Protoenstatite in MgSiO₃ samples prepared by conventional solid state reaction

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Enstatite (MgSiO₃) sample was prepared by conventional solid state reaction at 1500 °C, followed by cooling to ambient temperature with different cooling rates (0.04–500 °C/s). Quantitative analysis of enstatite phases in the samples by Rietveld refinement and ²⁹Si MAS NMR revealed that a large amount of metastable protoenstatite (30–40 mol%) along with clinoenstatite was preserved in all samples. The presence of protoenstatite was also confirmed by micro-Raman spectroscopy. The crystal structures of protoenstatite and clinoenstatite at room temperature were refined using the Rietveld method, and were essentially the same as those reported by previous studies. As the solid state reaction method is commonly used to prepare synthetic clinoenstatite, the present result implies that the ‘clinoenstatite’ starting materials used in previous phase equilibrium studies of MgSiO₃ pyroxene might contain overlooked protoenstatite, which could affect the interpretation for phase transition and thus those results should be reexamined.

Keywords: Protoenstatite, Crystal structure, Clinoenstatite, MgSiO₃, Phase relation

INTRODUCTION

Protoenstatite is one of the high-temperature forms of MgSiO₃ pyroxene, and its stability range is from 1000 to 1550 °C at ambient pressure (e.g., Presnall, 1995). There have been extensive studies on the phase transitions between low/high-clinoenstatite, orthoenstatite and protoenstatite (e.g., Huebner, 1980). It is often believed that protoenstatite is unquenchable to ambient temperature (e.g., Smyth, 1974). Although some earlier studies have reported quenched protoenstatite (e.g., Atlas, 1952; Sarver and Hummel, 1962), these studies commonly used ether natural samples (including talc) or synthetic ones with a mineralizer (such as LiF). For pure MgSiO₃, protoenstatite was often synthesized from treatment of a glass or melt. For example, Smith (1959) obtained protoenstatite sample for his crystal structural study of polycrystalline protoenstatite by treating MgSiO₃ glass at 1080 °C and 50 MPa. Lee and Heuer (1987) also reported quenched protoenstatite to ambient temperature by crystallizing MgSiO₃ glass at 1400 °C and dropping it into water. Reynard et al. (2008) obtained quenched protoenstatite by dropping MgSiO₃ melt into water. In our laboratory, the existence of partially quenched protoenstatite along with clinoenstatite was first recognized from ²⁹Si MAS NMR spectrum of a MgSiO₃ sample rapidly quenched from 1500 °C (Xue et al., 2002). Osako et al. (2016) studied grain size and cooling rate dependences on the protoenstatite to clinoenstatite transition starting from 1200 °C, and also recovered protoenstatite to ambient temperature. Unlike earlier studies, no melt or glass is involved in the last two studies. Thus, it is apparent that protoenstatite is partially quenchable to ambient temperature for pure MgSiO₃ even using conventional solid state synthesis method. This is an important point for experimental mineralogy and petrology, as MgSiO₃ starting material is typically prepared by such method. However, there has been no detailed study of quantitative (phase) analysis of enstatite samples synthesized by this common process, and no structural study of the recovered protoenstatite by Rietveld refinement. In this study, the crystal structures of protoenstatite and clinoenstatite at ambient temperature were refined using the Rietveld method, and the result of the quantitative analysis, along with results from Raman and ²⁹Si NMR spectroscopy, on the recovered samples are reported.

EXPERIMENTAL PROCEDURES

Starting MgSiO₃ sample (about 2 g) was synthesized...
from oxide mixtures of reagent-grade MgO and SiO₂ with 1:1 molar ratio. The mixture was pelleted, and heated in a platinum crucible at 1500 °C for 15 h using a home-made furnace consisted of four U-shaped MoSi₂ heater elements. After cooling, the product was reground and pelleted again, and heated at 1500 °C for 20 h, and cooled down to room temperature by 1 h. This (non-sintered) sample without any further processing was used as starting material for subsequent heat treatments.

In order to study the effect of cooling rate on the metastable recovery of protoenstatite to room temperature, four samples (0.25 g each) with different cooling rates were prepared. All samples were first kept at 1500 °C for 5 hr., and then sample #1 was cooled down to room temperature in 10 h using a programmable temperature controller. Sample #2 was cooled down in 1 h. Sample #3 was quickly taken out from the furnace at 1500 °C, and the bottom of Pt crucible was dipped into water (no contact between the sample and water). Sample #4 was similar to #3, but the sample was also dipped into water. Since the sample #4 was soaked in water, it was dried in an oven at 110 °C overnight. Rough estimation of cooling rate for the samples #3 and #4 would be ~ 500 °C/s, and oven at 110 °C overnight. Rough estimation of cooling rate for the samples #3 and #4 would be ~ 500 °C/s, and only lattice parameters and scale factors for cristobalite were refined. Initial structural parameters for protoenstatite were taken from optimized crystal structure by first-principles DFT calculation (Xue et al., 2017), and those for clinoenstatite were taken from single crystal refinement of Ohashi (1984).

Unpolarized Raman spectra of the samples were acquired using a home-built micro-Raman spectrometer with an Ar⁺ ion laser (488.123 nm and ~ 60 mW). The laser beam was focused onto the powder samples with a 50× objective lens, forming about 1 μm laser spot. Back-scattered light was then focused to a pinhole (diameter of 200 μm), and the light was collimated, and went through a RazorEdge filter (Semrock, Inc.) to reject Rayleigh scattering, and was finally focused to an entrance slit of the polychromator (with focal length of 500 mm, and a grating of 1200 gr/mm), and the dispersed light was detected by a liquid N₂ cooled CCD detector (PyLoN 100 BR eXcelon, Princeton Instruments). Accumulation time for the reported spectra was 3 min.

²⁹Si MAS NMR spectrum was obtained for the sample #3 using a Varian 9.4 T Unity–Inova NMR spectrometer and a 2.5 mm T3 MAS probe at a spinning speed of 20 kHz.

RESULTS AND DISCUSSION

Figure 1 shows typical Raman spectra obtained from the sample #2. Reynard et al. (2008) reported a quick way to identify enstatite polymorphs using Raman spectra. They proposed that a single peak at around 673 cm⁻¹ can be used as diagnostic feature for protoenstatite, whereas clinoenstatite and orthoenstatite both exhibit a doublet in the same frequency region. Therefore, the lower spectrum in Figure 1 can be assigned as protoenstatite in the sample #2. For orthoenstatite, a diagnostic peak appears at 82 cm⁻¹, whereas for clinoenstatite, a peak at 118 cm⁻¹ is characteristic. Therefore, the upper Raman spectrum shown in Figure 1 is assignable to clinoenstatite. No Ra-
man spectrum with 82 cm$^{-1}$ peak was observed. Therefore, our Raman measurements indicated that the sample #2 contains both protoenstatite and clinoenstatite, but no orthoenstatite. Protoenstatite was less frequently encountered than clinoenstatite from measurements of individual grains. Identical results were obtained for samples #1 and #4, and the starting material. These Raman results are not quantitative, but are consistent with results from powder X-ray diffraction given below.

The powder X-ray diffraction patterns of all the samples are shown in Figure 2 along with the fitted patterns by the Rietveld refinement. Clinoenstatite and protoenstatite were identified in all samples. The R-factors and proportion of protoenstatite obtained by the Rietveld refinements are summarized in Table 1.

The lattice parameters of protoenstatite obtained for the sample #3, which has the highest protoenstatite content, are: $a = 9.25655(9)$, $b = 8.73919(9)$, and $c = 5.31931(5)$ Å. These are in good agreement with those of Smith (1959), as compared in Figure 3 along with Figure 1.

![Typical Raman spectra of enstatite polymorphs in the sample #2. For clarity, the upper spectrum is displaced upward.](image)

*Figure 1.* Typical Raman spectra of enstatite polymorphs in the sample #2. For clarity, the upper spectrum is displaced upward.

![Results of the Rietveld refinements.](image)

*Figure 2.* Results of the Rietveld refinements. (a) Sample #1 (10H cooling from 1500 °C). (b) Sample #2 (1H cooling from 1500 °C). (c) Sample #3 (bottom of Pt crucible dipped into water). (d) Sample #4 (dropped into water). Red points are observed intensities, blue lines are calculated patterns, purple lines at bottom are the difference. Vertical ticks show the positions of reflections for protoenstatite, clinoenstatite, Si and cristobalite (from top to bottom). Insets are the expanded views for low-angle region.
high-temperature data. The cell parameters determined by in-situ high-temperature single crystal studies (Murakami et al., 1982; Yang and Ghose, 1995) deviate somewhat from those determined by in-situ powder X-ray diffraction (Jiang et al., 2002). The present lattice parameters are consistent with the trend of high-temperature data extrapolated to room temperature.

The refined crystal structural parameters of protoenstatite obtained for the sample #3 are shown in Table 2, along with the optimized structure from the first-principles calculation of Xue et al. (2017) (detailed structure not reported). These are very similar. The structural parameters of in-situ high-temperature studies of protoenstatite (Sadanaga et al., 1969; Murakami et al., 1982; Yang and Ghose, 1995) were also consistent with the present study. A short O2-O3 distance of 2.470(5) Å for the refined structure is noted. This short distance is apparently due to edge-sharing between SiO₄ tetrahedron and M₂O₆ octahedron. The result of Smith (1959) gave somewhat longer bond distance (2.627 Å). However, similar distances (2.48–2.51 Å) to our refinement are noted for the high-temperature structures of Yang and Ghose (1995) and that of the first-principles optimized structure (Table 2). Similar bond distances are also noted for the corresponding edge-shared O2A-O3A in the clinoenstatite structure (see the present result given below and Ohashi, 1984). Therefore, this short distance is not likely due to poor structural refinement of the present study. Similar observation is noted for the O3-O3-O3 angle as well.

The refined crystal structural parameters of clinoenstatite obtained for the sample #4, which has the lowest R-factors and higher clinoenstatite content, are given in Table 3. These structural parameters are similar to those from the single crystal refinements of Ohashi (1984).
The results of quantitative analysis (proportion of protoenstatite over total enstatite phases) by the Rietveld refinement method are shown in Table 1. Significant amounts of protoenstatite, up to 40 mol%, were found in all the recovered samples. The abundance of cristobalite (not shown in Table 1) was small, about 1 wt% in all samples.

For the sample #3, we also conducted quantitative \(^{29}\text{Si MAS NMR measurement (see Fig. 4). The}^{29}\text{Si spin lattice relaxation time constant (T}_1\text{) was first measured with the saturation-recovery method, and was found to be 1946 ± 693 s (-80.5 ppm), 2647 ± 496 s (-83.1 ppm) and 1559 ± 295 s (-84.8 ppm) for the three observed peaks. The reported}^{29}\text{Si MAS NMR spectrum was obtained with a π/2 pulse of 3.8 µs, an acquisition time of 0.16 s and a recycle delay time of 14000 s (>5T}_1\text{) to yield fully quantitative relative intensities. The three peaks near -80.5, -83.1, and -84.8 ppm have full-width-at-half-maximum (FWHM) of 0.14, 0.11, and 0.10 ppm, and relative integrated intensities of 31(2)\%, 33(2)\%, and 35(2)\%, respectively. The former two peaks at ~80.5 and -83.1 ppm can be readily assigned to the two Si sites in the clinoenstatite structure, and the third peak at -84.8 ppm can be assigned to the single Si site in the protoenstatite structure, according to previously reported NMR data on clinoenstatite and first-principles calculations on both phases (Xue et al., 2017) and also from the present diffraction study. The estimated relative abundance of 35(2)\% for protoenstatite in the sample #3 based on integrated NMR intensities is somewhat lower than that obtained for the same sample by the Rietveld refinement (39.6 mol%). For the Rietveld refinement, our samples were not ground, and relatively large grains in the samples are noted. These effects might be (partly) responsible for the relatively high \(R_{wp}\) (see Table 1) and the discrepancy in abundance compared to the NMR result. Nevertheless, the NMR result does confirm that significant amount of protoenstatite was present in the sample #3, and the relative abundance change among different samples revealed by the Rietveld refinement should be more reliable.

A cooling rate dependence would be expected for the relative abundance of recovered protoenstatite. Rapidly cooled sample #3 seems to preserve more protoenstatite as expected, although almost identical result was obtained for #1 and #2. Osako et al. (2016) observed cooling rate dependence on the recovery of protoenstatite. The supposedly most quickly quenched sample (#4), however, showed the lowest protoenstatite content. It should be noted that the sample #4 has experienced different handling than those of others. It was in direct contact with water. Also, additional heating to dry the soaked sample might have contributed to the difference. However, our preliminary high-temperature in-situ Raman study of the starting material revealed that protoenstatite was observed even at 800 °C, so the heat treatment in the oven at 110 °C may not be responsible for the lower protoenstatite content. Another possibility is that the stress generated when the sample directly contacted with water may enhance the transition. Further study is necessary for the water-soaked sample.

The present study revealed that even using the commonly employed solid state synthesis method, considerable amount (about 1/3) of protoenstatite could be preserved in the pure MgSiO\(_3\) sample. However, such high abundance of protoenstatite in recovered samples has often not been clearly recognized, except for some earlier studies described above and a recent study of Osako et al. (2016). This could be explained to some extent by the overlapping peak positions for protoenstatite and clinoenstatite in powder X-ray diffraction pattern, which makes casual identification of protoenstatite difficult. Another possibility is the contribution of mechanochemical reaction during grinding of the sample for the preparation of powder X-ray diffraction measurement. Sarver and Hummel (1962) and Lee and Heuer (1987) reported that grinding of the sample promoted transformation of protoenstatite to clinoenstatite. Smyth (1974) reported the martensitic nature of this transition. Thus, grinding could lead to lower or unrecognizable amount of protoenstatite in samples of previous studies.

Therefore, the clinoenstatite starting material used in previous phase equilibrium studies on MgSiO\(_3\) system and related systems might have contained protoenstatite as well. In term of this new insight, special interest to us is the controversial phase relation of clinoenstatite and orthoenstatite in the low-pressure and low-temperature region (Kanzaki, 1991). Boyd and England (1965) and
Grover (1972) proposed stability of clinoenstatite at the low-temperature and low-pressure corner of the \( P-T \) phase diagram, and this seems to be widely accepted (e.g., Presnall, 1995). However, no subsequent study has clearly demonstrated successful synthesis of clinoenstatite at their proposed \( P-T \) region, and there is no supporting evidence from studies of natural rocks either. Kanzaki (1991) argued that the shear stress existed in the piston-cylinder experiments of Boyd and England (1965) could have resulted in stabilization of metastable clinoenstatite. However, Grover’s result cannot be explained in this way, as his study was conducted in hydrostatic condition (i.e., hydrothermal runs). For this type of studies, the starting materials were often a mixture of clinoenstatite and orthoenstatite and a few intense peaks of powder X-ray diffraction patterns were likely used to estimate the relative proportion of clinoenstatite and orthoenstatite before and after the reversal runs. The ‘clinoenstatite’ used for such starting material was most likely prepared by solid state synthesis method as in the present study, and thus might contain protoenstatite. Since the transformation mechanism of protoenstatite to clinoenstatite is martensitic (Smyth, 1974), protoenstatite is more easily transform to clinoenstatite than to orthoenstatite. At lower temperature, even if no transformation of clinoenstatite to orthoenstatite takes place, protoenstatite may transform to clinoenstatite, contributing to the apparent increase of peak intensities for clinoenstatite. This might have misled to the interpretation of favorable stability of clinoenstatite at lower temperatures. Although this is only a speculation, these previous studies should be reexamined using well characterized starting materials.

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