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Highly alkaline, high-temperature hydrothermal fluids in the early Archean ocean

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ABSTRACT

Based on the petrology of hydrothermally altered Archean basaltic greenstones, thermodynamic calculations of phase equilibria were conducted to estimate the composition of a high-temperature (∼350 °C) hydrothermal fluid in an Archean subseafloor basalt-hosted hydrothermal system. The results indicate that the hydrothermal fluid was highly alkaline attributed to the presence of calcite in the alteration minerals under a high-CO_2 condition, and predict a generation of SiO_2-rich, Fe-poor hydrothermal fluids in the Archean subseafloor hydrothermal system. The chemically reactive mixing zones between alkaline hydrothermal fluids and slightly acidic-neutral seawater are characterized by inverse pH and chemical polarity to modern hydrothermal systems, leading to extensive precipitation of silica and iron oxyhydroxides on/under the seafloor. Such processes can be responsible for the abiotic formation of voluminous chert and subseafloor silica dike, the mechanism of silicification, and the pH-controlled generation of banded iron formation that has been arising mainly from the redox chemistry in the Archean ocean. Such high-temperature alkaline fluids could have had a significant role not only in the early ocean geochemical processes but also in the early evolution of life.

1. Introduction

Coevolution of environment and life through the history of the Earth is a fundamental issue of the Earth sciences today. Archean chert and banded iron formation (BIF) are of great interest because they harbor key trace elements and chemical–biological fossils for elucidating chemical properties of ancient seawater (Ohmoto, 1997; Holland, 1999; Bjerrum and Canfield, 2002) and early evolution of biological activity (Schopf, 2006). The formation processes of Archean chert and BIF have been explained mainly by the chemical reaction between hydrothermal fluid and seawater (Dymek and Klein, 1988; Van den Boorn et al., 2007). Most of the models seem to depend on an important assumption that the chemical property of Archean hydrothermal fluids was substantially similar to those of modern hydrothermal fluids, typically acidic, iron-rich hydrothermal fluids. However, the assumption is not yet justified because the hydrothermal fluids should originate from the source fluid, ancient seawater. If the Archean seawater is chemically different from the modern entity (e.g., slightly acidic-neutral and enriched with CO_2) (Grotzinger and Kasting, 1993; Ohmoto et al., 2004; Rouchon and Orberger, 2008), it should be presumed that different alteration processes occurred in an Archean subseafloor hydrothermal system, leading to the generation of different compositions of hydrothermal fluid in the modern Earth. Recently, it was pointed out that hydrothermal alteration of Al-depleted komatiite has the potential to generate alkaline-, Si-, and Fe-enriched fluid, which could influence the formation of BIF (Wang et al., 2009). However, many geological studies have demonstrated that both oceanic crust and plateau were dominated by basaltic rocks rather than by Al-depleted komatiite (Ohta et al., 1996; Komiya et al., 1999; Hickman, 2004; Furnes et al., 2007; Van Kranendonk et al., 2007), and that hydrothermal circulation in basalt-hosted systems had a significant role in the early ocean geochemical processes.

In this paper, thermodynamic calculations of phase equilibria are conducted on the basis of the hydrothermal alteration of Archean basaltic greenstones, which can provide the chemical property of a high-temperature hydrothermal fluid in the Archean basalt-hosted hydrothermal system. The results provide new insights on the formation processes of Archean chert and BIF. We finally discuss a potential ancient microbial ecosystem in the hydrothermal environment because seafloor hydrothermal systems have been considered as possible candidates for the origin and early evolution of life on Earth (e.g., Russell et al., 1993; Takai et al.,

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2004, 2006; Russell and Arndt, 2005; Russell, 2007; Martin et al., 2008).

2. Theoretical consideration

In the present hydrothermal systems, it is widely accepted that *in situ* pH ($pH_{in\ situ}$) and redox conditions of high-temperature hydrothermal fluids are strongly buffered by the mineral assemblage of plagioclase + epidote + anhydrite at the hydrothermal reaction zone. Anhydrite influences the redox condition of the hydrothermal fluid together with plagioclase and epidote (Seyfried and Ding, 1995). The anorthite component in plagioclase and the clinozoisite component in epidote control the $a\mathrm{Ca}^{2+}/a^2\mathrm{H}^+$ ratio of the hydrothermal fluid (Seyfried et al., 1991), while Ca^{2+} concentration is also controlled by metastable, igneous calcic plagioclase in fresh rocks (Berndt and Seyfried, 1993). This process maintains the value of $pH_{in\ situ}$ around 5 that is close to the neutral pH at high-temperature condition (Seyfried et al., 1991), which was confirmed by direct *in situ* pH measurements of deep-sea high-temperature hydrothermal fluid (Ding et al., 2005). Acidification of the hydrothermal fluid is caused by precipitation of metal sulfides, dissociation of H^+-bearing complexes due to decreasing temperature during emission on the seafloor (Ding et al., 2005).

There are, however, significant differences between the modern and Archean hydrothermal alteration processes. While carbonate minerals in modern oceanic crust are limited within the low-temperature alteration zone and lack in the deep high-temperature reaction zone (e.g., Alt, 1995), Archean seafloor basalts show extensive alteration and strong carbonatization attributed to the high-CO_2 concentration in seawater/hydrothermal fluid (Kitajima et al., 2001; Terabayashi et al., 2003; Nakamura and Kato, 2004; Shibuya et al., 2007), which led to almost complete albitization of igneous calcic plagioclase and calcite-bearing secondary mineral assemblages even at high-temperature conditions (~350–400 °C; Kitajima et al., 2001; Terabayashi et al., 2003; Shibuya et al., 2007). Furthermore, anhydrite was not precipitated in the Archean subseafloor basalt probably because of extremely low sulfate concentration in the anoxic ocean (Kump and Seyfried, 2005). Therefore, the mineral assemblage that influenced Archean high-temperature hydrothermal fluid is characterized by the presence of calcite and the absence of anhydrite and igneous plagioclase as compared with the modern equivalent, whereas epidote is one of the common representative alteration minerals in both Archean (e.g., Terabayashi et al., 2003) and modern high-temperature alteration zones (e.g., Alt, 1995).

3. Assumptions

3.1. Mineral activities of Archean hydrothermally altered greenstones

Greenstone sequence in the 3.5 Ga North Pole area, Pilbara Craton, Western Australia, was used as an example of hydrothermally altered basalts in the early Archean because early Archean seafloor hydrothermal alteration is exceptionally well preserved in this area (Kitajima et al., 2001; Terabayashi et al., 2003). This area exposes repeated basalt–chert sequences that originate from a submarine oceanic plateau formed by mantle plume magmatism (Smithies et al., 2005; Van Kranendonk et al., 2007). Layer-parallel faults are present at the structural top and bottom of the each basal-chert unit, but the basaltic sequences individually preserve a prefaulting seafloor hydrothermal alteration caused by the geothermal gradient of crust (Kitajima et al., 2001; Terabayashi et al., 2003). The metamorphic grade of each unit generally increases from sub-greenschist (e.g., prehnite–pumpellyite) facies to greenschist/amphibolite facies transition with depth (Terabayashi et al., 2003), which is also supported by an increase in temperature from 120 °C to 300 °C with depth estimated from fluid inclusions in hydrothermal quartz veins (Harris et al., 2009). The greenstones underwent various extents of carbonatization but the calcite-dominated zone generally exists at the topmost part of the unit (Terabayashi et al., 2003), which indicates that the stratigraphic change in the degree of carbonatization is also cut by the faults at the top and bottom of the units. This suggests that the calcite was formed during a seafloor hydrothermal alteration prior to fault imbrication. Although barite beds and veins are also present in a unit, the barite veins occur only in the shallower part, 0–100 m below the contact between pillowed basalt and chert/barite bed (Ueno et al., 2008), indicating lack of barite in the high-temperature alteration zone.

To estimate the composition of a high-temperature hydrothermal fluid, we used the greenstones altered at high temperatures (ca. 300–400 °C) with a mineral assemblage of calcite + plagioclase + epidote + chlorite + actinolite ± hornblende (stratigraphically lower part of "GS Zone" in Terabayashi et al., 2003). The greenstones generally preserve igneous textures such as intersertal, intergranular, and subophitic textures. Igneous plagioclase is replaced by epidote, secondary sodic plagioclase, and calcite, while minor igneous glass is replaced by chlorite, actinolite, hornblende, and calcite. Igneous clinopyroxene is partially retained and tends to be fringed by chlorite, actinolite, or hornblende. These secondary minerals are in contact with each other in many places and do not show crosscutting relationships. Such an intimate relationship of secondary minerals indicates that they crystallized simultaneously with each other. Therefore, a chemical equilibrium of the secondary minerals can be assumed. Although available mineral composition data are mainly derived from Terabayashi et al. (2003), some samples with insufficient mineralogical data were compensated by our analyses using an electron-probe microanalyzer (JEOL-JXA-8900RL) (see Appendix B). Although the minerals in natural samples have inherent compositional variations, the data provide constraints on mineral activities; the anorthite content in plagioclase is 1–5% and XFe^{3+} ($Fe_2O_3/(Fe_2O_3 + Al_2O_3)$) of epidote is 0.26–0.30, indicating that activity of anorthite is lower than 0.05 and that of clinozoisite is higher than 0.1. These values provide a lower limit of $pH_{in\ situ}$ in the calculation.

3.2. ΣCO_2 concentration

The total CO_2 concentration ($a\mathrm{CO}_{2(aq)} + a\mathrm{HCO_3}^- + a\mathrm{CO_3}^{2-}$) ($[\sum CO_2]$) of the Archean subseafloor hydrothermal fluid should be higher than the modern value because of the ubiquitous occurrence of calcite in the Archean greenstone, but the quantitative value has not been estimated. Therefore, we semiquantitatively constrained $[\Sigma CO_2]$ in the Archean hydrothermal fluid by comparing with modern basalt-hosted hydrothermal systems. At present, the $[\Sigma CO_2]$ in the hydrothermal fluid increases up to 0.2 mol/kg at evident magmatic events (Von Damm and Lilley, 2004), while the composition of the high-temperature fluid is strongly controlled by mineral-fluid equilibria even at a magmatic event (Lilley et al., 2003). However, calcite is completely absent in the modern high-temperature alteration zone (reaction zone) (Alt, 1995). The lack of calcite under high $[\Sigma CO_2]$ conditions indicates that $[\Sigma CO_2]$ of the Archean hydrothermal fluid was high enough to precipitate calcite in altered basalt, namely, higher than 0.2 mol/kg. Considering CO_2-rich seawater (Grotzinger and Kasting, 1993) and extremely frequent magmatic events to form thick oceanic crust (Sleep and Windley, 1982; Komiya, 2004) and plateau (Van Kranendonk et al., 2007) in the early Archean, the $[\Sigma CO_2]$ of Archean hydrothermal fluid is expected to be much higher than 0.2 mol/kg. Therefore, we simply used the value as a semiquantitative, minimum $[\Sigma CO_2]$