer equilibria for serpentinites with XFe in crysotile ranging from 0.1 to 0.025. H2 partial pressure contours are thick gray lines.
The stability field of the Ni-Fe alloy awaruite in the presence of serpentine, brucite, and magnetite is shown in Fig. 3, which illustrates the two-phase field of Ni-rich solid solutions plus awaruite (shaded area), and the region of awaruite stability (see Appendix). Also shown are isopleths (solid curves) of X_{Fe} in serpentinite for the assemblage serpentinite, brucite, magnetite, and awaruite as represented by equilibrium for reaction 5a, and isopleths (shaded curves) of partial pressures of H_{2(gas)} consistent with reactions 5b and 5c in Appendix. The curve labeled 500 bars denotes H_{2(gas)} saturation in the fluid, and the vertical dashed line denotes the composition of stoichiometric awaruite (FeNi_3). Fig. 3 is compatible with previous thermodynamic relations and field observations (3,28). That is, late magnetite-bearing assemblages replace earlier awaruite-bearing ones as the rock becomes increasing oxidized (3). Note that there is a minimum X_{Fe} in serpentinite for awaruite to be stable, which decreases with increasing temperature, which is a weak function of X_{Fe} in awaruite. The partial pressure of H_{2} needed to form awaruite increases with temperature. For example, at 200°C, awaruite of composition FeNi_3 cannot form unless the H_{2} partial pressure is in excess of 50 bars H_{2} is needed to form awaruite.

**Appendix**

“Ni” has been misspelled throughout the text. The correct spelling is “Ni”.

**Moon-Forming Impact and Ferric Iron in the Earth’s Mantle**

The Earth’s Moon formed when a Mars-sized object collided with the Venus-sized Proto-Earth. As summarized by Sleep et al. (44), the impact left the Earth surrounded by a rock-vapor atmosphere, which condensed in a few thousand years. The Earth’s water and CO_{2} formed a dense atmosphere heated from below. Internal heating became an insignificant effect on climate after ≈2 million years. By that time, liquid oceans condensed beneath a dense CO_{2} atmosphere, and the surface temperature was ≈200°C. The Earth’s gravity was able to hold CO_{2}, water,
and significant H₂. In contrast, the Moon did not retain these gases and lacks potentially habitable ground water.

Thereafter, the capacity of the Earth’s surface rocks to hold CO₂ in carbonates controlled the CO₂ pressure and hence (along with methane) climate (44–46). Rocks of the lithocap of this magma ocean were, however, insufficient to contain the available CO₂. Rather, the Earth’s interior sequestered CO₂ when the surface layer foundered, a process analogous to modern subduction of carbonates in altered oceanic basalts. This storage required that the foundered crust did not immediately degas its CO₂. Instead much of the CO₂ mixed into the deep interior (47). This situation prevails now in that only a modest fraction of subducted CO₂ immediately returns to the surface at arc volcanoes.

Our concern here is the effect of the aftermath of the Moon-forming impact on oxidation state of the Earth’s mantle. The Earth’s mantle contains a significant amount of ferric iron that is out of equilibrium with metallic iron in accreting bodies, which formed the Earth’s core (e.g., ref. 48). Ferric iron probably formed after the bulk of Earth’s metallic iron was sequestered in the core, at least partially after the Moon-forming impact. In addition, a “veneer” component of platinum group elements exists in the Earth’s mantle. This material formed along with the oxidation of metallic iron, much from the core of the impacting body. Water and preexisting ferric iron in the Proto-Earth’s mantle are the probable oxidants.

Mass balance indicates that these processes produced massive amounts of hydrogen gas (e.g., ref. 48). The ferric iron requires reduction of 4.5 × 10²² mol of water (60% of the mass of the current hydrosphere) to H₂. The platinum-group elements require 7.5 × 10²² mol of water (about the mass of the current hydrosphere). The hydrogen gas from each source (if all in the air at the same time) would have produced equivalent pressures of 20 and 30 bars, respectively for a total of 50 bars. That is, an equivalent pressure of 50 bars is a reasonable upper limit for the amount of H₂ in the aftermath of the Moon-forming impact.

The relative timing of the escape of atmospheric H₂ to space and the demise of CO₂ by forming carbonates is unknown. In addition, much of the hydrogen production (partially that from the oxidation of metallic iron) occurred at magmatic temperatures inside the Earth or when the Earth’s surface was still too hot for liquid water to form. Our calculations are inapplicable for a massive CO₂ atmosphere as carbon species are not included. However, we can represent the behavior of a element massive hydrogen atmosphere above the liquid-water ocean.

We consider the behavior of serpentine with the Fe²⁺/Mg ratio of the present mantle, by using Fig. 2. If no redox reactions occur this rock forms serpentine with XFe in serpentine of ∼0.1, which produces hydrogen at 160°C at all reasonable H₂ atmospheric partial pressures. At 20°C, this serpentine is in equilibrium with 30 bars of H₂ and produces H₂ at lower H₂ pressures. Even in the extreme case of 50 bars of surface H₂, oxidation of serpentine proceeds during hydrothermal circulation. For example, fluid saturated with 50 bars of H₂ descends from recharge point P (Fig. 4) into the subsurface as a closed system to point S. It then heats up and reaches equilibrium with moderately oxidized serpentine at point A. The water then ascends back to the surface, forming bubbles along the way on the path B–C–R. More than 90% of the H₂ present at point A eventually forms bubbles and escapes to the surface.

Thus significant oxidation of the mantle could have occurred at hydrothermal conditions on the early Earth or on other bodies where ultramafic rocks covered the surface. Conversely, the process on Earth was inefficient enough that most of the mantle’s iron is still ferrous, not 2/3 ferric, as in magnetite. Also, we still have an ocean. There is no obvious hydrothermal buffer that would yield the current mantle composition from a long-lived equilibrium process.

Conclusions About the Later History of the Earth

Ultramafic rocks are uncommon on the surface of the modern Earth. This situation prevailed soon after the Moon-forming impact when the Earth’s interior cooled to the point where the most common igneous rock was basalt, formed by partial melting of the mostly solid mantle. The dominant buffer since that time has been approximately QFM (reaction 2). Although uncommon, serpentinitized ultramafic rocks are important biotic environments on the modern Earth. They are also likely to have been a prebiotic environment on any silicate planet. These situations are likely to resemble the modern Earth, where both low- and high-temperature hydrothermal circulation occurs.

Figs. 2 and 3 suffice to delineate the environments where H₂ may be generated, and where the minerals magnetite and FeNi₃ may form. H₂ forms in molar to millimolar quantities at all temperatures even after much of the ferric iron in serpentine is oxidized. This finding is compatible with the observation of hydrogen in warm (40–70°C) oceanic hydrothermal vents (17), hot hydrothermal vents (16), 2-km deep waters within the Canadian Shield (18), and even natural flames above seeps on land (4). Magnetite is a stable phase in these environments. In contrast, FeNi₃ forms only at high XFe in serpentine, and hence high H₂ pressure. It is not expected to form at shallow depths or once the serpentine is extensively oxidized. The presence of this mineral in surface samples and placers, however, indicates that it oxidizes quite slowly at modern surface temperatures.

Appendix: Thermodynamic Calculations

We compute the phase relations depicted in Figs. 1–4 for equilibrium of reactions 1, 3, and 5 by using equilibrium constants derived from SUPCRT92 (49). Standard state conventions are unit activity at any temperature and pressure for stoichiometric minerals and H₂O, unit activity of a hypothetical one molal solution at infinite dilution for aqueous species, and unit activity of pure gases at any temperature and one bar.

We assume unit activities of quartz, magnetite, and water and compute activities of other solid phases, assuming ideal site-mixing solid solutions. The activity of fayalite is equal to 0.0064, which corresponds to the mole fraction of fayalite in olivine of mantle composition (0.08). We considered several compositions of serpentinite (Fe-Mg chrysotile) and Fe-Mg brucite; activities of mineral components chrysotile, Fe-chrysotile, Mg-brucite, and Fe-brucite (i.e., 3Fe(OH)₂ = XFe,chrysotile and 4Fe(OH)₂ = XFe,brucite, and vice versa for the Mg-endmembers) are computed consistent with the exchange reaction

$$3\text{Fe(OH)}_2 + \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \leftrightarrow \text{Fe}_2\text{SiO}_3(\text{OH})_4 + 3\text{Mg(OH)}_2$$

using a distribution coefficient of Kd = 0.5 reported by Evans and Trommsdorff (50), which is based on coexisting compositions of lizardite and brucite from serpentinites reported in the literature. The ratio of the mole fraction of Fe(II) in brucite to serpentine solid solutions is ≈2, which we assume to be independent of temperature and pressure at <300°C and 500 bars.

We compute the activity of Fe in FeNi₃ (awaruite) considering the stability of completely disordered FeNi₃ phase that corresponds to Fe metal with the activity of Fe equal to 0.25. We then compute the activity of ordered awaruite by noting that the entropy difference between the two ordering states is equal to the configurational entropy $S_{\text{conf}}$ ($S_{\text{conf}}$ is zero in the ordered phase and equal to 1.12 cal·mol⁻¹·K⁻¹ per atom in the formula unit for the disordered phase) and that the order/disorder transition temperature is equal to 500°C (28). Finally, the activity of FeFe₃O₄ as a function of temperature was calculated by using Eq3 (51) and the b-dot extended Debye-Hückel equation for a model sea water solution.
Thermodynamic data for H$_2$O, H$_2$(aq), H$_2$(g), and minerals (except metallic iron and Fe-brucite) are from the slop98.dat database (ref. 49 and http://geopig.asu.edu/supert92.data/slop98.dat). As a first-order approximation we use the thermodynamic data for greenalite reported in the slop98 database for Fe-chrysotile. We used thermodynamic data for metallic iron from Robie and Hemingway (52). Gibbs energy of formation and enthalpy of formation for Fe-brucite from Wagman et al. (53), which is consistent with Weast (54). Heat capacity of Fe-brucite is estimated by assuming zero heat capacity for the reaction

$$2 \text{Fe(OH)}_2 + \text{Mg}_2\text{SiO}_4 \rightarrow 2 \text{Mg(OH)}_2 + 2 \text{Fe}_2\text{SiO}_4 \quad [S2]$$

using heat capacity data from Helgeson et al. (55). Molar volume of Fe-brucite is based on density measurements of Fe(OH)$_2$ by Kozlov and Levshov (56).

Solubility curves of H$_2$g in water in Figs. 1–4 denote equilibrium for

$$\text{H}_2\text{g} \leftrightarrow \text{H}_2\text{aq} \quad [S3]$$

as a function of temperature at 30, 500 bars, etc. by using SUPCRT92 (49). We assume that H$_2$ behaves as an ideal gas under the pressure and temperature conditions considered. H$_2$ solubility curves represent the solubility of a pure H$_2$ gas.

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