Formation of Fe(III)-oxides on the magnetite surfaces in the low-temperature hydrothermal reaction

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Low-temperature hydrothermal experiments were conducted to investigate mineral formation on the magnetite surfaces. The synthesized magnetite single crystals grown up to approximately 100 µm in size had a truncated-octahedral shape enclosed by {111}, {100}, and {110} planes, but the {100} plane was composed of many micro/nano pyramid arrays. The as grown magnetite was hydrothermally treated in deoxidized water at 100 °C for 30 days. The molecular hydrogen generation was detected by methylene blue colorimetric measurement. SEM observations showed that after the hydrothermal reaction the magnetite (100) surfaces were selectively dissolved and enormous number of hematite (α-Fe₂O₃) nanoparticles were epitaxially grown on the magnetite (111) surfaces. At the shallow depth of the magnetite (100) surfaces within 200 nm, magnetite was transformed to maghemite (γ-Fe₂O₃). This is the first report that maghemite is formed as a Fe(III)-oxide by the low-temperature hydrothermal alteration of magnetite. Both the selective dissolution and maghemite formation on the magnetite (100) surfaces would be responsible for the anisotropic diffusion property of Fe²⁺ cations in magnetite.

Keywords: Magnetite, Hematite, Maghemite, Transmission electron microscopy, Epitaxial growth

INTRODUCTION

Since the discovery of hydrothermal chimneys and black smoker vents in 1979 (Corliss et al., 1979), a great variety of hydrothermal vents has been found (e.g., Hekinian et al., 1983; Normark et al., 1983; Haymon et al., 1991; Auzende et al., 1996; Stofflers et al., 2006; Connelly et al., 2012). After more than two decades of the pivotal discovery, the Lost City hydrothermal field (LCHF), a new type of submarine hydrothermal system, was discovered. The hydrothermal flow at this site is driven by exothermic serpentinization reactions in ultramafic oceanic crust (Kelley et al., 2001, 2002). The LCHF is furthermore characterized by high pH (9–11) and low temperature fluids (40–91 °C) enriched in H₂ (up to 15 mmol/kg) and CH₄ (1–2 mmol/kg) with 1 mmol/kg of CO₂ (Kelley et al., 2005; Ludwig et al., 2006; Proskurowski et al., 2006). Such a unique environment provides a suitable condition for bacterial and archaeal communities (Schrenk et al., 2004; Kelley et al., 2005; Brazelton et al., 2006).

Mayhew et al. (2013) performed laboratory experiments at 55 and 100 °C with natural peridotite, olivine, clinopyroxene, and magnetite to investigate the molecular hydrogen generation mechanism at low temperatures. The authors found a strong correlation between molecular hydrogen generation and the presence of spinels (magnetite and chromite). They also observed the Fe(III)-(hydr)oxide as a product of the hydrothermal reaction on the magnetite surfaces, although they could not uniquely identify the Fe(III)-bearing phases. Consequently, they have proposed that electron transfer from spinel particles to adsorbed water molecules or protons is the predominant pathway for H₂ generation (Mancey et al., 1993; Parkinson et al., 2011).

Furthermore, very recently, Mayhew et al. (2018) reported that the Fe(III)-(hydr)oxide minerals, hematite and goethite, are commonly observed in the highly serpentinized peridotites in the Samail ophiolite in the Sultanate of Oman, whereas magnetite is relatively rare and mainly associated with chromite. These observations are consistent with the results of Streit et al. (2012) who found that hematite is more common than magnetite in such highly altered rocks.

In this study, we performed the laboratory experi-
ments at 100 °C with synthesized pure magnetite single crystals. We carefully investigated the hydrothermally altered magnetite surfaces by scanning and transmission electron microscopy. Here, we report new formation of Fe(III)-oxide, maghemite (γ-Fe₂O₃) and hematite (α-Fe₂O₃), by the low-temperature alteration of magnetite.

**EXPERIMENTAL METHODS**

Single crystals of magnetite were prepared by a slight modification of the method described by Sato et al. (2014). Ferrous chloride tetrahydrate FeCl₂·4H₂O (FUJIFILM Wako Pure Chemical Corp., purity; >99.9 %) and sodium hydroxide (FUJIFILM Wako Pure Chemical Corp., purity; >97.0%) were used as starting materials. First, 5 mmol of FeCl₂·4H₂O was dissolved in 20 ml of distilled water with stirring. Second, 10 mL of NaOH aq. (4 mol/L) was added to the solution and a grey-green precipitate was formed. The solution was then sealed in a 28 ml Teflon-lined stainless steel autoclave and heated at 200 °C in an oven for 6 h. After the autoclave was cooled to the room temperature, black precipitates were collected by the magnetic separation technique. They were subsequently rinsed three times with distilled water and ethanol. Size of the magnetite single crystals obtained by this method was ranged from 5 to 10 µm. To increase the crystal size, the magnetite single crystals were transferred to a quartz capsule and sealed under vacuum. It was then heated at 1200 °C in an electric furnace for 3 days. By this solid-state crystal growth method, the magnetite single crystal size grew up to approximately 100 µm. The magnetite single crystals prepared were stored in a vacuum desiccator until used.

The synthesized magnetite single crystals were transferred to a glove box under a nitrogen gas atmosphere. About 2 g of the magnetite crystals were introduced into the 28 ml Teflon-lined stainless steel autoclave. Ultrapure water was in advance sufficiently bubbled with N₂ gas to remove dissolved O₂. 14 ml of the deoxidized water were added into the Teflon container. The autoclave was tightly sealed and then heated at 100 °C for 30 days. After the hydrothermal treatment, the magnetite crystals were removed from the Teflon container and dried at room temperature.

Dissolved H₂ in the water after the hydrothermal treatment (molecular hydrogen generation) was qualitatively checked by methylene blue colorimetry (Seo et al., 2012). The methylene blue reagent (MiZ Company, Kanagawa, Japan) was dropped into the waters before and after the hydrothermal treatment. Transmitted white light through the water was monitored with the complementary metal-oxide-semiconductor (CMOS) sensor in the smartphone camera. The visible spectra are analyzed using the Spectral Viewer software (Watanabe, 2017).

Scanning electron microscopy (SEM) analysis was performed with a JEOL JSM 6330F SEM with an accelerating voltage of 5 kV. After amorphous carbon was deposited on the sample surface, a cross-section was prepared with a JEOL JEM-9320FIB focused ion beam (FIB) system using a 30 keV Ga ion source. The FIB cross-section was analyzed using a JEOL JEM-2100F transmission electron microscope (TEM) operated at 200 kV equipped with scanning transmission electron microscopy (STEM). All image processing was carried out using Gatan’s Digital Micrograph and Image J softwares.

**RESULTS**

Figures 1a and 1b show the morphology of as grown magnetite. The synthesized magnetite single crystals had a truncated-octahedral shape enclosed by {111}, {100}, and {110} surfaces, which is approximately consistent with the previous report (Zhao et al., 2008). It is however especially important to note that the {100} surfaces are composed of many pyramid arrays of different size from hundreds nanometers to several micrometers (Fig. 1b). The all pyramids appear to have {111} surfaces and grown along the [100] axis.

After the low-temperature hydrothermal treatment, pH value of the water in the Teflon container was slightly decreased from 7.0 to 6.5. The results of the methylene blue colorimetric measurement are given in Figure 2.
With the hydrothermal treatment on magnetite, the intensity of the transmitted light through the methylene blue solution increased in the range of wavelength from 530 to 700 nm corresponding to the blue region. The result suggests the molecular hydrogen generation by the hydrothermal reaction with magnetite in the container.

Figures 1c and 1d display the morphological changes of magnetite (111) and (100) surfaces by the hydrothermal treatment, respectively. It is noteworthy that after the low-temperature hydrothermal reaction, an enormous number of spherical-shaped and spindle-shaped particles ranging up to 500 nm were formed on the magnetite (111) surfaces (Fig. 1c). As mentioned later, these nanoparticles are solely composed of hematite, α-Fe₂O₃. Unlike the magnetite (111) surface, on the other hand, these characteristic features were rarely found on the (100) surfaces (Fig. 1d). Figure 3 shows the HRTEM image of cross-section perpendicular to as grown (111) magnetite surface before the hydrothermal treatment. The fast Fourier transform (FFT) diffraction pattern is in good agreement with that of magnetite projected along the [1/2210] zone axis. Hence, there is no evidence that hematite nanoparticles were formed on the magnetite (111) surfaces before the hydrothermal treatment.

Based on the result that two types of distinguishable particles are found on the (111) surface (Fig. 1c), we investigated the possibility that several Fe(III)-(hydr)oxides, such as ferricyanide, hematite, and goethite, may be formed as a product of the reaction. Figure 4 shows the HRTEM images of the hydrothermally treated magnetite perpendicular to (111) surface. Both spherical-shaped and spindle-shaped particles are observed in Figure 4a. The regions (c) and (e) in Figure 4b correspond to the spherical-shaped and spindle-shaped particles, respectively. The FFT diffraction patterns reveal that these particles are composed of hematite single crystals (Figs. 4c and 4e). The different contrast between the two hematomalites would be attributed to the different crystal orientation.

The FFT image of the basement on which hematite particles are confirmed corresponds to magnetite (Fig. 4d). The atomic models of magnetite and hematite projected along the corresponding directions are overlapped for comparison (Figs. 4f and 4g). The FeO₆ octahedral layers parallel to the hematite (006) plane are perfectly matched with those of magnetite (111) plane. The similarity in the stacking of FeO₆ octahedral layers lead to the epitaxial growth of hematite on the magnetite (111) surface. On the other hand, because no epitaxial relationship existed between spindle-shaped hematite and magnetite (Fig. 4e), the spindle-shaped hematite should be precipitated from the solution.

As it can be seen in Figure 5a, a faint straight line running across the near-surface can be recognized. The selected area electron diffraction (SAED) pattern confirms that the region below the straight line is composed of magnetite. However, forbidden reflections of magnetite with space group Fd3m, hkl are not all odd or all even such as 011 and 122, were observed at both the region above the straight line and the part of the pyramidal object (Fig. 5b). In the present study, we carefully considered the possibility of multiple diffraction from magnetite because the multiple diffraction spots often lead to an incorrect assignment of the space group. We consequently determined that these extra spots are directly derived...
from a different phase with a different space group. The diffraction spots in the SAED pattern (Fig. 5b) are in complete agreement with the primitive cubic maghemite (γ–Fe₂O₃) with space group P4₁32. Maghemite is essentially identical to that of magnetite, but can be derived from magnetite by introducing 1/3 vacancies in the octahedral site, due to the oxidation of Fe(II) to Fe(III). It is especially noteworthy that magnetite was transformed to maghemite at the shallow depth of the magnetite (100) surfaces within 200 nm during the low-temperature hydrothermal alteration of magnetite.

**DISCUSSION**

In the low-temperature hydrothermal experiment, pH value of the water in the Teflon container decreased from 7.0 to 6.5, which is exactly in the same range as that reported in the previous study (Mayhew et al., 2013). Molecular hydrogen generation and formation of Fe-oxidized phases like ferrihydrite, hematite, and goethite are known to occur during the peridotite–water interaction (Olsson et al., 2012; Streit et al., 2012; Mayhew et al., 2013; Bach, 2016; Mayhew et al., 2018). A possible mechanism proposed on the basis of experimental results (Mayhew et al., 2013) is that the oxidation of Fe²⁺ released from primary minerals occurs in solution or it is promoted by interfacial electron transfer across the mineral surfaces. The later model may successfully explain the mineral evolution on the magnetite surfaces in the study.

Taking the possibility of multiple diffraction into account, we considered the forbidden reflections derived from screw axis or glide plane of magnetite. In general, when a structure projected along the incident beam has a
screw axis or glide plane, forbidden spots can appear (Nagakura and Nakamura, 1983). Forbidden reflections resulting from the face-centered lattice, on the other hand, never appear as multiple diffraction. In the space group $F\overline{4}3m = F4/ id\overline{3}2/m$, No. 227 in the International Tables for X-ray Crystallography, there is neither screw axis nor glide plane running along the [411] zone axis. Furthermore, the reflections such as 011 and 122 are the forbidden reflections resulting from the face-centered lattice. Therefore, the extra spots in the SAED pattern (Fig. 5b) cannot be generated by the multiple diffraction with strong Bragg reflections. Thus, we concluded that maghemite ($\gamma$-Fe$_2$O$_3$) was formed by the low-temperature hydrothermal alteration. Magnetite crystallizes in the inverse spinel structure, $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$, where Fe$^{2+}$ cations lie on octahedral sites and the Fe$^{3+}$ cations are distributed equally between octahedral and tetrahedral sites. By the transformation from magnetite to maghemite, 2/3 of the Fe$^{2+}$ cations in the octahedral site are oxidized to Fe$^{3+}$, while the remaining 1/3 diffuse from the lattice leaving behind vacancies (Bowles et al., 2011). The ordering of the vacancy within the octahedral positions gives rise to the symmetry change to primitive lattice (Pecharromán et al., 1995). The transformation from magnetite to maghemite is commonly found in oxidation of magnetite (Okudera et al., 2012; Jafari et al., 2015; Cuenca et al., 2016). Magnetite and maghemite have the same inverse spinel structure with octahedral and mixed tetrahedral/octahedral layers stacked along the [111] direction, resulting in the most thermodynamically stable (111) surfaces. As it can be seen in Figure 1, the (100) surfaces composed of many micro/nano pyramidal arrays have much larger specific surface areas than (111) surfaces. This result suggests that magnetite is selectively dissolved from the (100) surfaces by the hydrothermal reaction. In addition, the fact that maghemite is found only near the (100) surfaces would be also related to the anisotropic diffusion property of Fe$^{2+}$ cations in the magnetite.

The $\text{pH}_{\text{pzc}}$ (pH at the point of zero charge) is an important parameter since it determines whether the surface tends to be negatively charged or positively charged. For magnetite, the $\text{pH}_{\text{pzc}}$ at 100 °C is ranged from 6.00 to 6.24 (Vidojkovic and Rakin, 2017). The magnetite surface therefore becomes negatively charged at pH 6.5 in the low-temperature hydrothermal condition (Jolsterå et al., 2012). The Fe$^{2+}$ released from the magnetite would be preferentially adsorbed on the magnetite (111) surfaces because of the most thermodynamically stable surface. During the adsorption process, the Fe$^{2+}$ is oxidized to Fe$^{3+}$ by the electron transfer to adsorbed water molecules or protons (Mancey et al., 1993; Parkinson et al., 2011; Mayhew et al., 2013). As a result, hematite crystals are epitaxially grown on the magnetite (111) surface.

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**SUPPLEMENTARY MATERIALS**

Color versions of Figures 3 and 4 are available online from https://doi.org/10.2465/jmps.180717a.

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