論文 / 著書情報
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題目(和文)	コマチアイトと二酸化炭素に富んだ海水との反応で発生する水素についての実験的研究：初期地球における熱水流体への示唆
Title(English)	Experimental study on H2 generation by the reactions between komatiite and CO2-rich seawater: Implication for hydrothermal fluid in the early Earth
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	地球惑星科学　　コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　理学　）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This thesis reports experimental study on H_2 generation by the reactions between komatiite and CO_2-rich seawater. The results of the experiment are used to deduce chemistry of hydrothermal fluid in the early Earth.

In Chapter 1, the role of H_2-rich ultramafic-hosted hydrothermal systems are reviewed. The H_2-flux is important for early evolution of life and ecosystem as well as redox condition of the early atmosphere. The fluid chemistry of ancient hydrothermal systems has been poorly understood because of the uncertainty of host rocks and seawater composition. The early curst may have been komatiitic and the early seawater was probably rich in CO_2, however, it is poorly understood how the CO_2-rich seawater affected the fluid chemistry of the ultramafic-hosted hydrothermal system. In this study, systematic experimental studies were conducted to understand the fluid compositions in the komatiite-hosted seafloor hydrothermal system and evaluate the role of the CO_2-rich seawater.

In Chapter 2, I have conducted a simple reaction between olivine and a CO_2-rich NaCl fluid at 300°C and 500 bars in order to evaluate the effect of CO_2 qualitatively, and it is characterized as a preliminary experiment to investigate serpentinization under CO_2-rich conditions for the next experiments of using komatiite in Chapter 3. As a result, Mg-bearing carbonates were formed via the water-rock interaction. I found for the first time that the H_2 production rate was relatively lower than those of the CO_2-free system at the same temperature. The result suggests that the CO_2 in seawater may play a role for suppress H_2 production during the serpentinization process.

In Chapter 3, I focused on the komatiite-hosted hydrothermal systems. I monitored the reaction between synthetic komatiite and a CO_2-rich NaCl fluid at 100–350 °C and 500 bars up to 5372 hours. After the reaction, the komatiite was strongly carbonated and yield Fe(II)-bearing minerals mainly dolomite, ankerite and magnesite below 300°C, whereas the main carbonate was calcite at 350°C. Furthermore, the results show that the carbonation of komatiites clearly suppressed H_2 generation in the fluids. The steady-state H_2 concentrations in the fluid was very low (<1 mmol/kg) below 300°C, compared with the high H_2 (23 mmol/kg) observed in the CO_2-free system. The Fe content in carbonate minerals apparently correlated with the H_2 concentration, suggesting that the incorporation of ferrous iron into the carbonate minerals probably limit the oxidation of ferrous iron (i.e. magnetite formation), and thus suppressed H_2 produced by the reduction of H_2O. This suggests that flux of H_2 by serpentinization reaction may have been much lower than previously thought under the presumably CO_2-rich early seawater. In addition, the observed Mg concentrations (up to ca. 40 mmol/kg) below 300°C were higher than those in modern high-temperature hydrothermal fluids (<1 mmol/kg). This suggests that, in contrast to the modern hydrothermal systems, the komatiite-hosted hydrothermal systems might have served as a source of Mg in ancient ocean by the effect of CO_2-rich fluid.

In Chapter 4, the equilibrium state of the water-rock reaction was calculated and compared with the experimental results in Chapter 3 for mechanistic understanding of the reaction. I conducted thermodynamic calculations designed for komatiite-H_2O system at various temperatures (100–350 °C) and water-rock ratios (1–10) by using a software EQ3/6. Under CO_2-free condition, the estimated H_2 production is roughly consistent with the experimental results in Chapter 3. On the other hand, under CO_2-rich condition, the calculated H_2 production is much higher than the experimental results except for 100°C. The calculated mineral assemblages are also different from those of the experiments. Particularly, calculated amount of magnetite formation at equilibrium is higher than observed in the experiments. The difference between the equilibrium calculation and the experiment suggest that magnetite formation is kinetically prohibited in the actual experiment of komatiite-seawater reaction under CO_2-rich condition.

In Chapter 5, all the experimental results and thermodynamic calculations are summarized. In the early Earth, global H_2 flux from serpentinization is estimated to be order of magnitude smaller than those predicted previously if considering the high-CO_2 environment. In this case, the global H_2 flux from serpentinization is not a main factor for controlling redox state of the atmosphere, compared with the total volcanic H_2 outgassing. On the other hand, in terms of H_2 as an energy source for life, the H_2 concentration of the fluid at 350 °C corresponds to that of modern H_2–rich seafloor hydrothermal systems, such as the Kairei hydrothermal field, where hydrogenotrophic methanogens dominate in the prosperous microbial ecosystem. In contrast, the H_2-rich fluids may not have been generated by serpentinization at temperatures below 300°C in the komatiite-H_2O-CO_2 system. In addition, experimental result suggests that Mg flux from the komatiite-H_2O-CO_2 system is expected to be much higher than those of modern seafloor hydrothermal systems, which is comparable to modern riverine input. This implies that the komatiite hydrothermal system could have been a main source of Mg into the early ocean.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
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