Geoscience Frontiers xxx (2016) 1–10

HOSTED BY

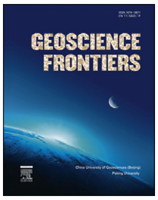
ELSEVIER

Contents lists available at ScienceDirect

China University of Geosciences (Beijing)

Geoscience Frontiers

journal homepage: www.elsevier.com/locate/gsf



Research paper

Reactions between olivine and CO_2-rich seawater at 300 °C: Implications for H_2 generation and CO_2 sequestration on the early Earth

Hisahiro Ueda[a,*], Yusuke Sawaki[a], Shigenori Maruyama[b]

[a] Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan
[b] Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan

ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form
17 September 2016
Accepted 3 October 2016
Available online xxx

Keywords:
Olivine
CO_2-rich condition
Early Earth
Hydrothermal alteration
Serpentinization
Experiment

ABSTRACT

To understand the influence of fluid CO_2 on ultramafic rock-hosted seafloor hydrothermal systems on the early Earth, we monitored the reaction between San Carlos olivine and a CO_2-rich NaCl fluid at 300 °C and 500 bars. During the experiments, the total carbonic acid concentration (ΣCO_2) in the fluid decreased from approximately 65 to 9 mmol/kg. Carbonate minerals, magnesite, and subordinate amount of dolomite were formed via the water-rock interaction. The H_2 concentration in the fluid reached approximately 39 mmol/kg within 2736 h, which is relatively lower than the concentration generated by the reaction between olivine and a CO_2-free NaCl solution at the same temperature. As seen in previous hydrothermal experiments using komatiite, ferrous iron incorporation into Mg-bearing carbonate minerals likely limited iron oxidation in the fluids and the resulting H_2 generation during the olivine alteration. Considering carbonate mineralogy over the temperature range of natural hydrothermal fields, H_2 generation is likely suppressed at temperatures below approximately 300 °C due to the formation of the Mg-bearing carbonates. Nevertheless, H_2 concentration in fluid at 300 °C could be still high due to the temperature dependency of magnetite stability in ultramafic systems. Moreover, the Mg-bearing carbonates may play a key role in the ocean-atmosphere system on the early Earth. Recent studies suggest that the subduction of carbonated ultramafic rocks may transport surface CO_2 species into the deep mantle. This process may have reduced the huge initial amount of CO_2 on the surface of the early Earth. Our approximate calculations demonstrate that the subduction of the Mg-bearing carbonates formed in komatiite likely played a crucial role as one of the CO_2 carriers from the surface to the deep mantle, even in hot subduction zones.

1. Introduction

Fluids circulating through ultramafic rocks are usually rich in reduced volatile constituents such as hydrogen and methane molecules (e.g., Neal and Stanger, 1983; Charlou et al., 2002, 2010; Etiope et al., 2011, 2016). These compounds could be important to sustain ecosystems, including chemolithoautotrophic microorganisms on the early Earth (e.g., Amend and McCollom, 2009; Russell et al., 2014). Even though hydrogen molecules provide the foundation for prebiotic chemical evolution and early energy metabolisms, the chemical reactions that regulate H_2 production remain uncertain. It is widely accepted that H_2 generation is tightly coupled with the oxidation of ferrous iron to ferric iron in parallel with the reduction of water molecule (e.g., Allen and Seyfried, 2003; Seyfried et al., 2007; McCollom and Bach, 2009). Multiple factors controlling H_2 generation have been suggested by previous studies such as the iron content of source minerals, the aluminum content of ultramafic rocks, the activity of silica, and the thermodynamic equilibrium between the mineral phases (e.g., McCollom and Bach, 2009; Klein et al., 2013; Shibuya et al., 2015).

Numerical modeling (Walker, 1985; Kasting, 1993; Elkins-Tanton, 2008) and geological records (Lowe and Tice, 2004; Ohmoto et al., 2004; Shibuya et al., 2007, 2012) indicate that atmospheric CO_2 levels on the early Earth were likely much higher than the present levels. Carbonate formation during the

---

* Corresponding author. Fax: +81 3 5734 3538.
E-mail address: ueda.h.ai@m.titech.ac.jp (H. Ueda).
Peer-review under responsibility of China University of Geosciences (Beijing).

http://dx.doi.org/10.1016/j.gsf.2016.10.002

Please cite this article in press as: Ueda, H., et al., Reactions between olivine and CO_2-rich seawater at 300 °C: Implications for H_2 generation and CO_2 sequestration on the early Earth, Geoscience Frontiers (2016), http://dx.doi.org/10.1016/j.gsf.2016.10.002

serpentinization of olivine under CO_2-rich conditions likely suppresses H_2 generation in fluids (Jones et al., 2010; Klein and McCollom, 2013; Neubeck et al., 2014); however, these studies examined temperature ranges up to 230 °C. McCollom et al. (2016) also conducted hydrothermal experiments using San Carlos olivine under CO_2-rich conditions (approximately 20 mmol/kg CO_2) at various temperatures up to 320 °C and emphasized the importance of temperature and iron partitioning for H_2 generation. However, due to the minor contribution of precipitated carbonate to the total mass balance, the influence of CO_2 on H_2 generation was not fully discussed in their study. Because the H_2 production rate derived from olivine hydration is greatest near 300 °C based on model calculations (Klein et al., 2013), the serpentinization of olivine under highly CO_2-rich conditions at such high temperatures should be tested via laboratory experiments.

Addition of carbon dioxide into experimental system has other key aspects. In the methane and hydrocarbons in the Rainbow and Lost City hydrothermal fields may have an abiotic origin (Charlou et al., 2002, 2010; Proskurowski et al., 2008), which could be important for the abiotic synthesis of building blocks on the early Earth. The production of abiotic methane possibly occur in association with Fischer-Tropsch-type reactions between molecular hydrogen from serpentinization and carbon compounds, such as CO_2 (Etiope and Sherwood Lollar, 2013), or direct olivine hydration in the presence of CO_2 (Oze and Sharma, 2005). However, recent hydrothermal experiments have demonstrated that significant amounts of methane are not generated by low temperature (50 °C) olivine hydration in CO_2-rich fluid (Neubeck et al., 2016.). Experiment in this study examines the possibility of methane production at higher temperature (300 °C). In the meanwhile, the early atmosphere may have contained all the Earth's carbon, corresponding to a partial pressure on the order of 10–340 MPa (Liu, 2004; Elkins-Tanton, 2008). If the majority of the carbon was in the early atmosphere, there must have existed large-scale carbon removal processes at a later time. On time scales of billions of years, the subduction of carbonated oceanic crust has the potential to transport carbon from the Earth's surface to its interior (Fig. 1). In current subduction zones, carbon in the crust remains stable as calcite during shallow dehydration and possibly hydrous melting according to phase equilibrium experiments (Yaxley and Green, 1994; Molina and Poli, 2000; Poli et al., 2009) and thermodynamic calculations (Kerrick and Connolly, 2001; Connolly, 2005). Moreover, the modern subduction of oceanic crust likely transports carbon into the deep mantle in the form of carbonated eclogite (Dasgupta et al., 2005). Sleep and Zahnle (2001) proposed catastrophic carbon removal from the ocean-atmosphere system via this process soon after solidification of the magma ocean. However, in the hot subduction zones on the early Earth, carbonate was likely released at shallow depths and might largely return to the atmosphere (Dasgupta and Hirschmann, 2010). Other mechanisms have been suggested to introduce carbon into the mantle, such as the subduction of (1) reduced carbon species such as graphite, (2) carbonate sequestered in deep subducting plates as altered peridotite, and (3) carbon trapped in lithospheric overriding plates (Sleep, 2009; Dasgupta and Hirschmann, 2010). Carbonate rocks on continents likely were minor prior to 2.0 Ga (Ronov, 1964; Veizer et al., 2003) and therefore could not account for a large inventory of carbon on the early Earth. Thermodynamic calculations indicate that Mg-bearing carbonate minerals are more stable than Ca-carbonate minerals in subduction P-T conditions on the early Earth (Aral et al., this volume). We focus on carbonate mineralogy formed in ultramafic rocks and its ability to remove CO_2 from the ocean-atmosphere system.

We performed a hydrothermal experiment to monitor the reactions between olivine and CO_2-rich seawater at 300 °C and 500 bars using a batch-type (closed system) hydrothermal reactor (Yoshizaki et al., 2009). The aims of this study are (1) to determine the quantities of hydrogen and methane molecules and (2) to determine the CO_2 absorption ability of ultramafic rocks via serpentinization under CO_2-rich conditions.

2. Sample preparation and experimental procedure

2.1. Starting material

Only olivine crystals from San Carlos (Arizona) were used in this experiment, and they were handpicked to exclude grains with obvious signs of weathering or inclusions of other minerals. The composition of the olivine was analyzed using an electron probe micro analyzer (EPMA). The analytical conditions for the EPMA were an accelerating voltage of 15 kV, a specimen current of 10 nA, and a counting time of 60–80 s. The results indicate that the olivine crystals have $Mg^\#$ values ($Mg^\# = 100 \times Mg/(Mg + Fe)$) ranging from 90 to 91 (Table 1). The olivine was crushed in an agate-ball mill and

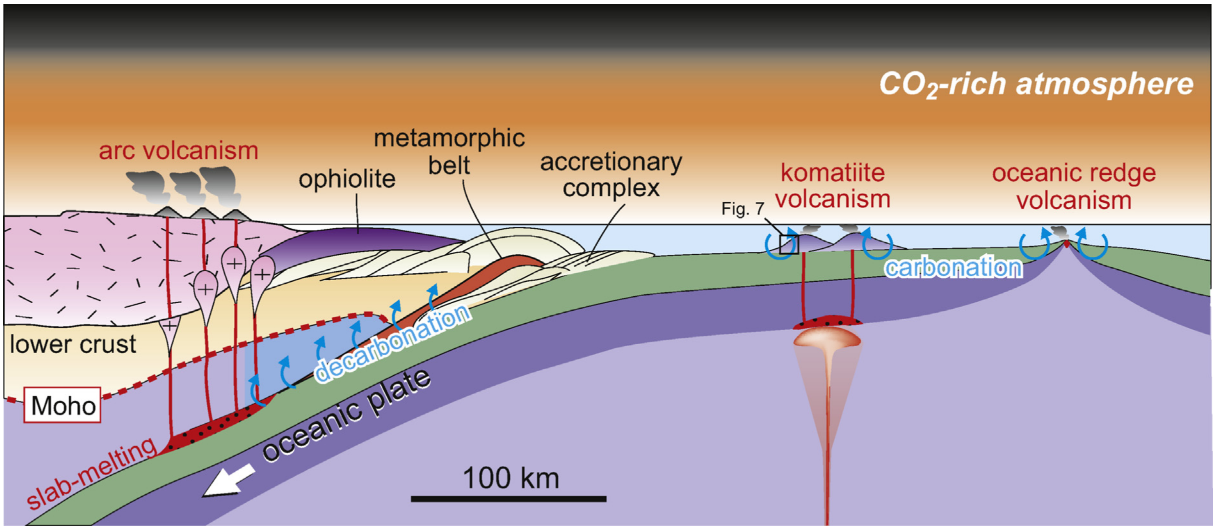


Figure 1. Schematic of surface environment on the early Earth. Under CO_2-rich conditions, carbonation of oceanic crust occurs in hydrothermal systems. The oceanic crust releases some amount of carbon (decarbonation) at the subduction zone depending on its P-T trajectory and carbonate mineralogy.

Please cite this article in press as: Ueda, H., et al., Reactions between olivine and CO_2-rich seawater at 300 °C: Implications for H_2 generation and CO_2 sequestration on the early Earth, Geoscience Frontiers (2016), http://dx.doi.org/10.1016/j.gsf.2016.10.002