



Stability of Fe³⁺-bearing majorite in the Earth's mantle

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Introduction

Recent discovery of an oxidized majorite inclusion in a garnet host (*Xu et al.*, 2017) has motivated us to investigate the stability of Fe³⁺-bearing majorite in the mantle. Majorite, characterized by excess Si in octahedral coordination, forms only at pressures higher than 6 GPa, and the majoritic component increases with increasing pressure. Direct recovery of majoritic garnet in mantle rocks has not been observed because of back transformation of majorite to garnet plus pyroxene upon exhumation. The preservation of Fe³⁺-rich majorite inclusions, particularly in a garnet host, requires new high-pressure experiments to understand the mechanism of recovery. It has been shown that ferric iron may play important roles in the mantle and subduction environment because of redox reactions and high intrinsic oxygen fugacity (e.g., *McCammon and Ross*, 2003; *Rohrbach et al.*, 2007; *Stagno et al.*, 2015). However, there has been very little understanding of the formation and stability of Fe³⁺-rich majorite in the mantle. The effect of Fe³⁺ content on the formation depth of natural majoritic garnets is also not well understood. In this study, we perform a series of experiments to synthesize Fe³⁺-rich majoritic garnets under mantle conditions using high-pressure multi-anvil apparatus. The experimental data are used to understand the role of ferric iron in the stability and formation of majorite under different mantle conditions.

Experimental Procedure

Synthesis experiments of Fe³⁺-bearing majoritic garnets were carried out in the multi-anvil apparatus from 6.5 to 15 GPa. The first set of experiments were designed to examine the effect of the Fe³⁺ content on the majorite geobarometer (*Tao et al.*, 2017), using a starting material with similar chemical composition to that of the natural Fe³⁺-majoritic garnet in eclogite xenolith from Earth's deep upper mantle (*Xu et al.*, 2017). It consists of mixing CaCO₃ and oxides (MgO, Cr₂O₃, Al₂O₃, Fe₂O₃, and SiO₂). All Fe is introduced as Fe₂O₃ in the starting material. We also mixed a second starting material with all Fe²⁺. The chemical composition is analogous to that of the natural garnet host (*Xu et al.*, 2017). The mixture of each starting material was ground under ethanol in an agate mortar for 1 hour and decarbonated twice in a furnace at 1000 °C for 24 hours. The all Fe²⁺ starting material was prepared under controlled oxygen fugacity. The chemical compositions of the two starting materials are listed in Table 1, and compared to the natural mineral compositions.

Table 1. Chemical compositions of starting materials, compared with nature mineral compositions

	Fe ³⁺ -sm	Fe ²⁺ -sm	Fe ³⁺ -rich Majorite	Garnet-II
	This study	This study	<i>Xu et al.</i> (2017)	<i>Xu et al.</i> (2017)
SiO ₂	43.49	42.30	44.20	42.40
TiO ₂	-	-	0.10	0.10
Al ₂ O ₃	6.96	22.03	7.09	22.13
Cr ₂ O ₃	1.08	1.08	1.10	1.09
FeO	-	8.04	18.47*	7.71*
Fe ₂ O ₃	20.15			
MgO	26.98	20.69	27.16	20.79
CaO	1.33	5.04	1.35	5.09
MnO	-	-	0.32	0.30
Na ₂ O	-	-	0.03	0.02
Total	100.00	100.00	99.82	99.60

*Total iron oxide

We used the 14/8 assembly (Bertka and Fei, 1997) for all the high-pressure experiments up to 15 GPa. It consists of an MgO octahedron with a ZrO₂ thermal insulator sleeve and a Re heater. The starting material was loaded, sealed into a Pt capsule. The pressure was calibrated using fixed phase transition points in CaGeO₃, SiO₂, and Mg₂SiO₄ (Bennett *et al.*, 2016). The temperature was measured using a Type-C thermocouple, inserted axially to the top of the Pt capsule. The recovered samples were polished and examined with scanning electron microscopy (SEM). The chemical compositions for the coexisting minerals were determined with a JEOL JXA-8530F field-emission electron probe. The Fe³⁺ contents of the majoritic garnets were analyzed using the “Flank method” (Höfer *et al.*, 1994; Höfer and Brey, 2007), that are in general agreement with results based on the charge balance calculations. Figure 1 shows a representative SEM image of a sample quenched from 12 GPa and 1200 °C, that contains majoritic garnet (Maj), olivine (Ol), pyroxene (Px), and magnetite (Mt).

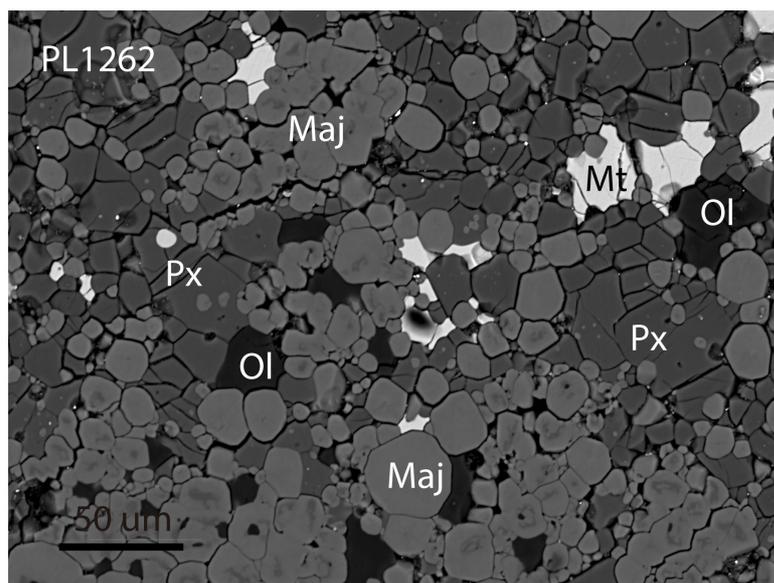


Fig. 1. Backscatter-electron image of recovered sample from high-pressure experiments at 12 GPa and 1200 °C, showing coexisting minerals, majoritic garnet (Maj), olivine (Ol), pyroxene (Px), and magnetite (Mt).

Results and Discussion

We performed a series of experiments from 6.5 to 15 GPa at temperatures up to 1600 °C to develop a new majorite geobarometer for Fe³⁺-bearing majoritic garnets, using the Fe³⁺ starting material. The experiments produced majorites with high Fe³⁺/ΣFe ratios (0.47-0.63) and low Al³⁺ contents. Using the same fitting procedure described by Collerson *et al.* (2010), we found that the synthesis pressure linearly changes with the cation substitution parameter. The linear relationship for Fe³⁺/ΣFe ~ 0.6 has a slope that is 2 times higher than that of the geobarometer defined for Fe³⁺/ΣFe = 0 (Tao *et al.*, 2017).

Fe³⁺-rich majorite in the mantle could form under high oxygen fugacity. However, the maximum Fe³⁺ content in majorite may be limited by the equilibrium element partitioning among the coexisting mineral even at the highest mantle oxygen fugacity. Majorite coexisting with magnetite and olivine/pyroxene has a typical Fe³⁺/ΣFe ratio of 0.48 at 12 GPa and 1200 °C, using both Fe³⁺ and Fe²⁺ starting materials. The alternative to produce high Fe³⁺-bearing majoritic garnets is through the reduction of carbonate accompanied by oxidizing the iron component in silicate. We carried out experiments to investigate redox reactions to form Fe³⁺-rich majorite through the reduction of carbonates including CaCO₃, FeCO₃, and MgCO₃. The starting material used in the experiments contains only Fe²⁺. The reaction with CaCO₃ produced high Fe³⁺/ΣFe ratios in majorite, 0.77-0.94, at 12 GPa and 1200 °C (Fig. 2). The majorite also contains high CaO and low MgO content. On the other hand, the reaction with MgCO₃ and FeCO₃ at the same condition produced majorites with low Fe³⁺/ΣFe ratios, < 0.33 (Fig. 2).

The Fe^{3+} content in majorite produced in carbonate reduction is strongly correlated with the CaO content and anticorrelated with the MgO content because of possible coupled substitutions in the structure. We also investigated the possible back transformation of Fe^{3+} -rich majorite. The Fe^{3+} -rich majorite is exceptionally stable and has a high kinetic barrier for the back transformation at low pressure because the decomposition has to involve an Fe^{3+} phase such as magnetite. The experiments provide new insights into the preservation of the Fe^{3+} -bearing majorite inclusion from deep mantle.

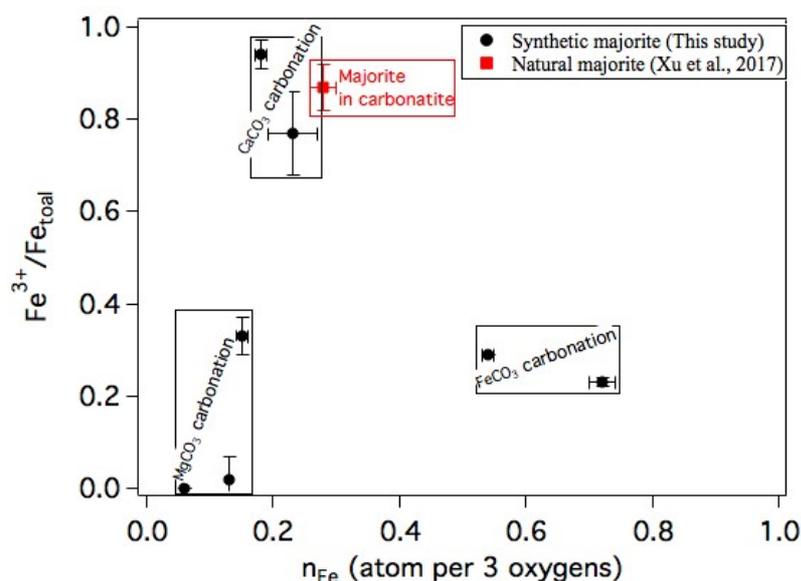


Fig. 2. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio v.s. n_{Fe} of the synthetic majorites produced through reaction with different carbonates, CaCO_3 , FeCO_3 , and MgCO_3 . The value for the natural majorite is also plotted for comparison.

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