Mechanism and kinetics of the a-b transition in San Carlos olivine Mg1.8Fe0.2SiO4

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Mechanism and kinetics of the α–β transition in San Carlos olivine Mg$_{1.8}$Fe$_{0.2}$SiO$_4$


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[1] The mechanism and kinetics of the α–β transformation in San Carlos olivine α-Mg$_{1.8}$Fe$_{0.2}$SiO$_4$ containing ca. 526 wt.ppm H$_2$O were studied in situ by time-resolved synchrotron X-ray diffraction (XRD) in the range 12.5 – 14.5 GPa and 870 – 1150 K. Time series of XRD spectra reveal the early formation of an intermediate phase that further transforms to wadsleyite (β-phase). This intermediate phase may be either a metastable ringwoodite (γ-phase) or the disordered spinelloid phase proposed in the pseudomartensitic reaction model. Both microstructural and kinetic data suggest that the transformation rates are controlled by growth processes after the early saturation of nucleation sites along olivine grain boundaries. Growth rates in the range 1.7×10$^{-12}$ – 2.1×10$^{-9}$ m.s$^{-1}$ are estimated by fitting the transformation–time data to the Cahn rate equation and defining an activation enthalpy for growth ΔH$_a$ = 204(55) kJ/mol. Compared to the previous studies performed on pure forsterite Mg$_2$SiO$_4$, these new kinetic results point out an increase of transformation rates with the iron content. Hence, the persistence of a metastable olivine wedge to depths > 660 km might be restricted to even colder and/or dryer subduction zones than previously estimated.


1. Introduction

[2] Olivine (Mg,Fe)$_2$SiO$_4$ (α-phase) is the major constituent of the Earth’s upper mantle. With increasing pressure, it transforms sequentially to wadsleyite (β-phase), with a modified spinel structure, then to ringwoodite (γ-spinel phase), and finally to perovskite + magnesio-wustite [e.g., Ringwood and Major, 1966; Akimoto and Fujisawa, 1968]. These phase changes have long been associated with the seismic discontinuities observed at 410, 520, and 660 km depth in the mantle, respectively [e.g., Ringwood, 1975]. In the cold interior of subducting plates, these phase transformations can be kinetically delayed [e.g., Stein and Stein, 1996], and olivine could persist metastably well beyond its equilibrium limit. Such a kinetic hindrance is of significant importance for the buoyancy and ultimate fate of subducting slabs. Because subduction is driven by the thermal structure and density increase related to phase transformations, the existence of a metastable wedge of olivine would profoundly influence the plate velocity, and ultimately the dynamics and morphology of slabs [e.g., Bina et al., 2001]. The mechanical properties of lithospheric materials would also be altered, as the stress state and the strength of slabs are strongly dependent on mineralogy and grain sizes [e.g., Karato et al., 2001]. Finally, shear instabilities postulated to occur during the transformation of metastable olivine to its high pressure polymorphs have been proposed for the origin of deep focus earthquakes [Kirby, 1987; Green and Burnley, 1989], as well as “outboard” earthquakes that occur away from Wadati–Benioff zones [Chen and Brudzinski, 2001].

[3] Direct seismic detections of a metastable olivine wedge are so far scarce. Examples of such observations include the Japan [Kawakatsu and Yoshioka, 2011] and the Mariana subduction regions [Kaneshima et al., 2007]. An alternative approach is to build thermo-kinetic models relying on accurate experimental data on the mechanism and kinetics of the α–β→γ transitions. The extensive work conducted on the transformation mechanism led however to conflicting results. A martensitic transition was proposed theoretically by Poirier [1981] based on the coherent shear of the olivine oxygen sublattice accompanied by “synchroscan” of the cations. The topotaxial relationship between the olivine and spinel phases (Mg,Fe)$_2$SiO$_4$ observed in either experiments [Lacam et al., 1980; Madon et al., 1989; Green and Burnley, 1989] or shocked meteorites [Price et al., 1982] support this shear-induced mechanism that would be favored by high differential stress and/or a large overstepping

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of the equilibrium conditions. In contrast, numerous experimental studies have documented microstructural evidences for a reconstructive transition involving grain-boundary or intracrystalline nucleation followed by interface-controlled growth [Sung and Burns, 1976; Brearley et al., 1992; Korschhofer et al., 1996; Kubo et al., 1998, Mosenfelder et al., 2001]. This mechanism is thought to be effective under near-equilibrium and high-temperature conditions.

Finally, an intermediate model is the pseudomartensitic mechanism that involves two stages: a shear-induced anionic re-arrangement followed by short-range diffusion of cations. This mechanism was first proposed by Furnish and Basset [1983] who observed during in situ X-ray diffraction (XRD) experiments that the coherent restacking of oxygen atoms appreciably precedes cations reordering during the \( \alpha \rightarrow \gamma \) transition in Fe\(_2\)SiO\(_4\). It is consistent with the transmission electron microscopy (TEM) observations of a disordered spinelloid phase that subsequently orders to produce the \( \beta \)-phase in Mg\(_2\)SiO\(_4\) quench products [Guyot et al., 1991; Brearley et al., 1992]. From the above literature data, it appears that the transformation mechanism might change with pressure, temperature, and stress conditions. However, the data are not yet comprehensive to infer the mechanism that operates under subduction environments.

[4] Early experimental kinetic studies have been carried out at low pressure on analogue materials Mg\(_2\)GeO\(_3\), Ni\(_3\)SiO\(_4\), and Co\(_2\)SiO\(_4\) (see Rubie and Ross [1994] for a review). However, the application to mantle olivine requires the extrapolation of kinetic parameters assuming that composition and absolute pressure do not affect transformation rates. More recently, kinetics data have been obtained on the \( \alpha \)-\( \beta \) and \( \alpha \)-\( \gamma \) transformations in synthetic Mg\(_2\)SiO\(_4\) and natural Mg\(_{1.8}\)Fe\(_{0.2}\)SiO\(_4\) compositions and conditions relevant to the upper mantle [Kubo et al., 1998; Liu et al., 1998; Korschhofer et al., 2000; Mosenfelder et al., 2001; Hosoya et al., 2005; Diedrich et al., 2009]. Most of these studies relied on quenched experiments performed in multi-anvil devices, aside from Kubo et al. [2004a] and Hosoya et al. [2005] who studied the transition in situ by XRD. These works concluded that overall transformation rates are controlled by growth kinetics rather than nucleation processes and suggested that the persistence of olivine to a depth of \( \sim 600 \)–\( 700 \) km is restricted to the cold interior of rapidly subducting slabs. However, they also pointed out the effect of transformation stress [Liu et al., 1998; Mosenfelder et al., 2001] and water [Hosoya et al., 2005; Diedrich et al., 2009] that could profoundly affect the extent of olivine metastability. This last point could be exceedingly important in hydrous subducted slabs as both olivine and its high-pressure polymorphs can contain significant H\(_2\)O in the form of hydroxyl point defects [e.g., Bolfan-Casanova et al., 2000].

[5] In this paper, we provide new kinetic data on the olivine–wadsleyite transition in a San Carlos mantle composition acquired by the in situ XRD method. The experiments were performed at relatively low-temperature conditions (870–1150 K) and small pressure oversteps of the transition boundary in order to reproduce the transformation in subduction zone environments. Time series of XRD spectra reveal the early formation of an intermediate metastable phase that further transforms to wadsleyite. Kinetic parameters derived from the experimental transformation–time data are compared with literature data and highlight an increase of transformation rates with the iron content. We discuss the implications of these new kinetic results on the metastability of olivine in subducting slabs.

2. Experimental Methods

[6] The starting material consisted of natural olivine crystals from the San Carlos peridotite (Arizona), ground in an agate mortar down to 2–3 \( \mu \)m in size. The composition of these crystals was Mg\(_{1.8}\)Fe\(_{0.2}\)SiO\(_4\) as determined by electron probe measurements. The water content was measured by infrared spectroscopy to \( 1.8 \pm 0.4 \) wt.ppm H\(_2\)O using the calibration coefficient of Libowitzky and Rossman [1997]. Prior to the experiments, powders were dried at 150°C in air for few days to avoid absorption of water. Angle-dispersive XRD experiments were carried out in a Paris-Edinburgh large volume press installed at beamline ID27 of European Synchrotron Radiation Facility (Grenoble, France) [Mezouar et al., 2005; Perrillat, 2008]. Sintered diamond anvils [Morard et al., 2007] were used to generate pressures up to 14.5 GPa. The sample assembly (Figure 1) was composed of a boron-epoxy pressure medium, a resistive heater, and an MgO sample capsule. The heater consisted of two LaCrO\(_3\) ceramic disks in electrical contact through two rhenium strips 50 \( \mu \)m thick, oriented parallel to the X-ray beam. The olivine and a thin layer of Au powder were packed in the MgO capsule. The maximal thermal gradient across the sample was estimated from numerical modelling to \( \pm 80 \) K at 873 K (Figure 1).

[7] Pressure and temperature conditions were determined from the diffraction lines of MgO and Au using the PVT equations of state of Martínez-Garcia et al. [2000] and Shim et al. [2002], respectively. Uncertainty on P and T depends on both the error in fitting the diffraction data and the uncertainty on the thermoeelastic parameters of the calibrants. It was estimated for each P–T conditions from the parallelogram area delineated by the intersection between the Au and MgO isotherms (Figure 2). Taking into account a \( \pm 0.002 \) \( \AA \) error on the distance of the Au and MgO diffraction lines, the precision on P and T was in all cases better than \( 0.4 \) GPa and \( \pm 80 \) K.

Figure 1. Details of the cell assembly and temperature profile at 873 K calculated using the program “CellAssembly” [Hernlund et al., 2006]. The interval between isotherms is 100 K. (1) boron-epoxy gasket, (2) steel ring, (3) MgO ceramic, (4) molybdenum disk, (5) LaCrO\(_3\) ceramic, (6) MgO capsule, (7) sample, (8) gold foil, (9) rhenium heater.
Samples were first compressed at room temperature to about 9 GPa and then annealed at 1100 K for 2–3 h within the stability field of the α-phase. The goal of this annealing is to relax the strain and reduce the density of defects resulting from the cold compression stage. The sharpening of diffraction lines on the XRD images testifies to these recrystallization processes. The achievement of equilibrium microtexture is clearly visible on the scanning electron microscopy (SEM) picture of a sample quenched after annealing (Figure 3a). It exhibits sharp olivine grain boundaries and 120° triple junctions. Following the annealing stage, temperature was reduced to ambient, and pressure was increased to the stability field of the β-phase. Then, temperature was increased again at a heating rate of 50 K/min up to the target value. To avoid a decrease in pressure related to the volume reduction of the reaction, a constant load was applied on the sample thanks to an automatic oil pressure drive system (Sanchez Technologies®). To monitor the extent of transformation as a function of time, a sequence of XRD spectra was acquired every 30 s to 4 min, with a collection time of 15 to 60 s. The incident monochromatic X-ray beam λ=0.6199 Å (Mo absorption K-edge) was reduced down to 50 × 50 μm² by two sets of carbide slits placed before the Paris-Edinburgh press. The diffracted X-rays from the sample were collimated through Soller slits [Mezouar et al., 2002] and collected on a MAR® 345 image plate over a 2θ interval from 4° to 18°. The two-dimensional XRD images were integrated after spatial distortion corrections using Fit2D [Hammersley et al., 1996]. Finally, transformation-time plots ζ(t) were constructed by Rietveld refinement of phase proportions using the GSAS package [Larson and von Dreele, 1994]. After completion of the reaction, i.e., disappearance of the diffraction lines of the α-phase, the samples were quenched to room temperature by switching off the power of the heater and then slowly decompressed. The recovered samples were cut and mounted on epoxy resin and polished for microscopic observations of texture and grain sizes. SEM images were acquired on a JEOL 840 microscope at the MATEIS laboratory (Lyon, France).

[9] Considering the potentially strong catalytic effects of even small amounts of H₂O in the sample charges, the water concentrations were determined using Fourier transform infrared spectroscopy (FTIR) measurements. For this purpose, recovered samples were ground and doubly polished to ~ 130 μm thin sections. The samples thickness was determined with a precision of approximately 2 μm with a Mitutoyo electronic micrometer. Unpolarized infrared spectra were obtained in air using a Vertex70 Bruker spectrometer coupled to a Hyperion microscope equipped with ×15 objective and condenser (at Laboratoire Magmas et Volcans, Clermont-Ferrand – France, and Institut de Planétologie et Astrophysique, Grenoble - France). Beam size ranged between 30 and 100 μm. The spectra were measured through a CaF₂ plate with a resolution of 2 cm⁻¹ and with up to 4000 scans between 2500 and 4000 cm⁻¹ in the O–H stretching region.

Figure 2. Pressure–temperature diagram showing the experimental conditions with relations between olivine (α), wadsleyite (β), and spinel (γ) phases (after Akaogi et al. [1989] and Katsura et al. [2004]). P and T were determined from the diffraction lines of Au and MgO using a cross-calibration of their PVT equation of state; uncertainties are displayed as gray-shaded area.

Figure 3. Electron backscattered images showing the characteristic microtextures of samples (a) after the annealing stage at 9.6 GPa, 1100 K during 3 h and (b) after the complete transformation to the β-phase after 6 h at 14.5 GPa, 980 K. For a better display, the gray scale has been stretched, and thereby contrasts reflect crystal orientation. The scale bar is 4 microns. The annealed sample shows a relatively homogeneous grain size of 2.5 ± 1.1 μm, well-developed triple junctions, and straight grain boundaries, whereas after reaction, it exhibits scalloped grain boundaries and a smaller grain size of 1.4 ± 0.6 μm.
All FTIR spectra (Figure 4) exhibit a broad absorption band in the range 3000 to 4000 cm$^{-1}$, attributable to molecular H$_2$O, which likely reflects the presence of water at grain boundaries. A group of four sharp absorption peaks near 3300 cm$^{-1}$ (i.e., 3275, 3326, 3360, and 3402 cm$^{-1}$) and a second group of two smaller peaks near 3600 cm$^{-1}$ (i.e., 3580 and 3615 cm$^{-1}$) are characteristic of the structural hydroxyls in wadsleyite as reported by Kohlstedt et al. [1996] and Kohn et al. [2002]. Finally, absorption bands near 2900 cm$^{-1}$, which are characteristic of C–H bending, eventually derive from the epoxy glue and acetone treatment and therefore were not considered for the determination of OH contents.

The hydroxyl contents were calculated from the integrated area of both sharp and broad absorption bands after background baseline correction and thickness normalization to 1 cm. The molar absorption coefficient $\epsilon_i =73,000$ L. mol$^{-1}$ cm$^{-1}$ [Deon et al., 2010] was used for the quantification of wadsleyite IR peaks, while the general calibration of Libowitzky and Rossman [1997] was used for the broad band. The OH content in each sample (Table 1) varies from 347 to 596 wt.ppm H$_2$O with an average value of 526 ± 119 wt.ppm H$_2$O. Though still low, the amount of water in wadsleyite is significantly higher than in the original olivine. It probably arises from water adsorbed in the cell assembly parts and powdered sample, and/or from the boron-epoxy medium.

### Results

#### 3.1. Mechanism of the Olivine–Wadsleyite Transition in Mg$_{1.8}$Fe$_{0.2}$SiO$_4$

Time-resolved XRD data were acquired in five runs over the 12.5 – 14.5 GPa and 870 – 1150 K P–T range (Figure 2 and Table 1). A typical sequence of diffraction patterns is shown in Figure 5. At the beginning of the transition, the decrease in intensity of olivine diffraction peaks is accompanied by the early appearance of a metastable intermediate phase whose diffraction lines are successfully indexed with the (220) (311) (400) (511) and (440) reflections of Fd3m spinel. This phase transforms progressively into wadsleyite, Imma space group, and at the end of the reaction, only the diffraction bands of wadsleyite are visible.

### Table 1. Experimental Conditions, Water Contents, and Estimated Values of Grain-Boundary Nucleation and Growth Rates

<table>
<thead>
<tr>
<th>Run #</th>
<th>$V_{\text{Au}}$ (Å)</th>
<th>$V_{\text{MgO}}$ (Å)</th>
<th>Pressure (GPa)</th>
<th>Temperature (K)</th>
<th>Free Energy Change $\Delta G_c$ (J/mol)</th>
<th>Water Content (wt ppm H$_2$O)</th>
<th>Nucleation Rate (m/s$^2$)</th>
<th>Growth Rate (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>64.55</td>
<td>69.94</td>
<td>14.5</td>
<td>980</td>
<td>−7017</td>
<td>571 (111)</td>
<td>-</td>
<td>1.9 (0.2) × 10$^{-11}$</td>
</tr>
<tr>
<td>#2</td>
<td>65.07</td>
<td>70.59</td>
<td>12.5</td>
<td>950</td>
<td>−2093</td>
<td>590 (29)</td>
<td>4.83 (0.5) × 10$^{-13}$</td>
<td>6.9 (0.6) × 10$^{-12}$</td>
</tr>
<tr>
<td>#3</td>
<td>64.68</td>
<td>70.22</td>
<td>13.2</td>
<td>870</td>
<td>−4401</td>
<td>596 (105)</td>
<td>-</td>
<td>1.7 (0.8) × 10$^{-12}$</td>
</tr>
<tr>
<td>#4</td>
<td>65.24</td>
<td>70.62</td>
<td>12.8</td>
<td>1050</td>
<td>−2561</td>
<td>-</td>
<td>1.2 (0.4) × 10$^{-10}$</td>
<td></td>
</tr>
<tr>
<td>#5</td>
<td>64.97</td>
<td>70.12</td>
<td>14.5</td>
<td>1150</td>
<td>−6983</td>
<td>347 (106)</td>
<td>-</td>
<td>2.1 (0.3) × 10$^{-9}$</td>
</tr>
</tbody>
</table>

*Pressure and temperature conditions were determined from the diffraction lines of MgO and Au using the PVT equations of state of Martinez-Garcia et al. [2000] and Shim et al. [2002], respectively.

*The free energy change $\Delta G_c$ at P–T is calculated from the thermodynamic data of Akaogi et al. [1989] and Jacobs and de Jong [2005].

*The FTIR measurements of OH contents were repeated at five to nine locations in each sample. The uncertainty in the water concentration is one standard deviation. Sample Run #4 was lost in the grinding process.

*Nucleation and growth rates were obtained by a fit of the experimental $\Delta f$ data to Cahn’s equation (1). Estimated uncertainties are listed in parentheses. When a solution for $N$ was not achieved, an arbitrary value of $N= 10^{-9}$ m$^2$/s was set.
The origin of this metastable phase may be twofold. On one hand, it may correspond to ringwoodite that nucleated and grew metastably according to the Ostwald rule. This could have occurred if the free energy sequence is $G_\alpha > G_\gamma > G_\beta$, so that ringwoodite is stable relative to olivine. On the other hand, this phase may be the intermediate spinelloid phase involved in the pseudomartensitic reaction mechanism [Chen et al., 2001]. In the latter model, the restacking of the anions transforms the hcp oxygen arrangement of olivine into the fcc oxygen sublattice of spinel and modified spinel. It results in a spinelloid phase with a disordered cation structure that further rearranges by short-range diffusion in a second step, to produce the $\beta$-phase. A detailed description of this intermediate phase can be found in Guyot et al. [1991]. Because of the random position of the cations, the spinelloid phase should exhibit more intense diffraction lines for the oxygen array than for the cations one [Furnish and Basset, 1983; Chen et al., 2001]. Unfortunately, this feature cannot be detected on the present XRD patterns, because of peak overlaps in the experimental phase mixture, i.e., the most intense (311) line of spinel is superimposed with the strong $\alpha$-phase (112) and MgO (111) peaks. However, the intermediate spinelloid phase has been clearly identified in the $\alpha$-$\gamma$ transition. Furnish and Basset [1983] in Fe$_2$SiO$_4$ reported the initial preferential growth of the only $\gamma$ phase peaks compatible with the oxygen sublattice, namely the (400) and (440) diffraction lines. Lauerjung and Will [1986] observed that at the beginning of the $\alpha$-$\gamma$ transition, in the Mg$_2$GeO$_4$ analogue, only diffraction peaks from a spinel-type oxygen array were present. Moreover, Chen et al. [2001] performed structure refinements of XRD spectra during the $\alpha$-$\gamma$ transition in fayalite and concluded to a delay in the reordering of cations relative to anions during the phase transformation. We therefore believe, though there is no direct evidence in the present XRD pattern, that the observed intermediate phase can be regarded as a disordered spinelloid and that the pseudomartensitic mechanism operates throughout the Mg$_2$SiO$_4$–Fe$_2$SiO$_4$ binary.

The pseudomartensitic mechanism is also consistent with many textural features observed in quenched experimental products and shocked meteorites. Guyot et al. [1991] studied by TEM partially transformed Mg$_2$SiO$_4$ samples and evidenced a structurally disordered spinelloid phase as an intermediate of the $\alpha$-$\beta$ reaction. The lamellar intergrowths of $\beta$ and $\gamma$ phases commonly observed in Mg$_2$SiO$_4$ [Brearley et al., 1992], in analogue compounds [Burnley et al., 1995], and in shocked meteorites [Price et al., 1982; Madon and Poirier, 1983] might also be interpreted as a result of the incomplete transformation of the metastable spinelloid into the $\beta$-phase.

The pseudomartensitic transition has often been considered as favored under high-stress conditions [e.g., Burnley et al., 1995]. In the present experiment, however, PT conditions were close to equilibrium, and the amount of differential stress, estimated from the method of Singh and Kennedy [1974] on MgO diffraction lines, was not detectable above 600 K, i.e., $\sigma < 0.05$ GPa. This is in agreement with the conclusions by Raterron et al. [2002] that the pseudomartensitic transition operates also under quasi-hydrostatic conditions and is driven by the local stress generated by the volume reduction of the reaction.

Microstructural SEM observations of the transformed samples (Figure 3b) give insights into the geometry of the nucleation and growth processes. In contrast to the texture of olivine after the annealing stage, the reacted samples show irregularly shaped and scalloped grain boundaries. The mean grain size decreased from 2.5(1.1) down to 1.4
The equation describing the transformation by the garnet.

The kinetic data were analyzed using the general rate reaction to

The transformation is advanced by reaction estimated from the decrease of the

The growth rates at any P-T conditions, assuming the transformation mechanism does not change. An expression of the

growth rate for the product phase in an interface-controlled transformation has been proposed by Turnbull [1956]:

where \( k_0 \) is a constant, \( T \) is temperature, \( \Delta H_a \) is the activation enthalpy for growth, \( P \) is pressure, \( \psi^* \) is the activation volume for growth, \( R \) is the gas constant, and \( \Delta G \), the free energy change of reaction at given P-T. Considering the limited pressure range investigated in the present study, the activation volume is not refined and is assumed to be zero. This assumption is justified by the low activation volume \( \psi^* \approx 1.7 \) (4.5) cm\(^3\)/mol determined by Kubo et al. [2004a] for the \( \alpha\)-\( \beta \) transition in Mg\(_2\)SiO\(_4\) and \( \psi^* \approx 0 \) (2) cm\(^3\)/mol estimated for the reconstructive growth of \( \gamma\)-Mg\(_2\)GeO\(_4\) [Burnley, 1995]. The \( \Delta G_{\text{r}} \) values are calculated from the thermodynamic data of Akaogi et al. [1989] and Jacobs and de Jong [2005] (Table 1). Values of \( k_0 \) and \( \Delta H_a \) are estimated from the slope and intercept of a least squares linear fit to the growth rate data on an Arrhenius plot ln\[G/\psi^* \text{exp}(\Delta G_{\text{r}}/RT)\] vs 1000/T (Figure 7). The best fit yields values for ln \( k_0 \approx -5.2 \) (8.1) m/s/K and \( \Delta H_{a} \approx 204 \) (55) kJ/mol, where uncertainties reported in parentheses are estimated from the propagation of the error on P-T conditions.

4. Discussion

4.1. Effect of the Iron and Water Contents on Kinetics

The present kinetic results are compared to the parameters obtained by Liu et al. [2004a] for the \( \alpha\)-\( \beta \) transition in Mg\(_2\)SiO\(_4\) synthetic samples. The latter experiments were conducted under nominally anhydrous conditions though low amounts of hydroxyl \( <750 \pm 100 \) wt ppm H\(_2\)O may have contaminated the sample like in the present study. Liu et al. [2004a] starting material was finned grained, and experiments were performed at small pressure oversteps relative to the \( \alpha\)-\( \beta \) equilibrium. Transformation–time data were acquired by in situ XRD and analyzed using the Cahn’s rate equation for interface-controlled reaction. These experimental and analytical methods are almost identical to the present study; in particular, the water contents are close. However, Liu et al. [2004a] reported growth rates more than one order of magnitude slower than in the present study. For example, our predicted growth rate at 13.7 GPa – 1273 K using equation (3) and the above kinetic parameters (ln \( k_0 = -5.2 \), \( \Delta H_a = 204 \) kJ/mol and \( \psi^* \approx 0 \) cm\(^3\)/mol) is \( G = 5.7 \times 10^{-10} \) m/s, while Kubo et al. [2004a] observed \( G = 8.5 \times 10^{-10} \) m/s. In addition, the activation enthalpy for growth \( \Delta H_a \approx 204 \) (55) kJ/mol is also significantly lower than the 391 (73) kJ/mol value (when \( \psi^* = 0 \) cm\(^3\)/mol) in Kubo et al. [2004a] and indicates a lower-temperature dependence of transformations rates. The comparison with the quench experiments is more tricky since the latter are performed at higher-pressure oversteps of the reaction boundary and suffer from a lower constraint in reaction duration. Liu et al. [1998] studied the transformation of Mg\(_{1+x}\)Fe\(_{2}\)SiO\(_4\) polycrystalline samples and reported some transformation rates, but not all, significantly faster than those measured by Kubo et al. [2004a]. For example, Liu et al. [1998] estimated a growth rate \( G = 1.4 \times 10^{-10} \) m/s at 1273 K – 18 GPa, while Kubo et al. [2004a] measured \( G = 8.5 \times 10^{-10} \) m/s at
Similar temperature. The activation enthalpy $\Delta H_a = 334$ kJ/mol estimated by Liu et al. [1998] is between the present value $\Delta H_a = 204$ kJ/mol and the one of Kubo et al. [2004a] $\Delta H_a = 391$ kJ/mol. The large errors on kinetic parameters cannot account for the discrepancy. The difference may originate from the different composition of the starting materials, in particular on the iron content of the San Carlos olivine that might enhance the $\alpha$–$\beta$–$\gamma$ transition rates.

[26] The pseudomartensitic reaction involves short-range Fe–Mg interdiffusion, which is a process controlled by composition [Chakraborty et al., 1999; Kubo et al., 2004b; Holzapfel et al., 2009]. For instance, Kubo et al. [2004b]
showed that the Mg–Fe interdiffusion rate in wadsleyte increases by almost one order of magnitude with increasing the iron concentration from $X_{Mg}=0.97$ to $X_{Mg}=0.90$ and decreasing grain size from 60 to 6 μm. Similarly, Yamazaki et al. [2005] studied the grain growth kinetics of ringwoodite by the quench method and observed faster growth rates in the iron-bearing samples than in the Mg$_2$SiO$_4$ end-member. Besides the effect of iron, the influence of water on the $\alpha$–$\beta$–$\gamma$ kinetics has been investigated owing to its relevance for olivine metastability in subducting slabs. However, experimental studies lead to conflicting results. Hosoya et al. [2005] investigated the $\alpha$–$\beta$ kinetics on 750–5000 wt.ppm H$_2$O synthetic Mg$_2$SiO$_4$ samples and inferred a power-law dependence of growth rate on the water content (Figure 7). In contrast, Diedrich et al. [2009] reported $\alpha$–$\gamma$ transformation rates on 300 wt.ppm H$_2$O hydrated San Carlos olivines up to four orders of magnitude faster than those predicted by Hosoya et al. [2005], suggesting a stronger catalytic effect at low water content. The present results showing a significant enhancement of kinetics of the $\alpha$–$\beta$ transition in the iron-bearing San Carlos olivine might well reconcile the previous studies and constrain more tightly the role of water on the phase transition. Indeed, Diedrich et al. [2009] determined kinetic parameters $\Delta H_f=237$ kJ/mol and $\ln k_0=-2.6$ (with $\nu^*=0$ cm$^3$/mol) close to the present kinetic results for Mg$_{1.8}$Fe$_{0.2}$SiO$_4$ containing 526 wt.ppm H$_2$O (Figure 7). Using these parameters, a growth rate $G=9.0 \times 10^{-12}$ m$^{-1}$ s$^{-1}$ is estimated at 14.5 GPa – 980 K slightly slower than our measured value $G=1.9 \times 10^{-11}$ m$^{-1}$ s$^{-1}$. Thus, it is likely that part of the discrepancy between the results of Hosoya et al. [2005] and Diedrich et al. [2009] could be explained by the role of iron, independently of the transformation type $\alpha$ to $\beta$ or $\alpha$ to $\gamma$-phase.

4.2. Implications for the Metastability of Olivine in Subducting Slabs

[21] In this section, the experimentally derived kinetic parameters of the olivine $\alpha$–$\beta$ transformation are used in a one-dimensional thermo-kinetic model to evaluate the metastable persistence of olivine in a subducting slab. The model assumes a grain-boundary reaction controlled by growth kinetics, as observed in our experiments. It ignores the effects of intracrystalline transformation and transformation stress that may occur in a subducting slab. The extent of transformation is calculated at each time step from the Cahn’s relation (1) and the growth rate determined from equation (3) using the kinetic parameters $\ln k_0=-5.2$, $\Delta H_f=204$ kJ/mol, $\nu^*=0$ cm$^3$/mol, and the thermodynamic data of Akaogi et al. [1989] and Jacobs and de Jong [2005] for the $\Delta G_f$ value. We investigated the transformation in a cold slab with a vertical subduction rate of 12 cm/yr and a thermal gradient of 0.6 K/km, as representative of the West Pacific subduction zones. The temperature of the lithospheric mantle at 300 km was set to 800 K, based on thermal model of Tetzlaff and Schmeling [2009]. The grain size in subducting plate is unconstrained and may lie in the range 0.01 – 10 mm [Riedel and Karato, 1997], a mean value of 5 mm was assumed in the calculation. This model is likely to be oversimplified as it does not consider the effect of latent heat released upon both kinetics and the thermal structure of the slab. For a more realistic model, the reader is referred to the recent work of Tetzlaff and Schmeling [2009]. Though schematic, the model provides an estimate of the effect of iron and water content on the metastable persistence of olivine at depth.

[22] The result of this thermo-kinetic model is presented in Figure 8. It is consistent with previous studies in predicting the presence of a metastable olivine wedge. However, the depth of the top of the metastable wedge reaches a maximum of 740 km, which is almost 70 km above the maximal depth of 810 km estimated from the kinetic parameters of Kubo et al. [2004a] for Mg$_2$SiO$_4$. Although the water content even more drastically reduces the persistence of metastable olivine (see Figure 8, calculations for 500–5000 ppm H$_2$O hydrous Mg$_2$SiO$_4$, Hosoya et al. [2005]), the influence of the iron content cannot be neglected. These new results do not preclude the viability of the transformational faulting hypothesis for the deep focus earthquakes. Indeed, considering the inhibition of growth by transformation stress would widen the metastable olivine wedge to greater depths, while the effect of latent heat release is to lower the $\alpha$–$\beta$ transition boundary and speed up reaction kinetics. Intracrystalline nucleation and/or grain size reduction would also strongly enhance transformation rate and reduce the extent of metastable olivine. However, the increase of reaction rate with the iron content evidenced in the present study implies that the development of a metastable olivine wedge to depths $>660$ km, corresponding to the deepest earthquakes, would
Figure 8. Fraction of olivine transformation as a function of depth for a cold slab with vertical subduction speed of 12 cm/yr and a thermal gradient of 0.6 K/km. Thermo-kineti c calculations were performed using the present kinetic results for Mg$_{1.8}$Fe$_{0.2}$SiO$_4$ ~ 500 wt.ppm H$_2$O (solid line) and the power-law dependence of growth rate on OH content with 500–5000 wt.ppm H$_2$O in Mg$_2$SiO$_4$ from Hosoya et al. [2005] (dash lines). For comparison purpose, in both models, the activation volume was set to a similar value of V* = 0 cm$^3$ mol$^{-1}$.

be restricted to even colder and/or dryer subduction zones than previously estimated.

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