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Perspective

A supercritical carbon dioxide layer in the Hadean atmosphere for the origin of life?

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Zhang et al. [1] reported the first direct detection of the natural supercritical CO_2 ($scCO_2$; critical point: 31.1 °C and 72.9 atm) in a deep-sea hydrothermal system. In their study, they measured *in situ* the Raman bands of $scCO_2$ bubbling from an approximately 95 °C hydrothermal vent. The Raman spectra indicated that the $scCO_2$ bubbles also trapped N_2 and CH_4 gases and unidentified organic carbons. This discovery suggests a scenario that a layer of $scCO_2$ might have existed in the Hadean atmosphere between the young ocean and the gaseous CO_2-dominated upper layers. Such a layer of $scCO_2$ in the atmosphere should have been highly active in trapping energetic small molecules and catalytic transition metals and polymerizing organic matters, thereby aiding the creation of a favorable planetary environment for prebiotic evolution toward life.

The origin of life is one of the greatest mysteries for mankind. One highly debated question is whether the organic matters for the prebiotic chemical evolution toward life on Earth were endogenous or exogenous [2]. The endogenous model argues that the geochemical reactions could and have selectively produced the organic matters [3,4]. However, they also debate whether these organic matters were photochemically synthesized in a cold atmosphere [5] or were cooked geochemically in hot, subsurface environments [3,4]. According to the current understanding, even if the early Earth had a proto-atmosphere accreted with reduced gases, such as CH_4, NH_3, H_2, and H_2S, the magma ocean process should have removed these gases and replaced them with a CO_2–H_2O atmosphere [6]. The Earth's early atmosphere was a highly "energetic" environment that allowed for the synthesis of organic matters. For instance, the direct interaction between the CO_2–H_2O atmosphere and the ultramafic crust in the Hadean eon could produce ample hydrocarbons [7]. However, the serpentinization (water–rock interaction) of the mafic- or ultramafic rocks at high temperatures (T), and the accompanying Fischer–Tropsch reactions might also have synthesized organic matters [4]. Although the ocean was a suitable habitat for the earliest living cells, it was not likely the environment for cells to originate because the early oceans were low in the contents of the essential materials and catalysts needed for the transition from geochemistry to biochemistry to happen [2].

As the organic matter delivered to Earth via comets/asteroids would be mostly destroyed by the impacts, it should not be considered the sole source of organic carbon in the Hadean eon [2]. In addition, such organic chemicals would have to be concentrated to make a primordial soup in Darwin's warm little pond before they could start the organochemical evolution toward life [2].

Where were the places on Earth those evolutionary processes had happened? As it is explained in Ref. [5], "Some like it hot, but not the first biomolecules". The research emphasizes that the small organic molecules, especially those carrying genetic information [2], required for the prebiotic evolution needed to be synthesized and accumulated at a low T for a long enough time for biochemistry to be established before being decayed. The other side of the coin is that "some like it hot", because Earth's atmosphere was probably already neutral very early on so that reactions in such an atmosphere could not produce enough organic matters [2]. So, roughly "Gene First" theory prefers a cold Earth while "Metabolism First" theory prefers a hot geochemical environment [8]. We think it is more reasonable to consider which process was more common on the early Earth that initiated a sufficient condition for another to start. In the view of thermodynamics, mineral (e.g., pyrite) catalyzed CO_2 reduction and carbon fixation [3] at high T should be common at the early habitable stage of Earth. For example, the synthesis of pyruvic acid, a small molecule for intermediary metabolism [9] is experimentally synthesized on iron sulfide at 250 °C and 200 MPa [3].

As an alternative to the atmosphere, the subsurface environments in Hadean were geochemically more capable of cooking a variety of organic matters. In these deep, hot geothermal environments, the highly-concentrated metal-sulfides or oxides may have catalyzed the syntheses of the vital organic compounds [4]. However, it was argued that the subsurface was probably not the environment for life to originate because of its low content of organic carbon and too slow the energy delivery processes to maintain the non-equilibrium order. Therefore, after considering these factors, the evolution from geochemistry to biochemistry, in which the transformation of the compartmentalized

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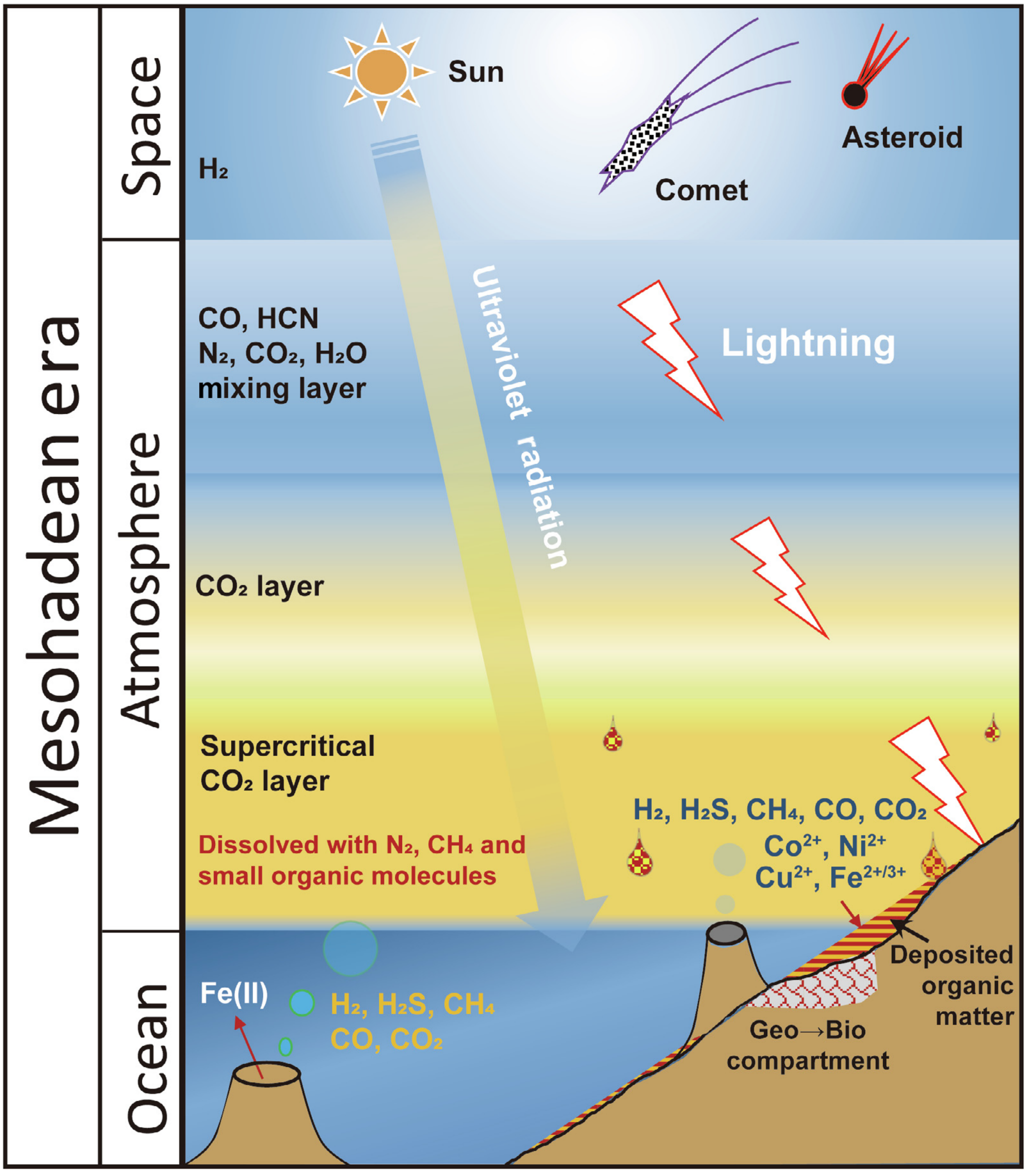

Fig. 1. The schematic of a supercritical CO_2 layer in the Mesohadean atmosphere. Based on our scenario, this $scCO_2$ layer in the atmosphere was the most productive planetary environment in the Mesohadean in making organic matters for the prebiotic organo-evolution toward life.

geochemical cells into the bacterial cells should have happened in the conduit to the ocean above [4].

Those studies indicate that neither the atmosphere nor the subsurface were sufficiently capable of supporting the whole prebiotic evolution toward life. However, the mechanism that combines the strengths of the atmospheric and the subsurface processes for the origin of life has not yet been found. Indeed, the geological subsurface and the atmosphere did not exchange much of energy or material in the Hadean eon because of the low energy flow and the lack of chemical reactive kinetics of matters that are the thermodynamic and kinetic requirements to support life [10].

By extrapolating the discovery by Ref. [1], we propose that there was once a layer of $scCO_2$ that existed between the gaseous CO_2-atmosphere above and an ocean of water below during the Mesohadean era (Fig. 1). Indeed, the densities of $scCO_2$ within its *T*-partial pressure (*P*) domain are lighter than that of seawater, but heavier than that of the gaseous CO_2 [11]. The $scCO_2$ layer contacted below with the global ocean and the sporadic super-volcanic islands (Fig. 1). It is suggested that about 167 million years after the accretion of Earth, the earliest ocean could have been formed from the precipitation of the atmospheric water vapor [6]. The *T-P* of the CO_2–dominated atmosphere could have simply defined the state of the $scCO_2$. It is calculated that a CO_2–H_2O atmosphere in equilibrium with the komatiitic crust could maintain a high CO_2 pressure (>73 atm) before and after H_2O precipitated into an ocean, and this high pressure lasted until the global *T* dropped to below 31 °C [12]. According to Ref. [5], the high global *T* could have continued to the early Archean, when life had already developed. However, the dropping of either *T* or *P* to below the critical point of $scCO_2$ would lead to the collapse of the $scCO_2$ layer in the atmosphere.

$ScCO_2$ is well-known for its capabilities of dissolving various non-polar organic molecules, polymerizing small organic molecules, and extracting of various transition metals [13]. It is showed that some important catalytic transitional elements, such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, among the others, could be extracted from a solid matrix (e.g., soil) and taken up by $scCO_2$ to make organotransition metal complexes [13], which are the right materials for prebiotic evolution toward complexity.

This putative $scCO_2$ atmospheric layer might have played a critical role in the prebiotic process of organo-geochemical evolution (Fig. 1). As an anhydrous organic solvent, the $scCO_2$ layer could enrich HCN, N_2, CH_4, and H_2S, the trace hydrocarbons photochemically synthesized in the atmosphere, and those emitted from the subsurface to make an atmospheric analog to Miller's glass flask [14]. HCN could be sourced from a CH_4-rich atmosphere (1000 ppmv) [15] or the out-space. With exposure to photochemistry, lightning and metal catalysts, small organic molecules could be polymerized [13]. Differently, the CO_2 reservoirs in the crust, including those under the $scCO_2$ *P-T* conditions, are made of almost pure CO_2 and inert in chemical reactions. These observations suggest that the putative $scCO_2$ layer in the Mesohadean atmosphere might have been a very important environmental setting where the vital prebiotic chemical evolution toward the origin of life occurred. The Hadean Earth should have frequent lightning storms in its dense CO_2 atmosphere (Fig. 1) [14]. In addition to the endogenous synthesis, organic matter delivered by comets or asteroids could also be trapped by this layer for exposure to further geochemical reactions.

The existence of this putative $scCO_2$ layer in the Hadean atmosphere may satisfy the requirements for both the cold- and hot-origin theories regarding organic matter synthesis and aggregation. This layer kept dissolving small energetic molecules and synthesizing them into organic deposits on the Earth's surface. Particularly, it also implies that this $scCO_2$ atmosphere could dissolve high contents of N_2 so that the atmospheric chemical reactions could synthesis more N-containing molecules such as amino acids [11,13]. The organic deposits made part of the compartmentalized geochemical cells [4] that are hypothesized to have fostered the emergence of the first living cells.

Conflict of interest

The authors declare that they have no conflict of interest.

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