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Serpentinization on Exoplanets: Indicators and Inference Methods

Serpentinization is a water–rock reaction where ultramafic silicate minerals (rich in Mg and Fe, like olivine and pyroxene) are hydrolyzed to form serpentine-group minerals, producing **molecular hydrogen (H_2)** as a byproduct [1] [2]. This process can also drive abiotic reduction of CO_2 into **methane (CH_4)** via Fischer-Tropsch-type reactions [3] [2]. On Earth and other solar system bodies, serpentinization is known to provide chemical energy and potentially support life, making it an important process in astrobiology [4] [3]. Inferring serpentinization on exoplanets relies on multiple lines of evidence, including surface mineralogy, atmospheric composition, and geophysical models. Below is a comprehensive overview of the methods and indicators used to detect or infer serpentinization processes on exoplanets, drawing from both observations and theoretical studies.

Spectral Signatures of Serpentinized Surface Mineralogy

One direct indicator of past or present serpentinization is the presence of **serpentine minerals (hydrous silicates)** on a planet's surface. Serpentine (e.g. lizardite, chrysotile) forms when water interacts with ultramafic rock, so detecting it remotely would be a strong sign of water-rock alteration. Recent work demonstrates that serpentine has distinctive **infrared spectral features** that could be observed on rocky exoplanets. For example, First *et al.* (2024) measured the mid-infrared emissivity spectra of basaltic rocks and their alteration products, finding that **hydrous minerals such as serpentine and amphibole exhibit identifiable IR signatures** [5]. These minerals have OH and lattice vibrational features that **signal the past presence of water**. The study showed that with sufficient observing time, JWST's Mid-Infrared Instrument (MIRI) could in principle distinguish serpentine-rich surfaces from unaltered basalts [6]. In practice, a planet would need to have minimal atmospheric interference or be viewed in thermal emission. For instance, modeling of the lava planet LHS 3844b (a hot bare rock) suggests JWST could detect differences in surface composition [7] [8]. If a temperate rocky exoplanet with thin atmosphere were observed, **a mid-IR spectral feature corresponding to serpentine (around ~10–12 µm and other band positions)** would strongly imply that basaltic crust had been hydrothermally altered by water [9] [5]. This method is analogous to orbital spectroscopy used on Mars: orbiters like CRISM have identified serpentine by its near-IR absorption at ~2.1–2.3 µm, mapping its distribution [10] [11]. Those Martian detections of Mg-serpentine in Noachian terrains indicate active serpentinization in Mars' past [12]. By extension, **a comparable spectral approach on an exoplanet (e.g. with a future direct-imaging telescope) could reveal serpentine or related phyllosilicates**, providing mineralogical evidence of serpentinization.

It's worth noting that detecting specific minerals on exoplanets is extremely challenging with current technology – even JWST can only probe bulk emission spectra of very hot rocks or large temperature contrasts. However, the development of spectral libraries and high-contrast imaging techniques is ongoing. Researchers are compiling libraries of **hydrated mineral spectra** to aid exoplanet interpretation; for example, a Cornell team is building a database of basalt alteration signatures to identify water-processed rocks on exoplanets [13] [9]. They highlight that **basalt that has interacted with water develops hydrated minerals like serpentine, which "look like a snake's skin" and are "easy to spot in the**

infrared spectra" [9]. In summary, **the presence of serpentine's spectral fingerprint** (either in emission or reflectance) on an exoplanet's surface would be a direct indicator of serpentinization, and scientists are actively preparing techniques to recognize such signatures [5].

Atmospheric Signatures of Serpentinization Byproducts

Even if we cannot resolve an exoplanet's surface, serpentinization can reveal itself through **atmospheric gases produced by water-rock chemistry**. The hallmark gaseous products are **H_2** and **CH_4.** Active serpentinization in a planet's crust or ocean floor continuously generates H_2, which can accumulate in an atmosphere if not fully lost [14] [15]. That H_2 can reduce dissolved CO_2 or carbon-bearing minerals to methane, meaning serpentinization is a source of **abiotic methane** [14] [2]. Scientists therefore look to atmospheric composition for hints of these gases: - **Hydrogen (H_2):** A significant H_2 atmosphere on a rocky planet might indicate ongoing outgassing from water-rock reactions (though H_2 could also be primordial or volcanic). Because H_2 is lightweight and escapes readily, a sustained presence of H_2 on a temperate terrestrial planet suggests a replenishing source. Hu *et al.* (2023) evaluated whether volcanism or serpentinization could maintain H_2-rich atmospheres on habitable-zone M-dwarf planets. They found that **typical volcanic or serpentinization rates would fall short of replacing H_2 lost to space** – even an optimistic serpentinization rate under Earth-like conditions is a few times too low to balance escape [16] [17]. Only with special conditions (e.g. direct water–mantle contact or unusually high outgassing efficiency) could a long-lived H_2-dominated atmosphere be sustained [18] [19]. This suggests that if future observations *do* find a small rocky exoplanet with an H_2-rich atmosphere, it might require exceptional serpentinization activity (or another mechanism). In larger sub-Neptunes, by contrast, H_2 is often primordial. But notably, **detecting excess H_2 on an Earth-sized planet in the habitable zone would be a strong clue of geochemical production**, since such planets cannot easily retain primordial H_2 over geologic time. For instance, a recent hypothesis is that **"Hycean" planets (ocean worlds with H_2 atmospheres) could have H_2 supplied by ongoing water–rock interactions** in their interiors. In these cases, one would expect to see H_2 coupled with other serpentinization products like CH_4 and perhaps NH_3 (ammonia).

- **Methane (CH_4):** Methane is a potential indicator of serpentinization – but also a potential biosignature – so its detection requires careful context. The mere presence of CH_4 in an exoplanet atmosphere does **not** uniquely signify life, because **abiotic processes (serpentinization, magmatic outgassing, even meteoritic impacts) can generate CH_4** [20] [21]. For example, Mars has trace methane which may partly come from subsurface serpentinization of olivine in the crust [22]. On exoplanets, one must distinguish between biogenic and abiogenic methane by examining accompanying gases and required fluxes. A key approach is looking for **redox disequilibria**. A classic biosignature scenario is CH_4 coexisting with abundant O_2 or CO_2 far from equilibrium. Abiotic methane from serpentinization typically occurs in reducing environments; if an atmosphere has mostly N_2–CO_2 with a bit of CH_4, that CH_4 could be geological. But if we see **a CH_4-rich, CO_2-poor atmosphere on a rocky planet**, it's hard to explain by known abiotic means [20]. Thompson *et al.* (2022) analyzed this in detail: They argue that **known abiotic processes cannot easily generate atmospheres rich in CH_4 and CO (reduced species) *while* keeping CO_2 low**, because maintaining a large CH_4 flux is difficult without life [20]. In their assessment, **methane detected at high abundance (>>0.1% by volume) on an Earth-sized, temperate planet with an otherwise oxidized atmosphere would likely exceed the maximum plausible abiotic CH_4 source** [23] [20]. One of the largest abiotic sources is serpentinization, yet even global serpentinization at rates far beyond Earth's would produce CH_4 fluxes much smaller than biology could [24] [25]. In fact, an extensive review of abiotic methane sources found **"none of the abiotic sources considered have estimated**

global CH_4 fluxes comparable to Earth's modern biogenic CH_4 flux" [24]. Most abiotic CH_4 generation (e.g. hydrothermal vents, metamorphic reactions) is **orders of magnitude lower** than biological emissions on Earth [21] [24]. This means if we detect a very methane-rich atmosphere in the habitable zone, a purely geological explanation (serpentinization or volcanism) would strain credibility unless the planet is extremely active. Conversely, a *low* level of methane (e.g. a few ppm to 0.1%) could well be consistent with ongoing serpentinization, especially if paired with other clues like hydrogen.

To strengthen the case for serpentinization, researchers consider **multi-gas fingerprints**. One suggestion has been to examine the ratio H_2/CH_4: in Earth hydrothermal systems, abiotic processes can yield high H_2/CH_4 ratios, whereas biological methanogens consume H_2 and lower this ratio. In theory, very high H_2/CH_4 might hint at abiotic origin. However, experiments show this ratio is highly sensitive to temperature and pressure; for instance, lab simulations of serpentinization found H_2/CH_4 ranges from >2000 at 310 °C to <10 at 400 °C [26]. This variability means **H_2/CH_4 is not a reliable discriminator of biotic vs abiotic methane** [27] [28]. Instead, a more robust indicator may be the presence of **other outgassing species**. Serpentinization can produce small hydrocarbons and **perhaps ethane or formate** in some conditions, and often is accompanied by **hydrogen sulfide (H_2S)** if sulfur-bearing minerals are present. Detection of a suite of reduced gases (H_2, CH_4, H_2S) alongside water vapor could point to ongoing hydrothermal chemistry.

Current observations: We are just beginning to probe small exoplanet atmospheres for such signs. A notable case is **K2-18 b**, a sub-Neptune (~8.6 M⊕) in the habitable zone of a red dwarf. Recent JWST spectroscopy of K2-18 b's atmosphere revealed a **H_2-rich atmosphere containing significant CH_4 and CO_2** [29] [30]. The combination of abundant methane, CO_2, and a lack of ammonia suggests this planet could host a water ocean under its hydrogen envelope [30]. While K2-18 b is not a rocky Earth-like planet, it is considered a potential "Hycean" world where an ocean interacts with a rocky interior. In such an environment, **serpentinization at the seafloor is a plausible abiotic source of methane** – analogous to hydrothermal vents on Earth. The detection of CH_4 and the implication of an ocean make K2-18 b a prime example where geochemical processes (including serpentinization) are being considered to explain the atmosphere [29] [30]. Moving forward, JWST and upcoming observatories will search smaller terrestrial planets for methane or hydrogen. For instance, temperate rocky planets like those in the TRAPPIST-1 system are targets for methane detection. If methane is found on a TRAPPIST-1 planet, scientists will use models (like those above) to test whether a realistic serpentinization rate could produce it or if a biotic source is more likely [20] [24]. Thus, **atmospheric composition – especially the presence and abundance of H_2 and CH_4 (with contextual gases)** – is a key indicator when inferring serpentinization on exoplanets.

Planetary Models and Geochemical Considerations

The likelihood and extent of serpentinization on any given exoplanet depend on the planet's properties: **composition of the mantle/crust, availability of liquid water, internal temperature, and tectonic regime**. A number of geophysical and geochemical models have been developed to estimate how these factors influence serpentinization and its detectable byproducts:

- **Bulk Composition (FeO content):** The amount of iron(II) in a planet's silicate interior is crucial, because serpentinization generates H_2 by oxidizing Fe^{2+} to Fe^{3+} (forming magnetite) [2]. Planets that formed from more oxidized materials (lower Fe^{2+}) will produce less hydrogen. Mars is an interesting example – its mantle has a higher FeO content than Earth's, and it is believed to have undergone extensive serpentinization early on [31] [12]. Experiments confirm that **Fe-rich olivine yields**

substantially more H_2 during serpentinization than Mg-rich olivine [32]. Klein *et al.* (2013) and recent follow-ups found that iron-rich olivine can produce **several times more H_2** than olivine with less iron [32]. This implies that an exoplanet's mantle redox state (often linked to its host star's composition) sets an upper limit on serpentinization flux. For instance, a planet around a star with high iron abundance might have a more Fe-rich mantle, potentially fueling more vigorous serpentinization [32] [33]. Conversely, a very oxidizing mantle might lock carbon in CO_2 and rock form (e.g. graphite) rather than allowing CH_4 outgassing [34] [35]. Modeling by Krissansen-Totton *et al.* considered **plausible FeO fractions, crust production rates, and conversion efficiencies** to estimate maximum abiotic CH_4 fluxes [36] [37]. They concluded that even under optimistic assumptions (FeO-rich crust, fast production of new serpentinizing crust), the global CH_4 output from serpentinization is likely at least an order of magnitude below Earth's biogenic methane output [24] [25]. These calculations provide context for exoplanet observations: a planet's composition can be used to predict whether serpentinization could supply a given atmospheric CH_4 level. If observations demand a higher flux than models allow, then abiotic serpentinization alone is insufficient [24].

- **Planet Mass and Interior Temperature:** A larger planet (super-Earth) tends to have higher internal pressures and longer-lived heat, which can influence serpentinization in two ways. First, a massive planet with active volcanism will continually expose fresh ultramafic rock to water through tectonics or volcanism, potentially creating more opportunities for serpentinization. However, if a planet is too massive (>~6–8 M⊕) and retains a thick primordial H_2 atmosphere, liquid water may not contact the surface (the planet could be a mini-Neptune instead of having a rocky seafloor). Studies like Hu *et al.* (2023) considered **1–7 M⊕ rocky planets** and found that for Earth-like compositions, even the higher gravity and interior heat of a super-Earth do not dramatically boost serpentinization H_2 flux enough to compensate for rapid atmospheric escape around active M-stars [16] [17]. So, planet mass alone doesn't guarantee detectable serpentinization signatures, especially if other processes (escape, lack of water) intervene. Interior temperature and cooling rate matter because serpentinization is exothermic and self-limiting at high temperature: above ~400 °C, different metamorphic reactions dominate (e.g. talc formation, brucite breakdown) that produce less H_2 [27] [28]. Thus, serpentinization is most effective at moderate temperatures (~50–300 °C), typically in the upper crust or seafloor. Geothermal gradients on more massive planets might keep deep crust too hot for serpentine stability, confining serpentinization to shallower layers. On smaller planets (Mars-sized or stagnant-lid planets), local serpentinization can occur but the overall flux might be limited by geothermal energy and water availability. **Geodynamic models** indicate that even on a stagnant-lid planet (no plate tectonics), water can infiltrate through fractures and cause serpentinization in the crust, especially early in the planet's history or after large impacts [38] [12]. For example, early Mars had infiltrating groundwater that serpentinized portions of the crust; the evidence is the scattered detections of serpentine and the calculation that significant H_2 (and possibly CH_4) could have been produced [12] [39]. Extrapolating this, a mildly geologically active exoplanet (even without Earth-like plate tectonics) could experience episodic serpentinization (e.g. following volcanism or impact fracturing) that releases bursts of H_2/CH_4 into the atmosphere.

- **Water Availability and Planetary Hydrology:** Serpentinization requires liquid water contacting rock. Thus, the presence of **surface or subsurface water** is a prerequisite. Planets in the habitable zone with surface oceans (or subsurface oceans, in the case of icy moons/super-Earths) are prime candidates. However, there is a caveat for very water-rich worlds: if an ocean is extremely deep, high-pressure ice (phases VI/VII) can form at the base, creating a barrier between liquid water and the rocky core. Such a planet – sometimes called a "waterworld" – might *reduce* serpentinization, because the rock and water are separated by an ice layer. The most favorable scenario for serpentinization is a planet with a **moderate ocean** (like Earth's or a few times deeper) where water percolates directly into a fractured crust. In fact, some theoretical studies propose that during the **initial cooling of a wet rocky planet**, there could be a phase when the entire newly formed crust is permeated by water, causing global serpentinization of the upper mantle. This could trap large amounts of water as hydrates and generate a one-time outburst of H_2/CH_4. Evidence for such processes comes again from Mars: serpentine deposits are found in ancient (Noachian) terrains, implying that as Mars cooled and liquid water became stable, it reacted extensively with ultramafic rocks [12]. The authors of the Mars serpentine mapping study infer that **serpentinization was likely more widespread on early Mars than the mineral map alone shows**, given the amount of hydrogen that would be generated from the detected deposits [12] [39]. By analogy, an early-Earth or early-exoplanet could undergo a burst of serpentinization that might imprint on its atmosphere or crust. In a modeling study by Krissansen-Totton *et al.*, they explored such "whole-planet" serpentinization scenarios by varying crust production and water interaction parameters [36] [40] – yielding probability distributions of CH_4 flux. These models help set expectations for what an abiotic methane signature might look like (likely a lower CH_4 baseline unless life amplifies it).

- **Tectonic Regime:** Plate tectonics continually exposes fresh peridotite at mid-ocean ridges and transports water into the mantle at subduction zones – both prime settings for serpentinization on Earth [38]. A planet with active plate tectonics would have ongoing serpentinization in its ocean crust and forearc regions. If an exoplanet is in a **stagnant lid** regime (single plate), serpentinization might be more localized (e.g. at impact sites, or in deep rift zones that occasionally open). Noack *et al.* (2017) and others have shown that stagnant-lid planets can still be habitable if enough volcanism and outgassing occur [41] [42] – we can include serpentinization-driven outgassing in that category. For habitability, some outgassing of H_2 and CO_2 is needed to build atmospheres, and serpentinization provides a path for outgassing H_2 even without volcanism, as long as water can seep down. Notably, Hu *et al.* (2023) point out that **"special mechanisms" like heat-pipe volcanism or direct water–mantle contact could enhance H_2 supply** in the absence of steady plate tectonics [18]. A heat-pipe mode (continuous volcanism as on early Io or early Earth) would crack the crust and let water in repeatedly, possibly sustaining serpentinization deeper and longer [18]. In summary, theoretical models suggest **serpentinization is likely on any rocky planet with liquid water and ultramafic rocks**, but the *intensity* and *duration* depend on geological activity and composition. Models allow us to estimate whether a given planet could produce enough H_2/CH_4 to be detectable. If observations of an atmosphere imply a higher flux than models deem possible (e.g. a small planet with CH_4 in amounts requiring >100× Earth's serpentinization rate), that would argue for biological input or an unknown mechanism [24] [25]. On the other hand, if modest methane is detected, models can show it is fully consistent with abiotic serpentinization given reasonable FeO content and water cycling [25] [36].

Lessons from Solar System Analogs

While our focus is exoplanets, studies within the solar system provide "ground truth" for serpentinization and inform exoplanet inferences:

- **Mars:** Orbital spectroscopy has identified serpentine minerals in ancient Martian crust, as noted above. These detections (though relatively sparse) prove that Mars had water-driven alteration of ultramafic rocks [12]. Researchers calculated the H_2 yield from the identified serpentine deposits and concluded that **Mars likely generated significant H_2 via serpentinization**, potentially affecting its early atmosphere and climate [12] [39]. Indeed, some climate models invoke H_2 (a powerful greenhouse gas when mixed with CO_2) to explain how early Mars stayed warm; serpentinization is a plausible source of that H_2 [43] [44]. This example shows how **mineralogical evidence combined with isotopic modeling (e.g. using D/H ratios) can link serpentinization to atmospheric gases**. In one study, scientists used Mars' atmospheric D/H (deuterium/hydrogen) ratio to estimate how much methane outgassing could come from water-rock reactions – finding up to ~40% of Mars's modern CH_4 budget might be abiotic [45]. Such analyses guide exoplanet studies: if we detect methane on a Mars-like exoplanet, we might consider isotope ratios or mineral context (if available) to assess an abiotic contribution.

- **Enceladus (Saturn's moon):** Enceladus provides a dramatic example of **active serpentinization detectable via plumes**. The Cassini spacecraft found that Enceladus's geyser-like plumes contain copious H_2, along with CH_4 and other organics, in water jets from the subsurface ocean [46] [47]. Chemical modeling of the plume indicated an alkaline, soda ocean with pH ~11–12, consistent with serpentinization in the rocky core producing hydroxide and hydrogen [48] [4]. In fact, **Cassini's detection of H_2 was considered a smoking-gun for ongoing serpentinization**: the only plausible source of so much H_2 in Enceladus's ocean is water reacting with Fe-rich rock, as in terrestrial hydrothermal vents [46] [15]. This example is instructive for exoplanets and exomoons. It shows that **serpentinization can be identified remotely by its chemical products** (even if we can't see the rock directly), and that these products (H_2, CH_4, high pH fluids) are linked to habitability. In Enceladus's case, the H_2 provides energy that could support a biosphere in the dark ocean, and the methane could be either abiotic or from methanogens feeding on H_2 [4]. The lesson for exoplanets: if we detect an atmosphere rich in H_2 and CH_4, especially with water vapor present, we should consider an "Enceladus-like" scenario of an ocean world with serpentinizing seafloor. Even though we cannot directly sample exoplanet plumes, upcoming missions might detect spectral hints of **outgassing in transiting exoplanets** (e.g. excess transit depth in H_2 or CH_4 lines). And future large telescopes could search for **disequilibrium combinations** like CH_4 + CO_2 + H_2 that might mirror the Enceladus chemistry on a planetary scale.

- **Earth:** Earth serves as the baseline: serpentinization occurs at mid-ocean ridges, subduction zones, and within tectonic ophiolites [38]. It produces H_2 at rates that sustain deep microbial communities (e.g. at the Lost City hydrothermal field) and creates distinctive serpentine minerals that we can detect in outcrops. Earth's atmosphere today has negligible H_2 and ~1.8 ppm CH_4 from geologic sources, because life and oxidation dominate the methane cycle. However, during the Archean Eon, abiotic methane may have been higher. Lab simulations and geological evidence suggest that hydrothermal serpentinization was widespread in early Earth's seafloor, potentially contributing to a methane-rich, low-oxygen atmosphere that set the stage for the origin of life [49] [21]. When assessing an exoplanet, scientists often invoke an **"Archean Earth analog"** for a planet with abiotic organic synthesis. For example, one study modeled an Archean-Earth-like exoplanet and the detectability of methane from low-temperature hydrothermal vents (simulating serpentinization-fueled microbial methanogenesis vs abiotic output) [50] [51]. They found that even with substantial vent activity, **biologically boosted methane would be easier to detect than purely abiotic methane** on a similar world [23]. This reinforces that while serpentinization can create methane, a *lot* of methane might hint at biology on top of geology. Earth also reminds us of **false positives/ negatives**: the presence of CO_2 + CH_4 in Earth's atmosphere today is *not* due to serpentinization but life, whereas an exoplanet with only modest CH_4 might still be alive (if life is low in productivity) or could be purely geochemical. Thus, we must use all available indicators in concert.

In conclusion, **inferring serpentinization on exoplanets requires a multidisciplinary approach**. Key methods include identifying **surface mineralogical evidence** of water-rock interaction (serpentine spectral features), detecting **atmospheric gases** like H_2 and CH_4 in ratios or contexts consistent with hydrothermal outgassing, and applying **geochemical models** to judge whether those observations fit abiotic processes. Observationally, we are on the cusp of these detections – JWST has begun to find relevant molecules on temperate exoplanets, and future direct-imaging missions will target surface and near-surface signatures. Theoretical and analog studies provide guiding benchmarks: for instance, serpentinization is a universal process expected on any wet, rocky world [14], but its observable effects might range from subtle (a few ppm methane) to significant (tens of percent H_2 atmospheres in rare cases). By combining spectral data, atmospheric analysis, and robust modeling, scientists can build a case for (or against) serpentinization on distant worlds. Each line of evidence strengthens the inference – much like a detective using mineral clues, "smoking gun" gases, and environmental context to solve the case of an exoplanet's hidden geology.

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