

REVIEW

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# Liquid and supercritical CO<sub>2</sub> as an organic solvent in Hadean seafloor hydrothermal systems: implications for prebiotic chemical evolution

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## Abstract

Prebiotic chemical evolution and the emergence of life in the seafloor hydrothermal systems of Hadean Earth is among the most plausible and popular hypotheses for the origin of earthly life. In contrast, many studies pointed out that this hypothesis intrinsically harbors a critical unsolved problem called the “water paradox”: Abundant water limits dehydration synthesis and instead facilitates hydrolysis of organic molecules during the early stage of chemical evolution. However, many of these criticisms have not referred to the abundant liquid/supercritical CO<sub>2</sub> (L/SC-CO<sub>2</sub>) fluids and pools in modern hydrothermal systems, which not only create dry environments but also behave as hydrophobic solvents at and beneath the seafloor. In this paper, we theorize the generation and preservation of a L/SC-CO<sub>2</sub> pool in modern seafloor hydrothermal systems and reinterpret the fossil hydrothermal systems preserved in early Archean seafloor basalts. The theoretical estimation of subseafloor phase separation and phase segregation of CO<sub>2</sub>-rich hydrothermal fluids suggests the presence of L/SC-CO<sub>2</sub> fluids and pools in Hadean seafloor hydrothermal systems. Because they behave as hydrophobic organic solvents, L/SC-CO<sub>2</sub> can potentially initiate the dehydration synthesis of organic molecules in seafloor hydrothermal systems. Moreover, at the interface between L/SC-CO<sub>2</sub> and H<sub>2</sub>O-rich fluid (seawater or hydrothermal fluid), amphiphilic molecules might be generated and triggered into self-assembled growth. Based on the abundant occurrence and physicochemical properties of L/SC-CO<sub>2</sub> fluids, we propose a new stepwise concept for the origin of life, whereby prebiotic chemical evolution was co-hosted and facilitated by L/SC-CO<sub>2</sub> in Hadean water-rich seafloor hydrothermal systems. This “liquid/supercritical CO<sub>2</sub> hypothesis” potentially overcomes the water paradox and strengthens the idea that earthly life was hatched in deep-sea hydrothermal systems.

**Keywords:** Origin of life, Liquid and supercritical CO<sub>2</sub>, CO<sub>2</sub> hydrate, Seafloor hydrothermal vent, Prebiotic chemical evolution, Phase separation, Organic solvent, Interface reaction, Metal dissolution

## 1 Introduction

An increasing interest in research on the origin of life (OOL) has emphasized two substantial aspects of OOL research: the process of prebiotic chemical evolution

and the birthplace of life. The former aspect began with the pioneering Miller–Urey experiments in a given primordial atmosphere (Miller 1953; Miller and Urey 1959) and was later sophisticated with genetics-centric theories such as RNA/Protein world hypotheses (Rich 1962; Gilbert 1986; Eddy 2001; Ikehara 2005; Robertson and Joyce 2012; Harish and Caetano-Anolles 2012) and metabolism-centric theories such as the autotrophic origin of life hypothesis (Wächtershäuser 1988, 1990, 1994; Huber and Wächtershäuser 1997, 2003; Russell and Hall

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1997; Martin et al. 2008; Russell et al. 2010). The latter aspect began with the primordial organic-soup hypothesis in oceans (Oparin 1924, 1957; Haldane 1929) and has been updated with several plausible candidates and models such as the seafloor hydrothermal vent hypothesis (Russell et al. 1988, 2021; Russell and Hall 1997; Takai et al. 2006; Russell et al. 2014; Shibuya et al. 2015, 2016; Yamamoto et al. 2017; Barge et al. 2019; Kitadai et al. 2018, 2019, 2021; White et al. 2020), on-land hot spring (warm little pond) hypothesis (Powner et al. 2009; Mulkidjanian et al. 2012; Maruyama et al. 2019; Damer and Deamer 2020), and others (e.g., panspermia hypotheses) (Arrhenius 1908; Hoyle and Wickramasinghe 2000). Both aspects can be overlapped to create unified scenarios and contexts of OOL, whereas each hypothesis has long been debated because it certainly embraces both advantages and disadvantages. In fact, seafloor hydrothermal vents and on-land hot springs are now considered as the most plausible birthplaces of life, but the hypotheses have been hotly debated recently (Damer and Deamer 2020; Marshall 2020; Russell 2021; Korenaga 2021; Rosas and Korenaga 2021). Furthermore, they have been extensively investigated in their analog environments on the present Earth (e.g., Takai et al. 2004; Suzuki et al. 2013; Suda et al. 2014) and Saturn's moon (Hsu et al. 2015; Sekine et al. 2015; Glein et al. 2015; Waite et al. 2017).

The hot spring hypothesis is supported by the availability of various energy sources (hydrothermal chemistry, sunlight, and cosmic ray irradiation), the supply of freshwater and atmospheric feedstock materials, and the condensation and polymerization of organics through possible wet–dry and freeze–thaw cycles on the ground surface (Powner et al. 2009; Mulkidjanian et al. 2012; Damer and Deamer 2020; Rosas and Korenaga 2021). In contrast, the ground surface of the Hadean should have been exposed to long-term cosmic ray irradiation, meteorite showers, and ultraviolet (UV) irradiation in the absence of an ozone shield. These natural processes have the potential to induce polymerization and molecular evolution of organics under appropriate conditions (e.g., McKay and Borucki 1997; Damer and Deamer 2020), but sustaining the prebiotic chemical evolution and the generation and continuity of primordial life would be difficult in such harsh environments. Furthermore, the spatiotemporal abundance and stability of hot spring environments on the exposed land might be stochastically weak points for the sustainable prebiotic chemical evolution and the generation and continuity of life as compared to those of deep-sea hydrothermal systems.

Since the discovery of hydrothermal systems on the modern ocean floor (Corliss et al. 1979), the seafloor hydrothermal vent hypothesis has been widely accepted as the birthplace of life and the hatchery habitat of the

last universal common ancestor (LUCA) because many thermophilic, lithotrophic, and potentially ancient lineages of microbes sustained only by geo-fuels have been identified in hydrothermal fluids (Corliss et al. 1981; Takai et al. 2004; Stetter 2006; Nakamura and Takai 2014). Recent reverse-evolution studies using an enormous dataset of prokaryotic genomes have reinforced the concept that early seafloor hydrothermal vents hosted the emergence of LUCA and the post-LUCA propagation and evolution (Weiss et al. 2016; 2018). However, whether the origins of life and LUCA were spatiotemporally related is still uncertain. Rather, the seafloor hydrothermal vent hypothesis for OOL has been established in terms of prebiotic chemical evolution, such as the generation of auto-catalytic and autotrophic proto-metabolisms in Hadean hydrothermal vents (Wächtershäuser 1988, 1990, 1994; Huber and Wächtershäuser 1997, 2003; Russell and Hall 1997; Martin et al. 2008; Russell et al. 2010; Yamamoto et al. 2017; Barge et al. 2019; Kitadai et al. 2018, 2019, 2021; White et al. 2020). In addition, limited but certain amounts of geological and geochemical evidences have constrained the environmental conditions that would support the seafloor hydrothermal vent hypothesis. For instance, seafloor hydrothermal vents can provide a sustainable and stable chemical energy supply for microbial metabolisms (McCollom and Shock 1997; Amend et al. 2011; Nakamura and Takai 2015) and are insulated from lethal extraterrestrial inputs (e.g., UV and cosmic rays and meteorite impacts) (Morbidelli et al. 2001; Takai 2019). Moreover, seafloor hydrothermal activities have existed since the initiation of plate tectonics in the Hadean (e.g., Komiya et al. 1999), and microfossils were found within the 3.5 Ga subseafloor hydrothermal deposits (e.g., Ueno et al. 2001). Nevertheless, all seafloor hydrothermal systems are present in seawater that generally inhibits dehydration synthesis rather facilitates hydrolysis of organics. This so-called water paradox or water problem is the most challenging inherent dilemma of the seafloor hydrothermal vent hypothesis.

In fact, various prebiotic organics have been synthesized in laboratory experiments under water-rich conditions that simulate seafloor hydrothermal systems (e.g., Yanagawa and Kojima 1985; Huber and Wächtershäuser 1997; Imai et al. 1999; Simoneit 2004; Kawamura et al. 2005a, b; Lemke et al. 2009; Sakata et al. 2010; Burcar et al. 2015; Barge et al. 2019; Kitadai et al. 2019, 2021). Early experiments on hydrothermal organic synthesis focused on the polymerization of amino acids from amino acid monomers, while recent geo-electrochemical experiments have synthesized various building-block organics (amino acids, organic acids, and thio-esters) from inorganic compounds (Kitadai et al. 2018, 2019,

2021). However, the amounts and sizes of the organic polymers generated in simulated hydrothermal solutions were demonstrably insufficient, possibly emphasizing the “water paradox” of seafloor hydrothermal vents.

Besides these two major hypotheses, there are a view that prebiotic chemical evolution might be facilitated by supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) fluids (e.g., Fujioka et al. 2009; Schreiber et al. 2012). The critical point of CO<sub>2</sub> ( $T_c=31.1$  °C;  $P_c=73.8$  bar) is located among the mild temperature and pressure conditions, which frequently occurs in those of geologic environments. Condensed CO<sub>2</sub> behaves as a nonpolar hydrophobic solvent in liquid and supercritical states (e.g., its solubility parameter is 14.6 MPa<sup>1/2</sup> at 40 °C and 20 MPa; Marcus 2018), and can be industrially used for polymer synthesis because of its high miscibility with many organic materials (e.g., Hyatt 1984; Cooper 2000; Shi et al. 2015). Thus, as potential environments facilitating prebiotic chemical evolution, Fujioka et al. (2009) assumed on-land soda fountains whereas Schreiber et al., (2012) proposed deep strike-slip fault zones in exposed proto-continents. However, partial pressure of CO<sub>2</sub> in atmosphere and ocean was probably reduced by water–rock reactions during formation process of primordial ocean to a level that L/SC-CO<sub>2</sub> is unstable (Ueda and Shibuya 2021). Moreover, the exposed land of continental crusts is not guaranteed to exist in the Hadean (Korenaga 2021). In addition, it might be difficult to examine these models in analogue sites on modern Earth. Nevertheless, these prior SC-CO<sub>2</sub> models certainly provide hints for solving the “water paradox” of the seafloor hydrothermal vent hypothesis because ongoing generation of liquid/supercritical CO<sub>2</sub> (L/SC-CO<sub>2</sub>) fluids is observed in several modern seafloor hydrothermal systems.

In this regard, this paper reviews previous studies of modern hydrothermal systems that host L/SC-CO<sub>2</sub> fluids and pools at and beneath the seafloor and theorizes the generation and preservation mechanisms. Archean geologic records that can be the evidence for L/SC-CO<sub>2</sub> fluids in seafloor hydrothermal systems are also reviewed. These discussions shed light on the possible key processes

of prebiotic chemical evolution driven by L/SC-CO<sub>2</sub> fluids and pools in Hadean seafloor hydrothermal systems.

## 2 Liquid CO<sub>2</sub> in modern seafloor hydrothermal systems

L/SC-CO<sub>2</sub> fluids and pools have now been recognized in some seafloor hydrothermal fields of the Okinawa Trough (Sakai et al. 1990a, b; Ishibashi et al. 1995; Inagaki et al. 2006; Konno et al. 2006; Kawagucci et al. 2011) and the Mariana Arc (Lupton et al. 2006, 2008) (Table 1). The hydrothermal vents in these fields generally emit CO<sub>2</sub>-rich fluids with or without lesser amounts of L/SC-CO<sub>2</sub> bubbles/droplets, which can be recognized both visually (e.g., Sakai et al. 1990b; Lupton et al. 2006) and acoustically (e.g., Nakamura et al. 2015). The CO<sub>2</sub> concentrations in hydrothermal fluids vary widely but are typically at least one order of magnitude higher than those in typical hydrothermal fluids of mid-ocean ridge systems (10–30 mM) (Table 1). However, these analyzed hydrothermal fluids are apparently mixtures of brine and gas-rich vapor phases because it is difficult to sample the brine and vapor phases, separately. Therefore, the reported CO<sub>2</sub> concentrations in hydrothermal fluids indicate the maximum and minimum values of the brine and vapor phases, respectively.

According to stable carbon isotope ratios of CO<sub>2</sub> in these hydrothermal fluids, CO<sub>2</sub> likely originated from a combination of mantle carbon and thermogenic CO<sub>2</sub> from sedimentary organics in the Okinawa Trough systems (Kawagucci et al. 2011). In the Champagne field (NW Eifuku) of the Mariana Arc, relatively heavy carbon isotopes point to decomposition of marine carbonates in the subducted slab, suggesting that a local melting process at subduction zone also potentially contributes to generation of a CO<sub>2</sub>-rich magma. (Lupton et al. 2006). In any case, the high CO<sub>2</sub> concentrations in fluids indicate that a considerable amount of CO<sub>2</sub> is injected into the reaction zone from surrounding heated organics-rich sediment layers and/or the underlying heat source (e.g., the magma chamber). As previously suggested, the upwelling of substantially CO<sub>2</sub>-rich hydrothermal

**Table 1** Modern seafloor hydrothermal systems with a L/SC-CO<sub>2</sub> pool beneath the seafloor

Site	Venting depth below sea surface (m)	Temperature of vent fluid (°C)	CO <sub>2</sub> concentration in hydrothermal fluid (mM)	δ <sup>13</sup> C <sub>CO2</sub> (VPDB)
JADE (Okinawa Trough)	1300–1550	< 220, 320	26–198	− 5.0 to − 4.7
Yonaguni Knoll IV (Okinawa Trough)	1370–1385	160–328	18.1–329	− 8.0 to − 7.2
Iheya North (Okinawa Trough)	1000	< 311	2.7–227	− 10.1 to − 6.1
Champagne, NW Eifuku (Mariana Trough)	1600	11–108	72.3–2711	− 1.8 to − 1.2

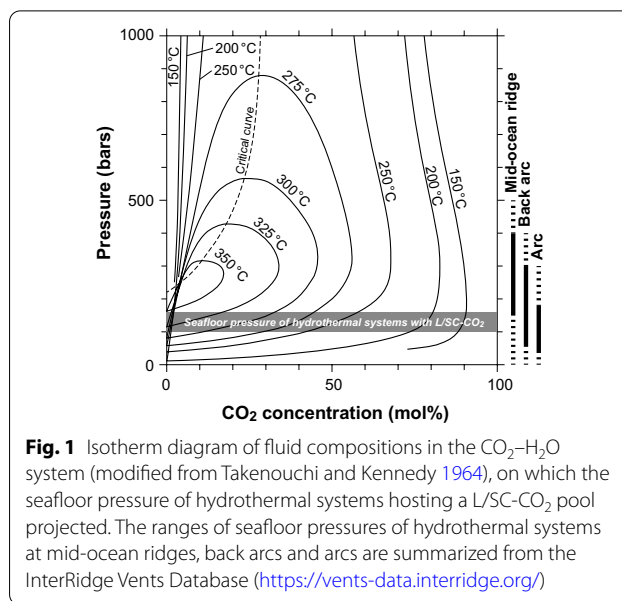
JADE: Sakai et al. (1990a, b) and Ishibashi et al. (1995), Yonaguni Knoll IV: Suzuki et al. (2001) and Konno et al. (2006), Iheya North: Kawagucci et al. (2011), Champagne, NW Eifuku: Lupton et al. (2006)

fluid inevitably drives phase separation through depressurization (e.g., Konno et al. 2006). Such processes likely generate a CO<sub>2</sub>-rich vapor phase during hydrothermal circulation, which should nucleate and grow L/SC-CO<sub>2</sub> fluids and pools at and below the seafloor. The following section discusses the mechanisms of phase separation in CO<sub>2</sub>-rich hydrothermal systems.

### 3 Generation and formation mechanisms of liquid/supercritical CO<sub>2</sub> fluids and pools in seafloor hydrothermal systems

#### 3.1 Phase separation by fluid upwelling as a CO<sub>2</sub> condensation process

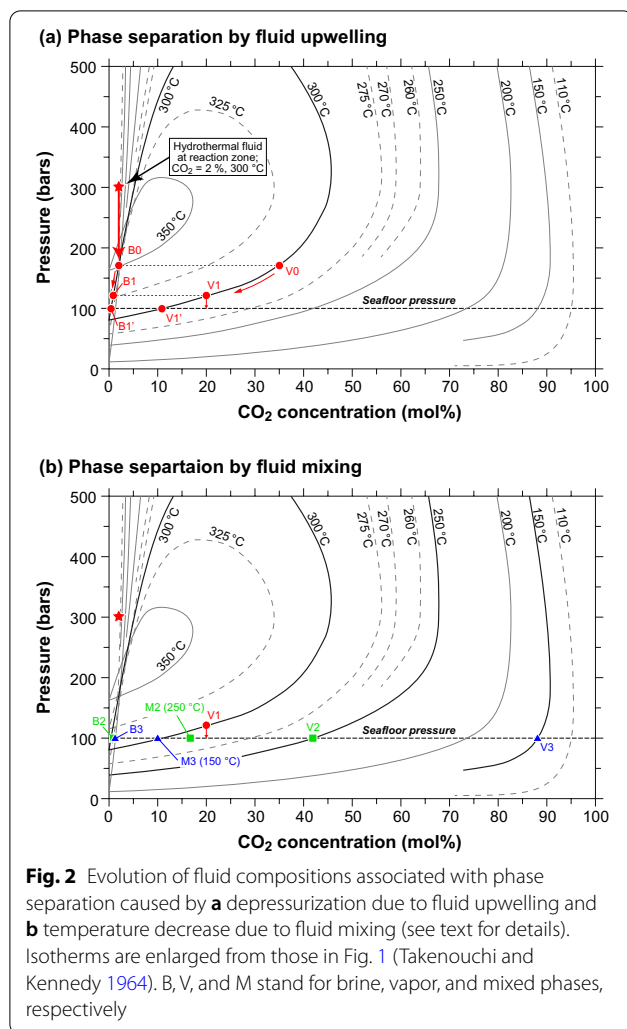
Phase separation is a frequent phenomenon in seafloor hydrothermal systems on the present Earth. It has been observed in the Rainbow (Charlou et al. 2002), East Pacific Rise (9°50' N) (especially immediately after magmatic events; Lilley et al. 2003), and Edmond (Gallant and Von Damm 2006) hydrothermal fields on the mid-ocean ridges, and even in the world's deepest hydrothermal system of the Piccard field, the Mid-Cayman Rise (McDermott et al. 2018). In addition, the processes of phase separation during subseafloor hydrothermal circulation are also well simulated by theoretical consideration and numerical modeling (Fox 1990; Scholl et al. 1993; Coumou et al. 2009). Subseafloor phase separation is generally recognized as a clear difference in salinity of the hydrothermal fluid against the seawater value. Higher and lower Cl concentrations in hydrothermal fluids than in seawater result from phase separation and segregation of brine and vapor phases during fluid upwelling (Butterfield et al. 2003). Phase separation occurs when the vapor pressure of water or partial pressure of the gases dissolved in the hydrothermal fluid exceeds the head pressure. Hence, a pressure decrease in the upwelling hydrothermal fluid causes phase separation, depending on the pressure, temperature, and fluid composition. If a hydrothermal fluid is significantly enriched in CO<sub>2</sub>, a high partial pressure of CO<sub>2</sub> likely causes phase separation during upwelling. Furthermore, the H<sub>2</sub>O–CO<sub>2</sub> system has a wide immiscibility field that changes with pressure and temperature (Fig. 1; Takenouchi and Kennedy 1964; Blencoe et al. 2001; Kaszuba et al. 2006). When a pressure and/or temperature change drives CO<sub>2</sub>-rich hydrothermal fluid into the immiscibility field on the *P*–*T* diagram, the fluid is physically separated into CO<sub>2</sub>-poor liquid and CO<sub>2</sub>-rich vapor phases. Actually, NaCl in fluids also influences conditions of phase separation in natural systems (Butterfield et al. 2003), but there is no available phase diagram of H<sub>2</sub>O–NaCl–CO<sub>2</sub> system with seawater salinity at present. Therefore, we tentatively use the phase diagram of NaCl-free system for the following discussions. It is noted that the immiscibility



fields probably expand slightly if seawater salinity is assumed for the fluids (e.g., Kaszuba et al. 2006; Dubacq et al. 2013).

Such processes are expected in present hydrothermal systems hosting abundant L/SC–CO<sub>2</sub> fluids and pools. For example, a hydrothermal fluid containing 2 mol% CO<sub>2</sub> (~1.1 mol/kg) is assumed to be generated at 300 °C in a reaction zone located 2 km beneath a 1-km-deep seafloor for simplicity. In the assumption, we lack geological and geochemical data supporting the depth of reaction zone and the CO<sub>2</sub> concentration of fluid. However, the assumed seafloor depth and temperature of reaction zone are broadly comparable to those of the Iheya North hydrothermal field in the Okinawa Trough, where dive observations with human-occupied and remotely operative vehicles have detected many L/SC–CO<sub>2</sub> droplets and bubbles exhaled along with high-temperature hydrothermal fluid flows (Kawagucci et al. 2011) (Fig. 2a and Table 1). As the hydrothermal fluid upwells, its hydraulic head pressure decreases and the fluid encounters the 300 °C immiscibility field at around 170 bar (700 m below the seafloor). At this point, phase separation begins with a very small amount of vapor phase containing 35 mol% CO<sub>2</sub> (V0 in Fig. 2a). Although the density differs between the vapor phase and the brine phase (B0; chemically almost identical to the original hydrothermal fluid), the vapor phase should occur as small droplets in the main brine phase due to its very small amount. As the upwelling proceeds, the brine phase continuously releases vapor phases and reduces its CO<sub>2</sub> concentration along the outer boundaries of the immiscibility field (Fig. 2a). Simultaneously, the volume of vapor phase gradually





increases and its CO<sub>2</sub> concentration also decreases along with the outer boundary of immiscibility field. When the bubbles of vapor phase reach a certain volume, the vapor phase (V1) might physically segregate from the main brine phase (B1) due to the density difference and might become concentrated during flow through the channels and mixing with low-temperature seawater (as discussed below). When the hydrothermal brine phase reaches the seafloor (100 bar) (B1'), its CO<sub>2</sub> concentration should be reduced to 0.3–0.4 mol% (170–220 mmol/kg) through the continuous release and segregation of the CO<sub>2</sub>-rich vapor phase. This value approximates the maximum CO<sub>2</sub> concentration of the hydrothermal fluids in the Iheya North hydrothermal field (Table 1). Meanwhile, the CO<sub>2</sub> concentration in the vapor phase reduces to approximately 11 mol% at 100 bar (near the seafloor) (V1'), but its amount relative to the brine phase increases with decreasing pressure if physical segregation is limited. In summary, depressurization from 170 to 100 bar

(from 700 to 0 m below the seafloor) causes continuous or progressive phase separation that condenses CO<sub>2</sub> into the vapor phase during fluid upwelling.

Above, the case close to Iheya North field was discussed in detail. We now briefly discuss the effect of varying the initial conditions. When the CO<sub>2</sub> concentration of the hydrothermal fluid generated in the reaction zone is higher than the above-assumed value, the amount of generated vapor phase relative to the brine phase increases and the CO<sub>2</sub> concentration in the vapor phase can reach 46 mol% (the right edge of the 300 °C immiscibility field in Fig. 2a). In contrast, if the temperature of the hydrothermal fluid in the reaction zone reaches 350 °C, the CO<sub>2</sub> concentration in the generated vapor phase is lower than at lower temperatures because the immiscibility field is narrowed. Therefore, high-temperature hydrothermal fluids (>350 °C) might be less likely to generate L/SC-CO<sub>2</sub> because the low CO<sub>2</sub> concentration in the vapor phase has less potential to generate the density difference that potentially drives the physical segregation between the vapor and brine phases. Nevertheless, the higher original CO<sub>2</sub> concentration in fluid leads to the greater amount of generated vapor phase, which might assist physical segregation of the vapor phase.

Under the above CO<sub>2</sub> concentration and temperature condition (CO<sub>2</sub>=2 mol%, 300 °C), the phases cannot separate below a water depth of 1700 m (170 bar) because the fluid composition is outside the immiscibility field. This indicates that upwelling of CO<sub>2</sub>-rich hydrothermal fluid does not necessarily cause phase separation if the seafloor is much deeper than 1700 m. For example, if the CO<sub>2</sub> concentration and temperature are approximately 2 mol% and 350 °C, respectively, the upwelling hydrothermal fluid reaches the 350 °C immiscibility field at a hydrostatic pressure corresponding to a depth of 2200–2300 m. Therefore, in typical mid-ocean ridge hydrothermal systems (e.g., 2500 m water depth at the seafloor), phase separation of hydrothermal fluids is not triggered by high CO<sub>2</sub> concentrations. This reasoning explains the lack of L/SC-CO<sub>2</sub> fluids and pools reported in/near mid-ocean ridge hydrothermal systems.

### 3.2 Phase separation by fluid mixing as a process of CO<sub>2</sub> purification

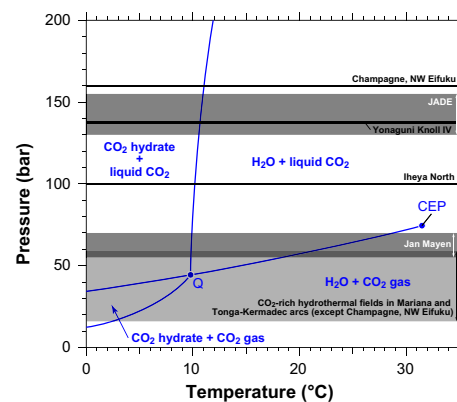
If the temperature decreases due to thermal conduction, an upwelling CO<sub>2</sub>-rich vapor phase segregated from the main flow channel would elevate its CO<sub>2</sub> concentration by releasing an H<sub>2</sub>O-rich phase. This mechanism is driven by the expanding immiscibility field in the H<sub>2</sub>O–CO<sub>2</sub> system as the temperature decreases (Fig. 1). This mechanism might work in some regions of hydrothermal systems hosting L/SC-CO<sub>2</sub> fluids and pools. In general, however, upwelling hydrothermal fluids actively

mix with cool seawater infiltrating down into the sub-seafloor environments, which effectively decreases the temperature of hydrothermal fluids (e.g., Butterfield et al. 2004). Although the mixing process usually dilutes the chemical species specifically dissolved in hydrothermal fluids (e.g.,  $\text{H}_{2\text{aq}}$ ,  $\text{H}_2\text{S}_{\text{aq}}$ , and  $\text{Fe}^{2+}$ ), the mixing-driven temperature reduction can enrich the  $\text{CO}_2$  only in  $\text{CO}_2$ -rich vapor phases. To briefly explain this mechanism, we assume simple initial conditions discussed above. First, a  $\text{CO}_2$ -rich vapor phase (V1;  $\text{CO}_2=20$  mol%) at  $300^\circ\text{C}$  is segregated from the main flow channel at 200 m below the seafloor (120 bar) during the fluid upwelling process with isothermal depressurization (Fig. 2a and b). Next, the vapor phase (V1) mixes with seawater near the seafloor (100 bar). For simplicity, the temperature and  $\text{CO}_2$  concentration of the seawater are assumed as  $0^\circ\text{C}$  and 0 mol%, respectively, because their actual values are negligible relative to those of the vapor phase. In this case, when the mixing ratio of seawater-to-vapor phase is 0.2, a mixed phase (M2) with a  $\text{CO}_2$  concentration of 16.7 mol% is formed at  $250^\circ\text{C}$  (Fig. 2b). This  $\text{CO}_2$  concentration falls within the immiscibility field at  $250^\circ\text{C}$ , which is unstable and causes phase separation generating a  $\text{CO}_2$ -poor brine phase (B2) and a  $\text{CO}_2$ -rich vapor phase (V2;  $\text{CO}_2=42$  mol%) (Fig. 2b). Similarly, when the mixing ratio of seawater-to-vapor phase is 1.0, the mixed phase (M3) has a  $\text{CO}_2$  concentration of 10 mol% and a temperature of  $150^\circ\text{C}$ . This mixed phase also falls within the immiscibility field at  $150^\circ\text{C}$  and separates into a  $\text{CO}_2$ -poor brine phase (B3) and a  $\text{CO}_2$ -rich vapor phase (V3;  $\text{CO}_2=88$  mol%). In natural systems, such mixing processes continuously occur in many places of the subseafloor hydrothermal circulation. Hence, the mixing ratio of the seawater/vapor phase generally increases over distance and time from the main flow channel or the reaction zone; accordingly, the width of the immiscibility field expands with decreasing temperature in the  $\text{H}_2\text{O}-\text{CO}_2$  system. This implies that once the  $\text{CO}_2$ -rich vapor phase has separated from the high-temperature hydrothermal fluids of the main flow channel, the  $\text{CO}_2$  enrichment can be accelerated by continuous mixing processes because the expansion of the immiscibility field due to the temperature decrease exerts a greater effect than  $\text{CO}_2$  dilution through mixing with seawater. Therefore, at the seafloor and in relatively shallow sub-seafloor regions dominated by the mixing process, nearly purified L/SC- $\text{CO}_2$  fluid is finally generated from the highly  $\text{CO}_2$ -enriched vapor phase. If there are appropriate geological structures such as alternation of porous and impermeable layers in the sediments and umbrella (flange)-shaped metal sulfide deposits, the L/SC- $\text{CO}_2$  fluids can be isolated and stored around the seafloor of the hydrothermal system (as discussed below). When spaces

become filled with L/SC- $\text{CO}_2$  fluids, L/SC- $\text{CO}_2$  pools would begin to form.

### 3.3 Geological processes that preserve liquid/supercritical $\text{CO}_2$ around the seafloor

Because the density of L/SC- $\text{CO}_2$  at the temperatures of modern deep seawater is lower than that of seawater at pressures lower than around 300 bar (e.g., Qanbari et al., 2011), the L/SC- $\text{CO}_2$  fluid should slowly rise through the fractures, voids, and cavities of subseafloor environments in hydrothermal systems shallower than 3000 m. On geological timescales, L/SC- $\text{CO}_2$  fluid might slowly permeate even the overlying impermeable sediments and eventually enter the seawater. To ensure the growth and long-term preservation of L/SC- $\text{CO}_2$  pools at and beneath the seafloor, other physical and chemical processes are required. At 100 bar and temperatures lower than approximately  $10^\circ\text{C}$ , liquid  $\text{CO}_2$  (L- $\text{CO}_2$ ) reacts with water to form clathrate hydrate (Fig. 3). As a solid,  $\text{CO}_2$  hydrate can agglomerate to fill the pore spaces of not only volcanics but also sediments. These agglomerates significantly reduce the permeability of sediments and block the leakage of L- $\text{CO}_2$  into the overlying seawater (Evrenos et al. 1971; Gauteplassa et al. 2018). Such self-sealing ability (hydrate formation) of L- $\text{CO}_2$  can promote the widespread occurrence and preservation of L/SC- $\text{CO}_2$  pools at and beneath the seafloor (Gauteplassa et al. 2020). Indeed,  $\text{CO}_2$  hydrate sealing the underlying L- $\text{CO}_2$  has been visually confirmed in the Yonaguni Knoll



**Fig. 3** A relationship between seafloor pressures of  $\text{CO}_2$ -rich hydrothermal fields and phase relations in the  $\text{CO}_2$ - $\text{H}_2\text{O}$  system (modified from Spycher et al. 2003).  $\text{CO}_2$ -rich hydrothermal systems seem to host a L/SC- $\text{CO}_2$  pool when seafloor pressures exceed the critical pressure of  $\text{CO}_2$ -rich fluid. In contrast, Jan Mayen field in the Arctic Mid-Ocean Ridge (Pedersen et al. 2010; Stensland et al. 2019) and  $\text{CO}_2$ -rich hydrothermal fields in the Mariana (except Champagne field) and Tonga-Kermadec arcs (Lupton et al. 2008) discharge  $\text{CO}_2$ -rich fluids as gas bubbles (with/without  $\text{CO}_2$  hydrate). Q, a quadruple point; CEP, a critical end point for the  $\text{CO}_2$ - $\text{H}_2\text{O}$  system

IV field and other fields of Okinawa Trough (e.g., Inagaki et al. 2006) and hydrate-sealed L-CO<sub>2</sub> droplets in deep seawater have also been verified near many hydrothermal fields (Lupton et al. 2006, 2008). In addition, although CO<sub>2</sub> hydrate can coexist with L-CO<sub>2</sub> at pressures above 35–45 bar at low temperatures, pressures higher than c. 74 bar are required for stabilizing SC-CO<sub>2</sub> that eventually becomes L-CO<sub>2</sub> when it cools beneath the seafloor (Fig. 3). Therefore, the formation of L/SC-CO<sub>2</sub> pools at and beneath the seafloor requires water depths of several hundred meters or more depending on temperature. This feature is consistent with the venting depths (>1000 m) of present hydrothermal fields bearing L-CO<sub>2</sub> pools (Table 1) and the emission of gas-phase CO<sub>2</sub> bubbles (and CO<sub>2</sub> hydrate) in CO<sub>2</sub>-rich hydrothermal fields at shallow seafloor depths (<700 m) (Lupton et al. 2008; Pedersen et al. 2010; Stensland et al. 2019). In contrast, L-CO<sub>2</sub> becomes heavier than seawater at pressures higher than approximately 300 bar (Qanbari et al. 2011). Therefore, in hydrothermal systems on seafloors deeper than 3000 m, the L-CO<sub>2</sub> does not ascend even when L/SC-CO<sub>2</sub> is generated in the deeper part by the above-discussed processes. In such cases, L/SC-CO<sub>2</sub> pools cannot form around the seafloor.

#### 4 Geological evidence of phase separation in early Archean seafloor hydrothermal systems

Fossils of ancient subseafloor hydrothermal systems are preserved in the Archean/Proterozoic greenstone belts (e.g., Kitajima et al. 2001a; Van Kranendonk 2006; Hofmann and Harris 2008; Rouchon and Orberger 2008). The Archean basaltic greenstones show a series of evidence of hydrothermal carbonation, suggesting that ancient seawater was extremely enriched in CO<sub>2</sub> (Nakamura and Kato 2004; Shibuya et al. 2013b). Furthermore, the carbonate content in the altered seafloor basalts decreased from the early Archean to the Paleoproterozoic (Nakamura and Kato 2004; Shibuya et al. 2012, 2013a, 2017), indicating that the CO<sub>2</sub> concentration in seawater decreased over this period (Shibuya et al. 2017). This finding is consistent with many other geologic records, such as paleosols and evaporates (Hessler et al. 2004; Lowe and Tice 2004; Kanzaki and Murakami 2015), and with climate models dealing with the faint young Sun paradox (Kasting 1993; Sleep and Zahnle 2001).

Since the early Archean seawater was indeed extremely enriched in CO<sub>2</sub>, the hydrothermal fluids in most of the early Archean seafloor hydrothermal systems may also have been enriched in CO<sub>2</sub> (e.g., Kitajima et al. 2001a). For example, the mineral assemblages of the seafloor basalts altered under high-temperature conditions (300–400 °C) indicate that the CO<sub>2</sub> concentration in the hydrothermal fluid exceeded 200 mmol/kg (Shibuya

et al. 2010). This range of values corresponds to the maximum CO<sub>2</sub> concentrations of hydrothermal fluids in the Okinawa Trough systems that host abundant L/SC-CO<sub>2</sub> fluids and pools (Table 1). Therefore, the early Archean seafloor hydrothermal systems could potentially generate L/SC-CO<sub>2</sub> fluids during hydrothermal circulation.

Other geological evidence is consistent with subseafloor phase separation. In the ca. 3.5 Ga North Pole area, Pilbara Craton, Western Australia, there is a bedded chert/barite (Dresser Formation, Warrawoona Group) and underlying thick basaltic sequence, in which ancient seafloor hydrothermal alteration is well preserved (Kitajima et al. 2001a; Terabayashi et al. 2003; Van Kranendonk 2006). In the basaltic sequence, the temperature of alteration increases stratigraphically downward, reaching approximately 350 °C at 1000 m below the ancient seafloor. At this depth, two types of mineral assemblages are found at nearly identical alteration temperatures: calcite-bearing (calcite–rutile–quartz) and calcite-free (epidote–actinolite–titanite) assemblages. The former and latter assemblages thermodynamically point to their coexistence with CO<sub>2</sub>-rich and CO<sub>2</sub>-poor (H<sub>2</sub>O-dominated) fluids, respectively. As these two fluids should have very different CO<sub>2</sub> concentrations, they might have been generated by subseafloor phase separation in the 3.5 Ga seafloor hydrothermal system (Kitajima et al. 2001b). This implies that L/SC-CO<sub>2</sub> fluids could be generated in Archean seafloor hydrothermal systems similarly to modern L/SC-CO<sub>2</sub>-bearing hydrothermal systems.

More direct evidence of subseafloor phase separation in the Archean greenstones is found in hydrothermal quartz deposits in the 3.5 Ga North Pole area. In this area, flow channels of hydrothermal fluids are well preserved as silica dikes and barite/quartz veins in the basaltic sequence (Ueno et al. 2006; Van Kranendonk 2006). Such hydrothermal deposits preserve ancient circulating fluids as many fluid inclusions in the quartz/barite crystals (Kitajima et al. 2001b; Ueno et al. 2006). The frequency distribution of homogenization temperatures of the fluid inclusions shows a single peak at approximately 150 °C in the deeper part of the basaltic sequence (>1000 m below the ancient seafloor), whereas samples from the shallower part (<1000 m deep) show wide ranges of homogenization temperatures (87–367 °C). Judging from this upward change in homogenization temperatures, phase separation likely occurred around 1000 m below the ancient seafloor (Kitajima et al. 2001b). Under a microscope, most of the fluid inclusions consist of two phases (H<sub>2</sub>O-rich liquid and vapor) at room temperature, but fluid inclusions containing L-CO<sub>2</sub> as a third phase are also seen (Kitajima et al. 2001b). This finding indicates extreme CO<sub>2</sub> enrichment in the L-CO<sub>2</sub>-bearing fluid inclusions, which probably corresponds to a vapor

phase generated by phase separation. Furthermore, the stable carbon isotopes of the CO<sub>2</sub>-rich fluid inclusions (ca. −7.4 to 0 ‰ vs. Vienna Pee Dee Belemnite) are generally explained by a mixture of mantle-derived CO<sub>2</sub> and seawater (Ueno et al. 2006). Therefore, even in the early Archean, the hydrothermal fluids enriched with seawater- and mantle-derived CO<sub>2</sub> probably underwent phase separation in the subseafloor hydrothermal systems, with consequent generation of CO<sub>2</sub>-rich vapor phases. In addition, the temperature of phase separation recorded in the fluid inclusions (ca. 150 °C) implies that phase separation occurred even in off-axis hydrothermal circulation systems (e.g., Kitajima et al. 2001b).

As discussed above, multiple lines of evidence in the Archean geological records show that CO<sub>2</sub>-rich vapor phases were formed by phase separation in early Archean seafloor hydrothermal systems. If the above-described condensation and purification processes were effective, nearly pure L/SC-CO<sub>2</sub> fluids are expected in these hydrothermal systems as observed in the modern equivalents, although this expectation must be validated in further analyses of the geological records. In particular, the Archean bottom seawater must have been sufficiently cool to form CO<sub>2</sub> hydrates beneath the seafloor (see above). The oxygen isotopes of phosphates in the Archean sediments indicate that the surface seawater was indeed cool during that period (26–35 °C) and did not significantly differ from the modern equivalent (e.g., Blake et al. 2010). Therefore, the temperature of the Archean bottom seawater was probably below ~10 °C, suggesting that hydrothermal systems hosting abundant L/SC-CO<sub>2</sub> pools could exist in the early Archean ocean.

## 5 Implications for prebiotic chemical evolution in Hadean seafloor hydrothermal systems

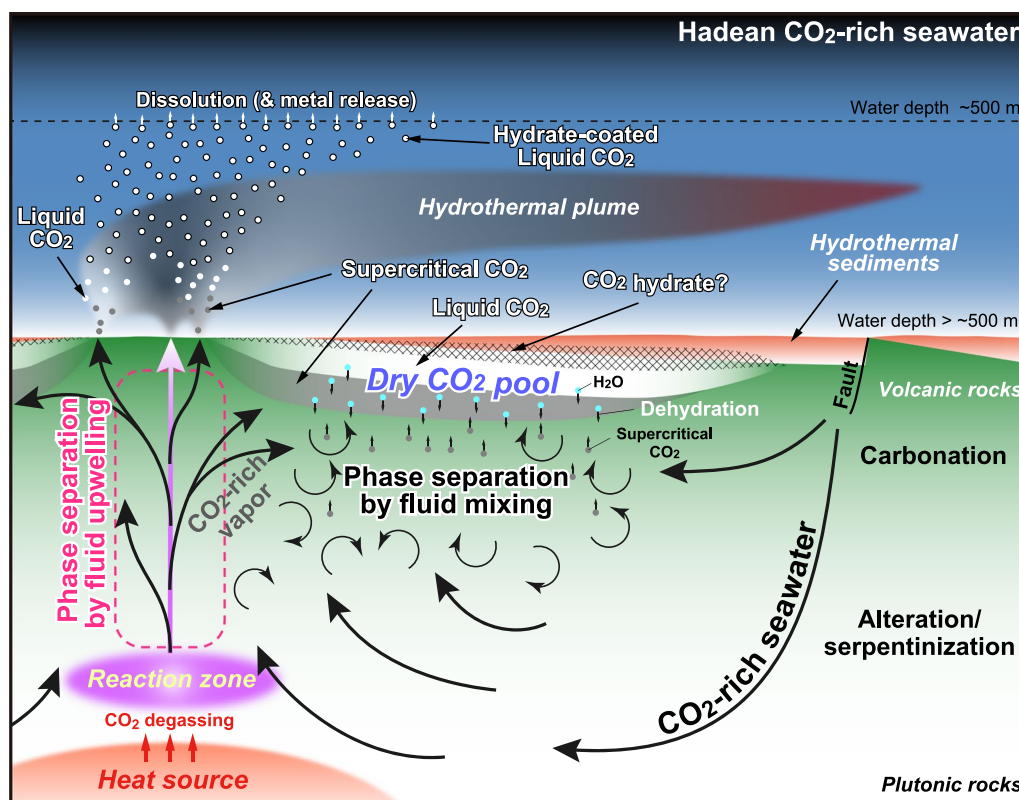
### 5.1 Liquid/supercritical CO<sub>2</sub> in Hadean seafloor hydrothermal systems

As discussed above, L/SC-CO<sub>2</sub> fluids and pools could be generated in the subseafloor hydrothermal systems of the early Archean. In the Hadean, the atmospheric and oceanic CO<sub>2</sub> levels were probably as high as those of the early Archean although the CO<sub>2</sub> levels had temporarily decreased through weathering of impact ejecta (Sleep and Zahnle 2001; Kadoya et al. 2020). Regarding solid Earth, the upper part of oceanic crust was highly carbonated through reactions with seawater (Nakamura and Kato 2004; Shibuya et al. 2012), and its subduction might cause decomposition of carbonates and resulting CO<sub>2</sub>-rich melt production at subduction zones. Moreover, komatiite magma could achieve buoyancy to erupt on the seafloor, likely because its enrichment of CO<sub>2</sub> decreased melt density (e.g., Anderson 1995; Shimizu et al. 2009), which would potentially inject abundant

degassed CO<sub>2</sub> into reaction zones in komatiite-hosted hydrothermal systems. Therefore, generation of L/SC-CO<sub>2</sub> fluids caused by phase separation is expected to be more frequent in Hadean seafloor hydrothermal systems than in modern systems (Fig. 4). Furthermore, during the weathering of impact ejecta, the Earth's surface temperature might have been temporarily lower in the Hadean than in the Archean (Kadoya et al. 2020). At this time, the deep seawater should have been sufficiently cool to initiate CO<sub>2</sub> hydrate formation at the interface between L-CO<sub>2</sub> and seawater at and beneath the seafloor, leading to the widespread formation of L/SC-CO<sub>2</sub> pools. Even if the temperature of deep seawater exceeded that of the stability field of CO<sub>2</sub> hydrates (~10 °C), sealing might have been provided by hydrothermal sediments (e.g., bedded chert and/or banded iron formation) chemically precipitated from hydrothermal plume (by mixing between hydrothermal fluid and seawater) instead of CO<sub>2</sub> hydrate (Fig. 4). Such sediments should be less permeable than those in modern seafloor hydrothermal environments because the hydrothermal fluid probably mixed with silica-saturated seawater, thus cementing the pore spaces and fractures as observed in Archean greenstone belts (e.g., Kitajima et al. 2001a; de Vries and Touret 2007; Shibuya et al. 2010). The sealing effects of CO<sub>2</sub> hydrate and/or chemical sediments may have prepared the conditions under which the seafloor hydrothermal systems could host abundant L/SC-CO<sub>2</sub> pools in the Hadean era when prebiotic chemical evolution and life's emergence took place. Accordingly, we propose that L/SC-CO<sub>2</sub> contributed to prebiotic chemical evolution in early seafloor hydrothermal systems. We call this hypothesis the “liquid/supercritical CO<sub>2</sub> hypothesis.”

In addition, the L/SC-CO<sub>2</sub> fluids associated with Hadean hydrothermal circulations likely played an important role in heavy metal cycles through the Hadean ocean. As heavy metals are highly soluble in L/SC-CO<sub>2</sub> under conditions with chelating agents (e.g., Smart et al. 1997; Erkey 2000; Lin et al. 2014), the L/SC-CO<sub>2</sub> pools generated in high-temperature hydrothermal systems (e.g., black-smoker-type systems) might have dissolved the heavy metals if natural chelating agents were present/generated. Furthermore, hydrate-coated CO<sub>2</sub> bubbles released from hydrothermal systems have also the potential to transport polymetallic nanoparticles upward and release them at shallower depths through their buoyancy and dissociation at depths around 500 m (e.g., Stensland et al. 2019) (Fig. 4). Therefore, the emission of L/SC-CO<sub>2</sub> fluids into seawater probably provided the chemical pump for the vertical distribution of heavy metals in the Hadean Ocean, in addition to active plume expansion derived from high-temperature hydrothermal vents (Fig. 4). This process would have contributed to the





**Fig. 4** Schematic of Hadean seafloor hydrothermal systems bearing a L/SC- $\text{CO}_2$  pool. The  $\text{CO}_2$ -rich seawater infiltrates the subsurface volcanic rocks and reacts with basalts or komatiites, causing carbonation and alteration of basalts or serpentinization of komatiites in the seawater recharge zones. When hydrothermal fluid reaches the reaction zone, it receives abundant degassed  $\text{CO}_2$  from an underlying magmatic heat source. During fluid upwelling, phase separation of the  $\text{CO}_2$ -rich hydrothermal fluid progressively occurs through depressurization, which likely condenses the  $\text{CO}_2$  in the vapor phase. If the  $\text{CO}_2$ -rich vapor phase is physically segregated from the main flow channel of the upwelling brine phase, it is continuously mixed with recharged seawater and/or cooler pore fluid, causing further phase separation by the temperature decrease.  $\text{CO}_2$  is then purified in vapor phase. Eventually, these condensation and purification processes generate many SC- $\text{CO}_2$  droplets beneath the seafloor. The SC- $\text{CO}_2$  is less dense than seawater and migrates upward. As it cools during the upward migration, its phase converts to L- $\text{CO}_2$ . These processes form a large L/SC- $\text{CO}_2$  pool beneath the seafloor. If the temperature of the bottom seawater is lower than approximately  $10^\circ\text{C}$ , reactions between L- $\text{CO}_2$  and the ambient seawater/pore fluid requisitely generate solid  $\text{CO}_2$  hydrates that cement the pores, voids and cavities of the hydrothermal sediments and permeable volcanics. This self-sealing effect by  $\text{CO}_2$  hydrates prevents the leakage of L/SC- $\text{CO}_2$  through the seafloor. In contrast, when  $\text{CO}_2$  hydrates are absent in the vicinity of warm/hot hydrothermal vents, L/SC- $\text{CO}_2$  leaks from the inner edge of the pool and enters the upwelling hydrothermal fluid just below the seafloor, where it is emitted in the form of bubbles. L- $\text{CO}_2$  containing these bubbles transforms to hydrate-coated L- $\text{CO}_2$  during upward migration through the water column. The bubbles disappear at depths around 500 m because L- $\text{CO}_2$  and  $\text{CO}_2$  hydrate are unstable at these depths. Eventually, both  $\text{CO}_2$  gas and the organic molecules dissolved in L/SC- $\text{CO}_2$  are released to the ambient seawater. If the hydrothermal vents are black-smoker type, the L- $\text{CO}_2$  bubbles will carry heavy metals upward to the shallower part of the water column

widespread formation of metal-rich chemical sediments in the Hadean and Archean oceans.

## 5.2 Possible roles of liquid/supercritical $\text{CO}_2$ in prebiotic chemical evolution

As L/SC- $\text{CO}_2$  fluids have similar chemical properties to hydrocarbon solvents (with a few notable differences) (e.g., Hyatt 1984), the L/SC- $\text{CO}_2$  pools in the Hadean seafloor hydrothermal systems would have provided novel reaction fields for prebiotic chemical evolution. At present, the reaction processes of prebiotic chemical

evolution is uncertain because we lack experimental data of the reaction properties of L/SC- $\text{CO}_2$  fluids and their interactions with seawater and hydrothermal fluid. In addition, in situ measurements of gaseous and condensed  $\text{CO}_2$  in natural seafloor hydrothermal systems are still challenging (e.g., Pasteris et al. 2004). In the following paragraphs, however, we briefly discuss three representative features of L/SC- $\text{CO}_2$  fluids: (1) provision of a dry environment, (2) behavior as an organic solvent, and (3) provision of an interface between L/SC- $\text{CO}_2$  and water.

The behavior as a dry environment is among the most important chemical characteristics of L/SC-CO<sub>2</sub> fluids and pools. The solubility of water in L-CO<sub>2</sub> is 0.003–0.004 mol% at 25 °C and >64 bar (Spycher et al. 2003), which is only approximately one order of magnitude higher than the content of saturated water vapor in air and is sufficiently low to facilitate dehydration synthesis. Therefore, the presence of L/SC-CO<sub>2</sub> pools in Hadean seafloor hydrothermal systems might resolve the “water paradox” that has stymied previous seafloor hydrothermal vent hypotheses—the filling of seafloor hydrothermal systems with abundant water is considered to limit organic synthesis and instead facilitate the hydrolysis of organic molecules. The dry environments of L/SC-CO<sub>2</sub> pools in seafloor hydrothermal systems would have been spatiotemporally abundant, stable, and safe, even in the Hadean era when the Earth was continuously bombarded with harmful extraterrestrial inputs such as solar UV radiation, cosmic rays, and meteorites (e.g., Morbidelli et al. 2001; Nishizawa et al. 2020).

Various organic molecules such as n-alkanes are highly miscible with L/SC-CO<sub>2</sub>, which reflects the behavior of L/SC-CO<sub>2</sub> as an organic solvent (Hyatt 1984; Swaid et al. 1985). In addition, most of the solutes in SC-CO<sub>2</sub> can also dissolve in L-CO<sub>2</sub>, while the difference in solubilities of a given solute between L-CO<sub>2</sub> and SC-CO<sub>2</sub> is a matter of degree (Hyatt 1984). Therefore, if organic molecules dissolvable in L/SC-CO<sub>2</sub> were synthesized somewhere in the hydrothermal circulation process (e.g., in the reaction and mixing zones), they could be finally transported and trapped in the L/SC-CO<sub>2</sub> fluids and pools. This suggests that L/SC-CO<sub>2</sub> pools can ultimately condense and store hydrophobic organics in hydrothermal systems. If L/SC-CO<sub>2</sub> pools establish dry conditions and promote the condensation of certain organics synthesized during hydrothermal circulation, they might be the efficient sites of dehydration synthesis and polymerization of L/SC-CO<sub>2</sub>-soluble organics in addition to other possible environments with L/SC-CO<sub>2</sub> (e.g., soda fountains and deep-reaching tectonic fault zones; Fujioka et al. 2009; Schreiber et al. 2012; Mayer et al. 2015; 2018). Furthermore, L/SC-CO<sub>2</sub> dissolves various types of organic molecules such as methanol and ascorbic acid (Hyatt 1984), which not only induce various synthetic reactions but also elevate the solubilities and reaction rates of other organic molecules via the entrainer effect in certain cases (Jouyban et al. 2005; Machmudah et al. 2006). Indeed, simple organic carbon species such as formate and C<sub>2</sub><sup>+</sup> alkanes are abiotically synthesized during serpentinization in modern seafloor hydrothermal systems associated with ultramafic rocks (Lang et al. 2010, 2012; McDermott et al. 2015). According to geo-electrochemical

experiments, the synthesis of simple building-block organics (amino acids, organic acids, and thio-esters) can be catalyzed by elemental metals/metal sulfide assemblages putatively included in early hydrothermal mineral deposits (Kitadai et al. 2019; 2020; 2021). Thus, in Hadean seafloor hydrothermal systems associated with ultramafic rocks (e.g., komatiite), and possibly in those hosted by other rocks, the L/SC-CO<sub>2</sub> pools might operate as factories that enrich and process certain organic molecules from the hydrothermal fluids and minerals and even from seawater.

The physicochemical properties of L/SC-CO<sub>2</sub> fluids and pools create different phases of fluids in water and form abundant interfaces between the water and hydrophobic fluids. Across these interfaces, hydrophilic molecules derived from H<sub>2</sub>O-rich fluid (e.g., heated seawater and hydrothermal fluid at >~10 °C) would react with hydrophobic molecules dissolved in L/SC-CO<sub>2</sub>, possibly forming amphiphilic molecules that can arrange along the interface and might self-assemble into membrane-like structures (e.g., Mayer et al. 2017). It can be speculated that physicochemical interactions among L/SC-CO<sub>2</sub> and H<sub>2</sub>O-rich fluids triggered by varying environmental conditions (e.g., temperature and pressure) lead to the formation of vesicles and droplets and their interactions (e.g., coalescence and splitting). According to previous seafloor hydrothermal vent hypotheses, cell-like mineral compartments formed within hydrothermal mineral deposits at the time of proto-metabolism emergence (e.g., Russell and Martin 2004). Of course, such self-assembled amphiphilic molecules created by interface reactions between water and L/SC-CO<sub>2</sub> may become immobilized in the mineral compartments of hydrothermal mineral deposits, where they cooperate with minerals as prebiotic cellular membranes.

In addition to the above-described features of L/SC-CO<sub>2</sub> fluids and pools, the high dissolution capacities of L/SC-CO<sub>2</sub> for heavy metals might have contributed to the formation of metal-bearing biomolecules (e.g., enzymes and co-factors) because SC-CO<sub>2</sub> can be industrially used for heavy metal extraction (e.g., Lin et al. 2014). Moreover, polynucleotides such as RNA and DNA, which are generally hydrolyzed in water, may have been stabilized and preserved in L/SC-CO<sub>2</sub> fluids and pools because dry small interfering RNA (siRNA) and dry plasmid DNA (pDNA) can be pharmaceutically prepared using SC-CO<sub>2</sub> (e.g., Okamoto et al. 2005; Okuda et al. 2013). These chemical characteristics of L/SC-CO<sub>2</sub> fluids and pools might increase the reactivity and stability of typical biomolecules. One can therefore hypothesize that the abundant L/SC-CO<sub>2</sub> fluids and pools in Hadean seafloor hydrothermal systems served as novel and important reaction fields for prebiotic chemical evolution.

In the proposed hypothesis, not all processes of prebiotic chemical evolution are associated with L/SC-CO<sub>2</sub> fluids and pools in the Hadean seafloor hydrothermal systems. Instead, the L/SC-CO<sub>2</sub> fluids and pools just facilitate significant steps of prebiotic chemical evolution such as condensation, storage, and synthesis of molecular building blocks, which were previously considered to be difficult in water-filled seafloor hydrothermal environments. Abundant L/SC-CO<sub>2</sub> fluids and pools are widespread at and beneath the modern hydrothermally active seafloors. They are associated with high- and low-temperature vent fluids and are found in the cavities and spaces of hydrothermal mineral deposits and also in sediments. In the Hadean, therefore, various simple organic compounds might be abiotically produced under various physicochemical conditions, in different zones of the whole hydrothermal circulation (e.g., reaction zone and mixing zone) and in different fluids and solids (e.g., high-temperature hydrothermal fluids, seawater, and various minerals). In this case, it would be possible that the many local environments in the seafloor hydrothermal system co-worked as a series of factories to drive prebiotic chemical evolution owing to the whole hydrothermal circulation. This study highlights that many of the Hadean seafloor hydrothermal systems could provide abundant L/SC-CO<sub>2</sub> fluids and pools by the whole hydrothermal circulation processes. Our new hypothesis, named the “liquid/supercritical CO<sub>2</sub> hypothesis,” is consistent with previous hypotheses related to seafloor hydrothermal systems, some of which refer to low-temperature alkaline vents (e.g., Russell and Hall 1997; Russell et al. 2014; Shibuya et al. 2016) or high-temperature vents (Takai et al. 2006; Shibuya et al. 2010, 2015). Our hypothesis synergistically strengthens the grand “seafloor hydrothermal vent hypothesis.”

## 6 Conclusions and future perspectives

L/SC-CO<sub>2</sub> fluids and pools can provide dry environments serving as organic solvents in water-rich seafloor hydrothermal systems. Based on preliminary experimental and analytic data in industrial and pharmaceutical laboratories, L/SC-CO<sub>2</sub> is considered to possess unique physicochemical properties enabling the potential dissolution and condensation of heavy metal elements and organics, and possible dehydration synthesis of certain molecules (e.g., Hyatt 1984; Swaid et al. 1985). Widespread L/SC-CO<sub>2</sub> fluids and pools in modern seafloor hydrothermal systems are theorized to form by phase separation and phase segregation processes of CO<sub>2</sub>-enriched hydrothermal fluid in the whole hydrothermal circulation at and beneath the seafloor. Considering the geological time scale of the Earth and re-interpreting many lines of evidence in the known

geological records, widespread L/SC-CO<sub>2</sub> pools in seafloor hydrothermal systems probably formed throughout Earth history and were likely more dominant in the Hadean and early Archean eras than in the modern era. Based on theoretical considerations and observations, we here propose that the abundant L/SC-CO<sub>2</sub> fluids and pools in the Hadean seafloor hydrothermal systems served as a novel and important reaction field for prebiotic chemical evolution, particularly of condensation, storage, and maturation of hydrophobic and amphiphilic molecules. Our “liquid/supercritical CO<sub>2</sub> hypothesis” potentially overcomes the intrinsic “water paradox” of the “seafloor hydrothermal vent hypothesis.”

The solvent and reaction properties of L/SC-CO<sub>2</sub> interacting with seawater and hydrothermal fluids are mostly unknown in natural seafloor hydrothermal environments and remain unclear even in laboratory studies. Therefore, the basic properties of L/SC-CO<sub>2</sub> should first be investigated under different physical and chemical conditions (e.g., temperature and pressure and with/without seawater and other gases) in the laboratory. The dissolubility, preservability, and reactivity of organic compounds such as amino acids, organic acids, nucleosides and nucleotides, proteins, nucleic acids, and lipids should also be studied in L/SC-CO<sub>2</sub> systems. Second, we need to characterize the types of inorganic and organic compounds that dissolve in the natural L/SC-CO<sub>2</sub> fluids and pools of modern seafloor hydrothermal systems. This investigation will require elaboration of seafloor sampling and preservation tools. The analyzed data of natural L/SC-CO<sub>2</sub> fluids and pools in modern seafloor hydrothermal systems, which contain both abiotically and biologically produced compounds, will help to reveal the in situ behaviors and properties of L/SC-CO<sub>2</sub> fluids and pools in the whole hydrothermal circulation processes. These laboratory and field experiments and analyses will provide key insights for predicting the types of compounds that dissolve and condense in L/SC-CO<sub>2</sub> fluids and the types of reactions occurring in the L/SC-CO<sub>2</sub> fluids and pools of modern and Hadean seafloor hydrothermal systems. The physicochemical conditions of the L/SC-CO<sub>2</sub> fluids and pools in Hadean seafloor hydrothermal systems can be predicted by analyzing the Archean geologic records (e.g., alteration of volcanic rocks and fluid inclusions). Particularly, the natural entrainers and chelating agents of L/SC-CO<sub>2</sub> are possibly constrained by compositions of fluid inclusions containing L-CO<sub>2</sub> in Archean hydrothermal deposits. Through these field observations, laboratory experiments, and theoretical approaches, our new “liquid/supercritical CO<sub>2</sub> hypothesis” will be further combined with the “seafloor hydrothermal vent hypothesis” for a comprehensive understanding of the OOL.

## Abbreviations

L-CO<sub>2</sub>: Liquid CO<sub>2</sub>; SC-CO<sub>2</sub>: Supercritical CO<sub>2</sub>; L/SC-CO<sub>2</sub>: Liquid and supercritical CO<sub>2</sub>; OOL: Origin of life.

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## Author contributions

TS and KT proposed the topic and conceived and designed the study. All the authors read and approved the final manuscript.

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## Availability of data and materials

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## Declarations

## Competing interests

The authors declare that they have no competing interest.

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