Decreasing extents of Archean serpentinization contributed to the rise of an oxidized atmosphere

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At present, molecular hydrogen (H₂) produced through Fe(II) oxidation during serpentinization of ultramafic rocks represents a small fraction of the global sink for O₂ due to limited exposures of ultramafic rocks. In contrast, ultramafic rocks such as komatiites were much more common in the Early Earth and H₂ production via serpentinization was a likely factor in maintaining an O₂-free atmosphere throughout most of the Archean. Using thermodynamic simulations, this work quantifies the global O₂ consumption attributed to serpentinization during the past 3.5 billion years. Results show that H₂ generation is strongly dependent on rock compositions where serpentinization of more magnesian lithologies generated substantially higher amounts of H₂. Consumption of >2 Tmole O₂ yr⁻¹ via low-temperature serpentinization of Archean continents and seafloor is possible. This O₂ sink diminished greatly towards the end of the Archean as ultramafic rocks became less common and helped set the stage for the Great Oxidation Event.
The Great Oxidation Event (GOE) after the end of the Archean marks the initial oxygenation of the Earth’s surface through a dramatic increase in the atmospheric O2 levels from minor amounts (<10^-3 of present atmospheric levels or PAL) to much higher values (10^-4–10^-5 PAL) around 2.4 to 2.1 billion years (Ga) ago2,3. While the production of O2 through oxygenic photosynthesis evolved much earlier4 and contributed to the localized accumulation of O2 well before the GOE5–11, it was only after the end of the Archean that O2 began to accumulate to significant levels in the atmosphere. It is proposed that the period preceding the GOE was characterized by the dominance of geochemical and biological processes that consume O2 (sinks) over its production (sources). As with an increase in O2 sources, decreasing magnitudes of O2 sinks in the form of reduced volatiles (e.g., H2, CH4) and solids (e.g., Fe(II)-bearing minerals) allow accumulation of O2 in the atmosphere towards the end of the Archean. Decreases in reduced volatiles could have been brought about by the escape of H2 from the atmosphere12–15 and a transition to outgassing of more oxidized volatiles from volcanism16,17. Alternatively, recent works have tied the rise of O2 to secular changes in the composition of the Earth’s continental crust18,21. The Earth’s crust has a vast potential to consume O2 via the oxidation of ferrous iron in primary minerals into ferric iron in minerals that formed during rock alteration and weathering, as depicted by the reaction

$$4\text{Fe(II)}\text{O}_3(\text{primary minerals}) + O_2 \rightarrow 2\text{Fe(III)}\text{O}_3(\text{secondary minerals}) + H_2.$$  

(1)

The transition from a continental crust composed dominantly of Fe-rich mafic rocks to one that is composed mostly of Fe-poor felsic rocks during the Archean resulted in a decrease in the reductive efficiency of the Earth’s crust that could have facilitated the initial oxygenation of Earth’s surface21. The absence of O2 does not impede the oxidation of rocks. At great extents of water-rock interactions such as those occurring in deeper aquifers where O2 and other dissolved oxidants are exhausted, ferrous iron in the protolith is oxidized to ferric iron in the alteration assemblages and, in turn, water is reduced into H2 as depicted by the reaction

$$\text{Fe(II)}\text{O}_3(\text{primary minerals}) + H_2\text{O} \rightarrow \text{Fe(III)}\text{O}_3(\text{secondary minerals}) + H_2,$$

(2)

supplying an additional sink for O2 through

$$O_2 + 2H_2 \rightarrow 2H_2O.$$  

(3)

The amount of H2 that can be generated through reaction (2) is far less dependent on the abundance of Fe present in the rock than the bulk composition23. An extreme example is the hydrous alteration of ultramafic rocks, which is known as serpentinization because most of the original minerals are replaced by serpentine. Serpentinization produces some of the most H2-rich rocks such as komatiites were much more concentrated than most basalt-hosted hydrothermal fluids37. This contrast is particularly distinct in lower temperature environments such as those occurring in continents. Ultramafic-hosted hyperalkaline groundwater can attain >1 molar H2 (e.g., Oman ophiolite38) while most basalt-hosted fluids rarely exceed 0.01 molar H2 (e.g., Columbia river basalt39). The greater potential for ultramafic rocks to generate H2 during alteration is attributed to their bulk compositions33. Previous thermodynamic simulations have related the compositions of a limited number of reacting rocks, mostly peridotites, and basalts, with the redox potentials of resulting hydrothermal fluid36,40,41. Using the expansive GEOROC database, thousands of simulations conducted in this work provide an inclusive assessment of the H2-generation potentials of rocks with compositions ranging from ultramafic to mafic. Equilibrium simulations yield aqueous compositions that are consistent with those measured from end-member low-temperature hyperalkaline fluids sampled from ultramafic bodies in ophiolites42, that are modern analogs of Archean ultramafic-hosted fluids. The approach to equilibrium even under ambient conditions is possible as the timescales required to attain reduced and hyperalkaline compositions may involve several thousands of years43. Results of simulations depicted in Fig. 1a, b, and Source Data S2 show the calculated amounts of H2 generated during.

**Results and Discussions**

**Serpentinization** is the key to significant H2 production. Although H2 production is tied to the oxidation of ferrous iron in rocks (reaction 2), the hydrous alteration of igneous rocks with similar ferrous iron content does not always yield similar amounts of H2. As an example, basaltic and ultramafic rocks have similar ferrous iron contents (6–14 weight percent, wt%, FeO) and, seemingly, the hydrous alteration of both types of rocks should generate similar amounts of H2 via reaction (2). However, fluids that are most enriched in H2, such as those venting at the Lost City and Rainbow hydrothermal fields34–36, are commonly associated with ultramafic-hosted environments with some inputs from intermingling mafic rocks35. Ultramafic-hosted hydrothermal fluids can attain >10 molar H2 that is several times more concentrated than most basalt-hosted hydrothermal fluid37. This contrast is particularly distinct in lower temperature environments such as those occurring in continents. Ultramafic-hosted hyperalkaline groundwater can attain >1 molar H2 (e.g., Oman ophiolite38) while most basalt-hosted fluids rarely exceed 0.01 molar H2 (e.g., Columbia river basalt39). The greater potential for ultramafic rocks to generate H2 during alteration is attributed to their bulk compositions33. Previous thermodynamic simulations have related the compositions of a limited number of reacting rocks, mostly peridotites, and basalts, with the redox potentials of resulting hydrothermal fluid36,40,41. Using the expansive GEOROC database, thousands of simulations conducted in this work provide an inclusive assessment of the H2-generation potentials of rocks with compositions ranging from ultramafic to mafic. Equilibrium simulations yield aqueous compositions that are consistent with those measured from end-member low-temperature hyperalkaline fluids sampled from ultramafic bodies in ophiolites42, that are modern analogs of Archean ultramafic-hosted fluids. The approach to equilibrium even under ambient conditions is possible as the timescales required to attain reduced and hyperalkaline compositions may involve several thousands of years43.
low-temperature (25 °C) alteration of Fe-bearing igneous rock types at a water-to-rock ratio of 1 (i.e., alteration of 1 kg of rock in 1 kg of water). Predictions are summarized for hydrous alteration of 9,414 Fe-bearing igneous rocks from the GEOROC database with compositions ranging from those that are ultramafic, i.e., rocks that have high MgO content such as peridotites and komatiites at the right side of Fig. 1a, b, to those relatively depleted in MgO (left side of Fig. 1a, b) such as picrites and basalts. Further details on the relationship between the composition of reacting rocks and their H2-generation potentials are shown in Fig. S1. All of these rocks have similar FeO contents (6–14 wt%, Fig. S1a). Basalts and picrites originate from smaller extents of mantle melting while komatiites were generated by larger extents of melting that occurs at higher temperatures, which usually resulted in rocks with higher Mg and lower Si (Fig. S1b), Ca (Fig. S1c), and Al (Fig. S1d) contents44. Most of the peridotites exposed in the seafloor and in the continents are uplifted harzburgite, which are the residual rocks that remained after melting of the mantle and hence are characterized by high Mg content and low Si and Al values. As shown in Fig. 1a, there is a marked decrease in the H2-generation potentials between rocks with MgO content lower and higher than 35 wt%, even among rocks without much difference in their FeO abundances. Model results also depict a gradual decrease in H2-generation potentials as the reacting compositions become less Mg-rich (towards 20 wt% MgO), as shown in Fig. 1b. These results corroborate natural observations that ultramafic-hosted fluids are more enriched in H2 than those hosted in basalts. The generation of highly reduced fluids during alteration of Mg-rich rocks is also supported by the presence of accessory minerals only stable in reduced conditions such as NiFe alloys (awaruite) found in some altered ultramafic rocks45.

The key to the transitions in the H2-generation potentials during rock alteration documented in Fig. 1a, b is the formation of serpentine. Mg-rich rocks favor the formation of serpentine during rock alteration, as shown in Fig. 1c, which depicts the overall abundances of secondary minerals (in mole fraction) calculated to form. In the models, initial stages of serpentinization, characterized by high water-to-rock ratios, typically leads to the formation of Fe-bearing serpentine minerals that host ferric iron: hisingerite [(FeIII)2Si2O5(OH)4] and cronstedtite [(FeIII2(FeIII)(FeIII)Si)O5(OH)4]. In contrast, serpentinization at rock-dominated conditions favors the formation of greenalite [(Fe(II)2)Si2O5(OH)4], which is a Fe-bearing endmember component of serpentine that only hosts ferrous iron. Simulations incorporate an ideal-site solid solution model that involves the above Fe end-members and Mg end-member serpentine (chrysotile, Mg3Si2O5(OH)4). Model results are consistent with analysis of natural serpentinites where higher Fe(III)/ΣFe values were measured in serpentine thought to form at higher water-to-rock ratios than those that precipitated at rock-dominated conditions46. As shown in Fig. 1d, which depicts the distribution of Fe in the secondary assemblages predicted to form at a low water-to-rock ratio of 1, the Fe end-member serpentine favored to form is greenalite followed by cronstedtite. The amount of hisingerite that formed at the low water-to-rock conditions simulated in this work is insignificant and plots below the range shown in Fig. 1d. Aside from the water-to-rock ratio, the
composition of reacting rocks also controls the distribution of Fe in the precipitating serpentine. Crocsedite is most favored to form during alteration of rocks with high MgO content (>40 wt%, see Fig. 1d). As the MgO content of the reacting rock decreases from 40 to 20 wt%, the formation of crocsedite is drastically reduced. In contrast, the formation of greenalite generally remains constant and only decreases (along with serpentine) when the MgO content of the reacting rocks is between 20 and 25 wt%. The decreasing potential to form crocsedite relative to greenalite results from the decreasing MgO and increasing SiO₂ contents of the rocks as crocsedite has a lower Si content (1 mole per formula unit) than greenalite (2 moles per formula unit)⁴⁸. The decrease in the crocsedite content in the precipitating serpentine with decreasing MgO means that less Fe will be oxidized resulting in less H₂ production, as shown in Fig. 1b, d.

Another Fe(III)-bearing phase, andradite garnet [Ca₃(Fe²⁺⁴⁺)₃-Si₃O₁₂], is also favored to form during alteration of Mg-rich rocks and provides additional pathways for H₂ formation⁴⁸. Not all Mg-rich rocks favor the formation of garnet, which also depends on their CaO content, resulting in highly variable H₂-generations potentials for rocks with MgO contents between 30 and 40 wt%. In contrast, rocks that are poorer in Mg (MgO ≤20%) do not favor serpentine and garnet formation during rock alteration. Instead, alteration of these Mg-poor but more Si- and Al-rich rocks stabilizes minerals such as chlorite, talc, and clay minerals (Fig. 1c, d). Most of the iron mobilized from the primary minerals is incorporated into these secondary minerals without much oxidation because these minerals preferentially accommodate ferrous iron into their crystal structures. Consequently, less H₂ is generated as the iron oxidation process depicted by reaction (2) occurs at lesser extents compared to conditions where serpentine and garnet form extensively. Overall, results show that non-redox-sensitive components of rocks (e.g., Mg, Si, Al, Ca) determine the distribution and fate of Fe during secondary mineralization, and therefore the redox processes that generate reduced volatiles during fluid-rock interactions. Further discussions on how various types of mineralization control H₂ production can be found in the supplementary document and are illustrated in Fig. S1.

A statistical summary of the H₂-generation potentials of rocks with MgO content <10, >45, and those ranging from 10–45 wt%, at intervals of 5 wt%, subjected to various water-to-rock ratios (100, 10, 1, 0.2) is shown in Fig. 2. Full data can be found in Source Data S2. The distribution of H₂-generation potentials of rocks within a compositional group is further shown in Fig. S2. Rocks with MgO content >35 wt% have the potential to generate the most H₂ but of highly varying amounts owing to their differing capacities to stabilize various Fe(III)-bearing phases during hydrous alteration. Rocks with similar MgO content can have variable SiO₂ contents, which lead to varying potentials to precipitate Fe-bearing secondary phases (see Fig. S1b). Those with higher SiO₂ contents favor formation of greenalite relative to crocsedite. Hence, less H₂ can be generated as Fe(II) from primary minerals is mobilized into greenalite unoxidized⁴⁷,⁴⁹. Rocks with MgO content between 20–35 wt% have potentials to generate moderate amounts of H₂ only at higher water-to-rock ratios. Rocks with MgO content <20 wt% do not yield high H₂ at any water-to-rock ratios simulated in this work.

Decreasing O₂ sink via continental serpentinization during the past 3.5 Ga. In the modern Earth, ultramafic rocks comprise only ~0.2% of the continental surface⁵⁰, mostly as uplifted harzburgites and other peridotitic rocks in ophiolites and orogenic massifs. Volcanism of ultramafic lavas is rare throughout most of the Proterozoic but is known to have been more prevalent during the Archean⁵¹. In the Archean, ultramafic rocks such as komatiites are estimated to have comprised a significant component of the continental crust (~10–20% during the early Archean⁵²,⁵³). This elicits scenarios of substantial fluxes of serpentinization-derived H₂ that can maintain an atmosphere with elevated H₂ levels during the Archean⁵⁴,⁵⁵.

The global O₂-consumption potentials via H₂ production during low-temperature serpentinization during the past 3.5 Ga were calculated using Eqs. (4) and (5) (see methods) following estimates of H₂ generation (x₃OH, Tmole H₂ km⁻³) shown in Fig. 1 and summarized in Fig. 2. In these calculations, we assume a serpentinization rate (rFe) of 10⁻⁶ km yr⁻¹, a maximum value for low-temperature ophiolitic aquifers with low reactive surface area⁵⁵. For the extents of ultramafic rocks in continents (aFe, km²), we used the average distribution and continental presence calculated by Greber et al.⁵³ and Dhuime et al.⁵⁶, respectively. Tang et al.⁵² disagree with Greber et al.⁵³ on the bulk composition and timing of the transition from mafic to felsic crust during the Archean. However, both studies are consistent in their estimates of past ultramafic distribution, and both estimate the significant presence of komatiites in continents during the early Archean (10–20%) and a greatly diminished distribution towards the end of the Archean. Multiplying all the above values together yields the annual global H₂ generation (Tmole H₂ yr⁻¹) and consequently the annual global O₂ consumption (Tmole O₂ yr⁻¹). Results of calculations are depicted in Fig. 3, and Source Data S3, which shows the O₂-consumption potentials of H₂ produced during alteration of rocks with given ranges of MgO content. We only show results for these relatively Mg-rich rocks as the continental compositional estimates by Greber et al.⁵³ pertain to komatiites and perhaps other ultramafic bodies, which we used as a proxy for Mg-rich rocks. Analyses of remnant komatiites in cratonic belts yield MgO values ranging from ~18 wt% in evolved spinifex-textured lavas to ~45 wt% in olivine-rich cumulates⁵¹. Binning the wide range in the MgO content of rocks used in our calculations to every 5 wt% accounts for uncertainties in the compositions of komatiites when they are first exposed during the Archean. While Greber et al.⁵³ and Tang et al.⁵² also estimated the amount of basalts present in continents during the past 3.5 Ga, results of alteration simulations for rocks with MgO content <20 wt %, encompassing all basalts and most picrites, yield negligible potentials to generate H₂ and consume O₂ (Figs. 1 and 2), and thus are not included.

As shown in Fig. 3, the global O₂ consumption arising from the alteration of various Fe-bearing rocks with MgO content >20% greatly decreased at ~2.5 Ga ago, and this decrease is directly attributed to the decrease in the extent of exposures of Mg-rich rocks in the continents. A marked decrease in komatiite distribution from ~7% to ~1% of continents from 3.0 to 2.5 Ga ago⁵³ caused a sevenfold decrease in the O₂-consumption potentials during this time interval and contributed to the rise of O₂ by the end of the Archean. This monotonic decrease may not be characteristic of the late Archean if the occurrences of several 2.7 Ga greenstone belts⁵⁸,⁵¹ are a consequence of increased komatiite volcanism at this time period and not solely a result of exceptional preservation. Nevertheless, komatiite occurrence is significantly diminished by the end of the Archean and thus would not change model outcomes depicting the Archean-Proterozoic transition shown in Fig. 3. Note that results shown in Fig. 3 are solely dependent on the ultramafic distribution in continents (aFe component of Eq. 4) as the rate (rFe), and H₂-generations potentials (x₃OH) are assumed to be constant across time for each investigated Fe-bearing igneous rock. The alteration rate, H₂-generations potentials, and therefore the O₂-consumption potentials could have larger values for the
Archean due to the warmer conditions and more acidic or reactive starting fluids derived from an atmosphere with higher $pC02$, Thus, results of our calculations should be considered conservative and decreases in the O2-consumption values during the past 3.5 Ga could be even more dramatic than those depicted in Fig. 3. Simulation results also show that alteration of rocks with MgO content $>$35 wt% has the greatest potential to consume O2 (Fig. 3a, b). Median potentials for rocks with MgO content ranging from 20 to 35 wt% are far lower (Fig. 3d–f). Those with MgO content between 30 and 35 wt% mostly have similar potentials compared to those with less Mg but a few rocks within this compositional range have similar potentials to consume O2 as those with higher MgO content (see upper thinner lines in Fig. 3c).

From 1.0 Ga ago to the present, ultramafic rocks are estimated by Greber et al. to comprise at most 0.2% of the continents, consistent with abundances determined by analysis of global present-day geological maps. Median values yielded by models show global H2 production ranging from 0.08 to 0.18 Tmole yr$^{-1}$ and correspondingly, O2 consumption ranging from 0.04 to 0.09 Tmole yr$^{-1}$ for the past 1.0 Ga (Fig. 3 and Source Data S3). These values are consistent with other estimates of modern-day outgassing rates in continental serpentinitization environments (0.02–0.18 Tmole H2 yr$^{-1}$). Model results are also within range, but on the lower bound, of estimates of global H2 production associated with serpentinitization of oceanic ultramafic rocks (0.17–0.70 Tmole H2 yr$^{-1}$). These values are insignificant relative to the overall modern global O2 sources and sinks (>15 Tmole O2 yr$^{-1}$ (refs. 16,31,32)). The magnitude of net O2 production on the early Earth remains unconstrained though recent analysis of the carbon isotopic record and extent of organic carbon burial show that Archean primary productivity may have been comparable to modern values. If Archean net O2 production was similar to that of the present (>15 Tmole O2 yr$^{-1}$), global O2 consumption via serpentinitization of Archean continents alone would have been a major sink for oxygen given that consumption of >2 Tmole O2 yr$^{-1}$ (~13% of sources) and, in some extreme cases, >4 Tmole O2 yr$^{-1}$ (~27%) is possible between 3.5 and 3.0 Ga ago if the reacting rocks are Mg-rich (MgO >35 wt%, Fig. 3). Consequences of variable continental extents as well as additional contributions from seafloor serpentinitization are discussed below.

**Effect of variable extent of ultramafic exposure in continents.** The calculations summarized above use estimates of past continental mass from Dhuime et al., which predicts that the amounts of continents throughout the Archean are intermediate to more extreme values estimated by earlier studies. To further explore the consequences of these variations, we calculated the potential for consuming different levels of O2 via serpentinitization given variable extents in the exposures of Mg-rich rocks in continents. Outcomes of calculations are shown in Fig. 4a which depicts the proportion of simulations that result in the consumption of >2 Tmole O2 yr$^{-1}$ given the abundance of Mg-rich rocks (in km$^2$) and an alteration rate of 10$^{-6}$ km yr$^{-1}$.

Given the range in the exposure of Mg-rich rocks present at the mid-Archean (3.0 Ga, light grey region in Fig. 4a), up to 100, 90, and 46% of models simulating rocks with MgO >45, 40–45, and 35–40 wt%, respectively, result in the consumption of >2 Tmole O2 yr$^{-1}$. Only up to 17% of the models involving rocks with MgO content between 30–35 wt% result in a similar amount of O2 consumption. Consumption of >2 Tmole O2 yr$^{-1}$ is still possible if most Archean komatiites have MgO content <30 wt% but are less likely as only ~5% of simulations result in H2 production that can offset this rate of net O2 production. The above values depict results of models assuming maximum exposure using the continental growth model of Armstrong who argues for the present-day extent of continents throughout most of the Archean. Using the recent model of Dhuime et al. yields lower but still significant values. In contrast, smaller masses of continents proposed by other works would yield lower likelihoods of H2 generation from continental serpentinitization during the Archean.
These results imply that for continental serpentinization to be a significant sink for O$_2$ throughout most of the Archean, continental presence must be significant (i.e., at least 60% of the present-day value at 3.0 Ga)$^{56}$ and occurrence of Mg-rich (MgO \(>35 \text{ wt\%}\)) rocks must be extensive. Thus, the majority of H$_2$ production occurs in Mg-rich ultramafic bodies such as peridotite massifs or komatiite flows with significant olivine cumulates$^{46}$. Cumulates are often associated with deeper portions of komatiite flows but fluids are known to infiltrate and interact with deep-seated rocks$^{58}$. Furthermore, deep-seated rocks can readily react with groundwater during and after continental emplacement like in modern ophiolitic bodies where peridotites are exposed to surficial conditions and enable the generation of most present-day H$_2$-rich, hyperalkaline springs. Results of additional calculations assuming slower rates (10\(^{-6.5}\) km yr\(^{-1}\)) are depicted in Fig. S3, which shows that a much smaller proportion of simulations result in significant H$_2$ production and O$_2$ consumption. Therefore, for serpentinization to be a significant source of reduced gas throughout most of the Archean, the rate of serpentinization should be at least 10\(^{-6}\) km yr\(^{-1}\). While this represents an upper limit on rates perceived to occur in modern low-temperature ultramafic aquifers$^{55}$, such a rate could have been normal under warmer and more dynamic Archean surface conditions.

Simulations by Kadoya et al.$^{20}$ show that in addition to volcanic volatiles, additional flux of reduced gas generated via serpentinization amounting to consumption of at most 2 Tmole O$_2$ yr\(^{-1}\) would result in oxidation of the atmosphere by 2.4 Ga ago. Larger fluxes from serpentinization such as 3 Tmole O$_2$ yr\(^{-1}\) could have delayed the GOE to 1.9 Ga ago$^{20}$. Assuming the amount of Mg-rich rocks present in continents \(\sim 3.0\) Ga ago, up to 35% or 80% of models result in consumption of >3 Tmole O$_2$ yr\(^{-1}\) via alteration of rocks that have MgO content 35–40 wt% or >40 wt%, respectively (Fig. 4b).

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**Fig. 3 O$_2$ consumption via continental serpentinization during the past 3.5 Ga.** Global consumption rate for O$_2$ (Tmole yr\(^{-1}\)) was calculated assuming an alteration rate of 10\(^{-6}\) km yr\(^{-1}\) for rocks belonging to various compositional groups: a MgO >45, b 40–45, c 35–40, d 30–35, e 25–30, f 20–25 wt%. Extents of continental mass and exposure of komatiites are from Dhuime et al.$^{56}$ and Greber et al.$^{53}$, respectively. Bold curve depsects median values. The lower and upper dotted curves represent 25th and 75th percentiles of model results, respectively, while the lower and upper thinner curves depict 5th and 95th percentiles of model results, respectively.
of models results in scenarios that can offset the same amount of O2 during alteration of rocks with lower MgO contents. Thus, if the estimated amount of Mg-rich ultramafic rocks (MgO >35 wt %) present in continents at ∼3.0 Ga remained by ∼2.4 Ga ago, then the abundance of reduced volatiles released from both serpentinization and volcanic outgassing would have delayed the GOE to a much later period. However, the extent to which ultramafic rocks were present in continents declined significantly from 3.0 to 2.5 Ga ago, as shown by the dark grey shaded regions in both plots in Fig. 4 where the amount of ultramafic rocks present in continents ∼2.5 Ga ago should be not more than 3 million km². Consequently, the decreased presence of ultramafic rocks in continents would have resulted in lower potentials for an O2 sink. As shown in Fig. 4, close to 0% of models encompassing all compositional ranges explored by this work result in consumption of >2 Tmole O2 yr⁻¹ by 2.5 Ga ago, ensuring the accumulation of O2 in the atmosphere and setting the stage for the Great Oxidation Event.

Contributions from seafloor serpentinization. In addition to H2 produced by serpentinization in continents, significant amounts of H2 can be generated through water-rock interactions in the subseafloor. Modern seafloor serpentinization contributes as much, perhaps more, H2 than that generated via continental serpentinization58. While the extent of ultramafic exposures in the seafloor during the Archean is poorly known, the importance of additional H2 generated from seafloor processes warrants preliminary discussion. A hotter mantle during the Archean would generate Mg-rich oceanic crust that could have favored H2 production. However, a hotter ambient mantle that yields erupting lavas with MgO contents between 15 and 25%, higher than present seafloor basalts, would still not generate enough H2 to result in significant O2 drawdown (Fig. 4a). Rocks with MgO contents of 25–30%, which require a much hotter mantle source44, would still need to comprise >150 million km² of the seafloor (~40% of present-day) for the likelihood of offsetting >2 Tmole O2 yr⁻¹ to exceed 50% (Fig. 4a). Variable thickness of highly impermeable sedimentary layers can cover and prevent extensive exposures of the igneous oceanic crust, especially that which is older, and control communication between seawater and basement rocks67. Less pervasive sedimentation in the Archean seafloor would likely favor greater extents of water-rock interactions and higher potentials to produce H2.

Most of the outgassing of H2 in modern seafloor environments is limited to slow-spreading environments where tectonically exposed residual peridotites readily interact with seawater66. Faster spreading rates68 and thicker oceanic crust69 that likely characterized the Archean would not favor emplacement of deep-seated Mg-rich residual peridotites and cumulate rocks into the surface. Instead of spreading centers, Mg-rich rocks are believed to have erupted during the Archean in hotter plume-generated settings such as oceanic plateaus formed by large igneous provinces70. Oceanic plateaus can be extensive and are estimated to comprise ∼5% of present-day seafloor (~18 * 10⁶ km²)71. If similar extents (15–21 * 10⁶ km²) of oceanic plateaus comprised of rocks with MgO contents <30% were present during the Archean, the likelihood of generating H2 that can offset >2 Tmole O2 yr⁻¹ is still low (<5% of models, blue field in Fig. 4). A similar extent of exposure of rocks with MgO content >35% would have
resulted in much higher potentials to offset a similar rate of net O₂ production. However, Mg-rich cumulate komatiites typically comprise a minor component of eruptive komatiite flows that are likely to have been compositionally heterogeneous. H₂-rich seeps could have been sourced from deep-seated aquifers in komatiitic bodies where interactions with cumulate rocks are more likely. Results of calculations of H₂ outgassing in a heterogeneous igneous province comprised of variable mixtures of mafic (MgO <10%) and relatively more Mg-rich lithologies are shown as colored symbols and curves in Fig. S2a,b, respectively. As H₂ production in rocks with MgO >35% is far more substantial than in rocks with lower Mg contents, at least 40% (dark blue-violet curves in Fig. S2b) of a given quantity of fluids present in mafic-ultramafic igneous provinces encompassing 18 km² of the seafloor (orange line in Fig. S2b) would need to interact with rocks with MgO >35% to consume >2 Tmole O₂ yr⁻¹. A hotter mantte on the early Earth would likely result in more extensive occurrences of plume-generated igneous bodies than present (i.e., >18 km²), which would increase the likelihood of offsetting production of >2 Tmole O₂ yr⁻¹.

Cessation of Archean serpentinization as a driver for the GOE. This work quantifies the extents of ultramafic presence in continents and the seafloor required for significant outgassing of H₂ during low-temperature serpentinization that would have helped maintain an O₂-free atmosphere throughout most of the Archean. Recent constraints on the composition52,53 and extent56 of Early Earth continents yield scenarios where outgassing of serpentinization-derived H₂ that can offset O₂ production of >2 Tmole yr⁻¹ is possible. Similar or greater extents of H₂ production via serpentinization of the Archean seafloor are possible but remain poorly constrained and may depend on the extents of ultramafic rocks present in plume-generated oceanic plateaus composed of Mg-rich ultramafic rocks. Those with >35% MgO are more likely to generate significant fluxes of H₂ that can result in larger sinks for O₂. Whereas they are abundant throughout most of the early- and mid-Archean, exposures of ultramafic rocks diminish significantly by the end of the eon. Almost all our simulations yield close-to-zero potentials to consume significant amounts of O₂ via H₂ production from rock alteration by the end of the Archean and help set the stage for the GOE.

Additional constraints on the extents of ultramafic presence in continents and the seafloor will refine global H₂-generation and O₂-consumption rates on the Early Earth. Quantifying H₂ outgassing during both low- and high-temperature serpentinization of ultramafic rocks present in plume-generated oceanic plateaus, as well as other marine settings like ocean ridges, passive margins, and subduction zones, during the Archean will yield more comprehensive global models of serpentinization-derived H₂ outgassing. Serpentinization is only one of the many sources of redoxants to the Earth’s surface (e.g., volatiles that are volcanically and microbially derived). We hope that our simulations will ultimately contribute to an integrated model that incorporates evolution of various redox sources and sinks, many of which can be facilitated by the secular change in the composition of Earth’s continents and seafloor, that will yield forward models predictive of surface redox conditions.

Methods

Overview. The annual global outgassing of H₂ (mole H₂ yr⁻¹) derived from the serpentinization of komatiites and other Fe-bearing igneous rocks at a given point of Earth’s history, H₂, can be described by the equation

\[ H_{2,\text{yr}} = n_{\text{FeOT}}A_{\text{FeOT}}x_{\text{Fe}} \]  

where \( n_{\text{FeOT}} \) = rate of rock alteration (km yr⁻¹), and \( A_{\text{FeOT}} \) = the H₂-generation potential of a given volume of Fe-bearing igneous rocks (mole H₂ km⁻³).

As shown by reaction (3), consuming a mole of O₂ would require two moles of degassed H₂, which means that the global O₂ consumption can be estimated via

\[ O_{2,\text{yr}} = 0.5H_{2,\text{yr}} \]  

(5)

Calculation of the H₂-generation potential of a given volume of rock (\( x_{\text{FeOT}} \)). The amount of H₂ that can be generated through the serpentinization of a given volume of rock, given by \( x_{\text{FeOT}} \) in Eq. (4), can be variable and will depend on the compositions of the reacting rock and fluid, as well as the extent of the rock alteration process. Simulations of hydrous alteration of 9,414 Fe-bearing igneous rocks of variable compositions were conducted using the reaction-path code EQ3/672 together with a customized thermodynamic database (see below) to calculate \( x_{\text{FeOT}} \) values. Automation of rock alteration simulations and data processing was conducted following ref. 77. These calculations simulate the hydrous alteration of a rock by a fluid and determine the compositions of coexisting solid phases and fluid constituents attained at thermodynamic equilibrium at each step of overall progress in rock alteration. Our models account for H₂ generation at various extents of water-rock reaction, quantified as the water-to-rock ratio. An increase in reaction progress is analogous to a decrease in the water-to-rock ratio, as the reacting water encounters more rock while infiltrating deeper into the subsurface. Active serpentinization-generated H₂-rich seeps are known to be products of rock-dominated systems (i.e., low water-to-rock ratios56,42,74). In addition, we found that at water-to-rock ratios <100 the simulation results show that the compositions of fluid, gas, and solid phases generated during the alteration of a given rock sample would be similar despite reaction with fluids of variable starting dissolved O₂ concentration (see Fig. S4). At low water-to-rock ratios, alteration products will be predominantly dictated by the composition of the reacting rock rather than the reacting fluid. Given these constraints on serpentinization-generated fluids, we used the results of simulations at low water-to-rock ratios (<100) to estimate past fluxes of H₂. The rock alteration models assumed to form hydrous minerals and the simulations were terminated by this point in the overall rock-alteration process.

We did not include dissolved CO₂ in our idealized fluids owing to scarcity of information on mineral carbonation reactions in the deep past. However, note that the 95% confidence interval for the initial CO₂ content in the Archean47,48 would have been much higher than present in the Archean. Consequently, the pH of meteoric-derived fluids infiltrating the continental subsurface could have been lower75 and affected reaction rates. Moreover, while the inclusion of CO₂ in the reacting fluid can permit predictions of the amount of CH₄ generated, which is another sink for O₂ generation of abiotic CH₄ during low-temperature serpentinization has been questioned47. Future work on the concentrations of dissolved CO₂, as well as other solutes in the reacting fluid, would refine model results. Aside from dissolved CO₂, the starting dissolved sulfate73 and Si⁴⁷ concentrations of reacting fluids can also influence the overall process of rock alteration. It has been argued that an elevated Si concentration can suppress H₂ production47. However, the extent to which H₂ production is suppressed at variable water-to-rock ratios (i.e., water-dominated vs rock-dominated conditions) is unknown. It is likely that at low water-to-rock conditions (e.g., water-to-rock ratio = 1), which is the focus of this work, the compositions of the reacting rock exert more influence than the starting compositions of the reacting fluids. This is illustrated by the results of calculation (3) depicted in Fig. S4, which shows the potential for a given rock composition at low water-to-rock conditions despite interaction with fluids that have variable starting dissolved O₂ content. Future simulations can disentangle the relationship between H₂ generation, water-to-rock ratios, and the starting composition of reacting groundwater or seawater.

The idealized calculations allow us to adequately track changes in fluid chemistry during rock alteration as demonstrated by several studies on sites of serpentinization actively occurring today42. Simulated temperature is set to 25 °C to model low-temperature continental and subsurface aquifers where serpentinization is thought to be actively occurring. Compositions of reacting rocks formed under the precompiled list of Fe-bearing igneous rocks (komatiite, picrite, peridotite, harzburgite, dunite) in the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/). While we did not include the GEOROC precompiled file for lherzolite, the precompiled file for peridotite includes several lherzolites to account for those present in uplifted orogenic masses57. Other rocks in the ultramafic olivine-orthopyroxene-rich rock type (e.g., websterite, pyroxenite) were not included as these lithologies comprise a minor component of uplifted ultramafic bodies54. Only these samples with complete lithologies were a minor component of uplifted ultramafic bodies54. Only these samples with complete lithologies were included. Duplicates and samples containing high volatile contents (>1% CO₂, S) were removed. Only major element data for MgO, SiO₂, Fe₂O₃, CaO, K₂O, and Na₂O on an anhydrous basis were used in the calculations. FeO was calculated if it was not reported and if both FeO and Fe₂O₃ were indicated (FeO = FeO + 0.9Fe₂O₃). Reacting rocks include trace amounts of Cl (40 ppm) to yield aqueous solutions with dissolved Cl concentrations ranging from 1 to 10 mmolal, which are similar to those measured from hyperalkaline spring fluids42. Overall, a total of 9,414 different Fe-bearing igneous rocks of variable compositions were used for the rock alteration models. Simulations include at least 500 rocks with MgO <10 and >45 wt% and each 5 wt%
interval from 10 to 45%. Further statistical analyses were conducted using these compositional groups. Compositions of all rocks used in the simulations as well as calculated water-to-rock ratios are compiled in Source Data S1.

Thermodynamic data used in the simulations are calculated with the SUPCRT code using standard state thermodynamic data for aequous species, including the revised Hégeson-Kirkham-Flowers equations of state. Data for minerals were mostly taken from Hégeson et al., with the addition of estimated thermodynamic data, consistent with the above database, for Fe(II)-serpentine (greenalite) and tach (minnesotaite) from Wolery and Jove-Colon, Fe(I)-serpentine (crondstedite and hisingerite) from Leong and Shock, Fe(II)-brucite from McCollom and Bach, and clay minerals from Catalonia.

Notes on the rate of rock alteration (rFe). The rate of serpentinization, rFe, can be informed by experimental work. Recent experiments by McCollom and Donaldson1 show that H2-generation rates during low-temperature serpentinization are much slower than rates determined by earlier studies to the point that H2 can be undetectable on the timescales of laboratory experiments. Reaction extents calculated xFe at different water-to-rock ratios are compiled in Source Data S1.

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Author contributions

J.L. and E.S. designed the project. J.L. and T.E. performed thermodynamic calculations and statistical analyses. J.L. wrote the paper with contributions from all authors. All authors contributed to the discussions of calculation results.

Competing interests

The authors declare no competing interests.

Additional information

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