Si-magnetite nano-precipitates in silician magnetite from banded iron formation: Z-contrast imaging and ab initio study

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ABSTRACT

Si-bearing magnetite or silician magnetite is common in low- and high-temperature rocks. However, details about possible Fe-silicate or Si-Fe-oxide discrete phases/nano-precipitates were not available due to the limitations of conventional high-resolution TEM. Combining Z-contrast imaging and ab initio calculation using density functional theory (DFT) method, we have derived both composition and crystals structure of the discrete nano-precipitates within host magnetite. The nano-precipitates of Si-magnetite with composition of [\(\text{Fe}_2\text{SiO}_4\)](\(\text{Fe}^{3+}\))\(\text{Si}^{4+}\)\(\text{O}_2\) or \(\text{γ-Fe}_2\text{SiO}_4\) occur in silician magnetite from a banded iron formation from Western Australia. In the Si-magnetite precipitates, Si replaces Fe\(^{3+}\) in tetrahedral sites of the magnetite structure and vacancies are introduced in the octahedral Fe\(^{2+}\) sites. The Si-magnetite precipitates distribute along \{111\} of the host magnetite. Widths of the precipitates are even multiples of \(d_{111}\) of magnetite, such as \(2d_{111}\), \(4d_{111}\), and \(6d_{111}\). Ordering of the vacancies in the Si-magnetite will result in symmetry of \(P4_32\), which is a subgroup of \(Fd\overline{3}m\) for magnetite. Stacking of Si-magnetite and magnetite (111) layers along the [111] direction also occur in magnetite. The nano-precipitates result from exsolution of Si-magnetite from the host silician magnetite at low temperature. The occurrence of the thin nano-precipitates within the magnetite host results from the minimization of interfacial energy between the precipitate and the host magnetite. Relatively high concentrations of aqueous silica and Fe-silicate complex species in pore fluid might enhance the incorporation of Si into the silician magnetite during crystallization of the magnetite.

Keywords: Si-magnetite, silician magnetite, banded iron formation, Z-contrast imaging, DFT

INTRODUCTION

There are more than 30 reported studies documenting the presence of silician magnetite included in a wide range of rock types from low to high temperatures. These rock types include banded iron formations, mid-ocean ridge serpentinites, volcanogenic massive sulfide (VMS) deposits, skarns, and porphyries, as well as high-temperature igneous occurrences ranging from felsic to gabbroic compositions, pegmatites, and carbonatites (see a summary by Huberty et al. 2012). Early studies report a range in SiO\(_2\) of up to 8 wt% for silician magnetite, especially the magnetite from Porphyry and Skarn ore deposits (Shimazaki 1998; Shiga 1988, 1989; Westendorp and Watkinson 1991; Wang et al. 2001; Imai 2001; Ohkawa et al. 2007; Huberty et al. 2012).

Results from in situ X-ray micro-diffraction and TEM observations indicate that Si atoms occupy magnetite lattice sites, instead of existing as silica inclusions (Newberry et al. 1982; Huberty et al. 2012). Guinier-Preston (G.P.) zone-like textures have been observed in a few instances suggesting the presence of nanoscale \(γ\)-Fe\(_2\)SiO\(_4\) domains (Huberty et al. 2012). However, further details related to possible Fe-silicate discrete phases/nano-precipitates were not available due to the limitations of conventional high-resolution TEM (HRTEM), which is a phase contrast imaging method. In this study we present evidence related to the presence of Si in a Si-magnetite lattice in the form of a discrete nanophase, or nano-precipitates within the host magnetite derived from Z-contrast imaging methodology. The Z-contrast imaging can clearly reveal positions of atom and vacancy columns along electron beam direction. Crystal structures of nanophasess in a fayalite-laihunite (or \(α\)-Fe\(_2\)SiO\(_4\)) series have been solved by combining Z-contrast imaging and density functional theory (DFT) method (Xu et al. 2014).

SAMPLES AND EXPERIMENTAL METHOD

The samples in this study come from drill hole (DDH)-47A located ~15 km south of Wittenoom, Western Australia. Rock removed from DDH-47A was used to define the stratigraphic subdivisions of the Brockman Iron Formation, Hamersley Group, Mt. Bruce Super Group and is the type section core for the Dales Gorge Member (Trendall and Blockley 1968). Our samples are taken from quarter-core sections of DDH-47A selected by Cornelius Klein in 1978. Klein donated these samples to the Department of Geoscience, UW-Madison, and they are cataloged in the collections of the UW-Madison Geology Museum (UWGM500). Details regarding the samples have been described previously (Huberty et al. 2012).

Scanning transmission electron microscopy (STEM) analyses were carried out using a FEI Titan 80-200 aberration corrected scanning/transmission electron microscope operated at 200 kV. The microscope is equipped with CEOS probe aberration corrector, an EDAX high-resolution EDS detector, and Gatan image filtering system. Probe current was set at 24.5 pA. All the Z-contrast images were acquired using camera length of 160 mm, to maximize the difference among different elements. High-angle annular dark-field (HAADF) STEM imaging (or Z-contrast imaging) is capable of a spatial resolution of ~0.1 nm using the...