1 **Revision 2 Potential Link between Antigorite Dehydration and**

2 **Shallow Intermediate-Depth Earthquakes in Hot Subduction Zones**

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16 **ABSTRACT**

17 　　The distribution of earthquakes at intermediate depths corresponding to pressures

18 <2 GPa in several hot subduction zones (such as Cascadia and southwestern Japan)

19 coincides with the breakdown of antigorite to forsterite and talc; thus, this reaction may

20 have triggered these earthquakes. However, previous studies have overlooked the

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21   potential significance of this reaction. Here, we performed a series of time-dependent

22   dehydration experiments on antigorite at a pressure of 200 MPa and temperature range

23   of 500-650 °C. The results show that dehydration is controlled by a heterogeneous

24   nucleation and growth mechanism and has an activation energy of 354±24 kJ/mol. The

25   formation of fine-grained forsterite and large talc crystals is consistent with kinetic

26   results indicating Avrami exponents $n=\sim1.4$-1.1 and ~2.7, respectively. Fluid

27   production rates at 600 and 650 °C are 2.54×10^{-6} and 4.69×10^{-5} $m^3_{fluid}m^{-3}_{rock}s^{-1}$,

28   respectively, which are much faster than those of mantle deformation, causing high

29   fluid pressure in hot subducting mantle but not necessarily embrittlement. We

30   emphasize the role of kinetic mechanisms in controlling the sizes of reaction products,

31   which likely determine the mechanical behavior of serpentinized fault zones.

32   Superplasticity or velocity weakening of fine-grained forsterite and velocity weakening

33   of antigorite by water and/or talc may be responsible for earthquake nucleation and

34   propagation in a heterogeneous system, which can be either dehydration products

35   within a serpentinized fault zone or the mixture of antigorite fault and surrounding

36   peridotite in hot subduction zones (<2 GPa).

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38   **Keywords**: Antigorite; Talc; Forsterite; Kinetic mechanism; Subduction zone;

39   Shallow intermediate-depth earthquakes

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41   INTRODUCTION

42   Serpentine is a main hydrous phase in oceanic plates and the most abundant

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43   water-bearing mineral in altered ultramafic rocks (Hyndman and Peacock, 2003), with

44   water contents up to ~13 wt.% (Schmidt and Poli, 1998; Shao et al., 2014, 2021; Ulmer

45   and Trommsdorff, 1999). There are three main forms of serpentine: chrysotile, lizardite,

46   and antigorite (Rinaudo and Gastaldi, 2003). Among them, antigorite is persistent in

47   subduction zones to a depth of ~200 km and is thus called high-temperature serpentine

48   (Ji et al., 2013; Reynard, 2013; Reynard et al., 2007; Shao et al., 2014). Previous

49   studies have shown that the temperature stability field of antigorite, from 1 to 5 GPa, is

50   close to the isotherm of the lower plane of a double seismic zone (DSZ) (e.g., Abers et

51   al., 2013; Peacock, 2001; Yamasaki and Seno, 2003), which means that the hypocenter

52   distribution of intermediate-depth earthquakes in the subducted mantle fits the

53   distribution of antigorite. However, a recent study by Ferrand (2019) suggested that

54   many of the upper-plane earthquakes actually appear in the uppermost mantle, as

55   clearly evidenced for northern Chile. Therefore, antigorite dehydration is commonly

56   used to explain the seismic activity in the entire DSZ (Dobson et al., 2002; Omori et al.,

57   2004; Peacock, 2001).

58   In a pioneering study by Raleigh and Paterson (1965), seismogenic faulting is

59   claimed to be triggered within the dehydrating antigorite itself due to fluid

60   overpressure. This is the original model of so-called 'dehydration embrittlement',

61   which is possible only when the Clapeyron slope of serpentine dehydration is positive

62   (i.e., at $P<$~2 GPa). However, several experimental studies on syndeformational

63   antigorite dehydration have found that antigorite is weakened but deforms aseismically

64   (Chernak and Hirth, 2010, 2011; Gasc et al., 2011, 2017; Okazaki and Hirth, 2016;

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65   Proctor and Hirth, 2015; Shao et al., 2021), which might be comparable to slow

66   earthquakes occurring in hot subduction zones (e.g., Chernak and Hirth, 2010; French

67   et al., 2019; Okazaki and Katayama, 2015). Some studies have improved the model

68   and considered that seismogenic faulting should occur in more brittle surrounding

69   rocks rather than the dehydrating antigorite itself (e.g., Brantut et al., 2017; Ferrand et

70   al., 2017). For example, Ferrand et al. (2017) proposed dehydration-driven stress

71   transfer (DDST) to generate earthquake events in fresh peridotite at the edge of

72   antigorite-rich zones. However, seismicity is triggered by dehydration of very limited

73   amounts of antigorite (Ferrand et al., 2017; Xia, 2013), implying that these earthquakes

74   are not the result of fluid overpressure. Concurrently, Brantut et al. (2017) proposed a

75   new dehydration embrittlement model, in which a positive feedback between pore fluid

76   pressure, shear compaction, and the dehydration rate of antigorite was considered to

77   induce nucleation and propagation of earthquakes in the surrounding rocks forming the

78   subducted slab. Thus, the role of fluid in triggering the lower plane earthquakes is still

79   inconclusive. Furthermore, both the DDST and the new dehydration embrittlement

80   models, unlike the original dehydration embrittlement, are specifically for the case

81   where the net volume change of the dehydration reaction is negative. These facts

82   suggest that none of the models can explain seismicity related to the dehydration

83   reaction of antigorite with positive volume change, which is the reaction of antigorite

84   breakdown to forsterite and talc.

85   To explain intermediate-depth earthquakes, several dehydration kinetics studies of

86   serpentine minerals have been performed over the past two decades using various

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87   methods, such as time-resolved X-ray diffraction (XRD) (Chollet et al., 2011; Gualtieri

88   et al., 2012; Inoue et al., 2009; Perillat et al., 2005), high-temperature infrared

89   microspectroscopy (Sawai et al., 2013), and thermogravimetric analysis (Balucan et al.,

90   2011; Liu et al., 2019; Weber and Greer, 1965). However, published conclusions

91   regarding the kinetic mechanism are significantly different (Balucan et al., 2011;

92   Gualtieri et al., 2012; Liu et al., 2019; Perrillat et al., 2005; Sawai et al., 2013). In

93   addition, these studies were conducted under conditions of either ambient pressure

94   (e.g., Liu et al., 2019; Sawai et al., 2013) or high pressures [e.g., 1.1-1.5 GPa in

95   Perrillat et al. (2005) and ~4 GPa in Chollet et al. (2011)], but data under relatively low

96   pressures (<1 GPa) are lacking. Furthermore, no microstructural observations of run

97   products were performed in most of these previous studies to support their analyses of

98   the kinetic mechanism of antigorite dehydration. These previous dehydration kinetics

99   studies all suggest that antigorite dehydration can trigger earthquakes based on either

100   the original dehydration embrittlement (related to fluid overpressure) (e.g., Chollet et

101   al., 2011; Perrillat et al., 2019) or the DDST model (Liu et al., 2019). According to the

102   results of syndeformational dehydration experiments with antigorite (e.g., Chernak and

103   Hirth, 2011; Gasc et al., 2011), however, fast fluid production rates calculated based on

104   kinetic parameters alone cannot account for the potential link between antigorite

105   dehydration and seismicity (e.g., Liu et al., 2019; Perrillat et al., 2005). The

106   microstructural morphology (controlled by the kinetic mechanism) and thus the

107   mechanical behavior of reaction products should not be ignored. In addition, the

108   reaction of antigorite breakdown to forsterite and talc has not yet been considered in

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109   most of these dehydration kinetics studies (e.g., Chollet et al., 2011; Inoue et al., 2009;

110   Liu et al., 2019; Perrillat et al., 2005). This reaction fits most shallow

111   intermediate-depth seismicity in hot subducting mantle beneath Cascadia and

112   southwestern Japan (Abers et al., 2013; Ferrand, 2019), indicating the geophysical

113   significance of this dehydration reaction.

114   In this paper, high-pressure and high-temperature (high-PT) experiments were

115   carried out on antigorite using a Tuttle-type autoclave (cold-seal hydrothermal vessel).

116   Our goal is to study the dehydration kinetics of antigorite by isothermal experiments

117   and analyze the kinetic mechanism by both Avrami modeling of the experimental data

118   and microstructural observations of run products, which provide constraints on the

119   fluid production rate and the mechanical behavior of run products, respectively. Finally,

120   the experimental results are extrapolated to hot subduction zones ($P < 2$ GPa) to

121   interpret the shallow intermediate-depth seismicity occurring in these zones by

122   emphasizing the role of the kinetic mechanism in controlling the size and, thus,

123   mechanical behavior of dehydration products.

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125   **METHODS**

126   **Starting Material**

127   The material used in the dehydration kinetics experiments is known as Xiuyan

128   jade in Chinese culture, has a mineral composition of mainly antigorite with trace

129   amounts of dolomite and apatite (<1%), and was collected from Xiuyan Manchu

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130   Autonomous County (Liaoning Province, China) (Shao et al., 2014, 2021). Whole-rock

131   X-ray fluorescence (XRF) analyses reveal that the starting material contains 44.25

132   wt.% SiO_2, 41.83 wt.% MgO, 0.28 wt.% CaO, 0.03 wt.% Na_2O, 0.06 wt.% Al_2O_3, 0.97

133   wt.% TFeO (total iron given as FeO), and 12.19 wt.% water. The nearly pure antigorite

134   crystals were crushed and ground into powder with various grain sizes, from which

135   mean particles of ~10-15 μm were selected and stored in a furnace at 110 °C,

136   eliminating absorbed molecular water. To determine the structure of the starting

137   material that may affect the phase stability and thus the dehydration kinetics, we

138   investigated the starting material via XRD at the Institute of Geology, China

139   Earthquake Administration (IGCEA), Beijing, and transmission electron microscopy

140   (TEM) at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS),

141   Guiyang, Guizhou Province. The TEM investigation was carried out on a suspension

142   that was made according to the powder technique described by Shen et al. (2020). The

143   XRD analyses suggest that the starting material is characterized by lattice constants

144   with a=5.42 Å, b=9.24 Å, c=7.27 Å, and β=91.32°. Figure 1 shows a high-resolution

145   TEM image of a representative grain and a histogram of the m value, which is equal to

146    $(a^*/5.42)\times2+1$, where a^* is the length of the a-axis and 5.42 Å represents the length of

147   the subcells along the a-axis in this material, that is, the lattice constant a. m represents

148   the number of tetrahedra in a single chain along the wavelength a^*. The results show

149   that the m value ranges from 13 to 18, with the most frequent value being 15; thus, this

150   value can be used as the polysome m value of the starting material.

151   **High-PT Experiments**

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152   All dehydration kinetics experiments were performed at a pressure of 200 MPa

153   and temperatures of 500-650 °C with durations ranging from 1 to 745.5 hours (h)

154   (Table 1) using a Tuttle-type autoclave (Figure 2) at the Guangzhou Institute of

155   Geochemistry, Chinese Academy of Sciences (GIGCAS). The antigorite powder was

156   loaded into gold capsules of two sizes: one had an outer diameter of 5.0 mm, and the

157   other had an outer diameter of 4.6 mm. Both gold capsules had a wall thickness of 0.25

158   mm and a length of 18 mm. Gold is commonly used in high-temperature experiments

159   because it is chemically inert. One side of a capsule was welded with a tungsten inert

160   gas high-frequency pulse welder (PUK3, Lampert Werktechnik, Germany) before

161   loading, and the other side was welded after loading with either just sample powder

162   (the system was water unsaturated at least at the beginning of the experiment) or

163   sample powder plus excess deionized water (the system was water saturated

164   throughout the experiment). A leak check was performed before all experiments. For

165   initially water-unsaturated samples, we immersed capsules in alcohol for at least 1 h

166   and then placed them in a drying furnace at 110 °C for at least 2 h. For water-saturated

167   samples, the capsules were directly placed in the drying furnace at 110 °C for at least 2

168   h. To determine whether the sample capsule was a closed or open system, the sealing

169   conditions of the sample capsule had to be confirmed. Thus, it was necessary to weigh

170   each sample capsule before and after the experiments and compare the weights to

171   determine the sealing conditions. Capsules with a weight difference of < ~0.5 mg were

172   considered completely sealed, which could be further supported by the increased

173   widths of these capsules after removal from the vessels. Capsules whose shapes stayed

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174   the same as before the experiments were considered open, and the experimental results

175   from capsules with this characteristic are not reported in this study. Water-saturated

176   experiments can be further confirmed by the presence of free water in the recovered

177   samples. The capsules were loaded into the bottom of the hydrothermal vessel,

178   followed by a filler rod (~6 cm in length) for the vertical vessel, with the purpose of

179   preventing convection. Pressures were generated by pumping water into the vertical

180   vessel and were measured by a pressure gauge with a precision of ±10 MPa (Huang et

181   al., 2017). To monitor temperature, an external K-type thermocouple was inserted into

182   a hole near the bottom of the vessel. Temperature was controlled with an accuracy of

183   ±2 °C. At the end of the experiment, the vessel was chilled by immersion in ice water,

184   thereby decreasing the temperature of gold capsules to <100 °C within a few seconds.

185   **XRD and Microstructural Observations**

186   After all the high-*PT* experiments, the sample powders were recovered from the

187   capsules and then ground for XRD analysis, except for two complementary

188   experiments from which sample powders (Atg103 at 600 °C and initially

189   water-unsaturated conditions for 48 h and Atg112 at 650 °C and water-saturated

190   conditions for 3 h) were recovered for microstructural observations under a Zeiss

191   Sigma scanning electron microscopy (SEM) system equipped with an Oxford X-Max

192   50[N] energy-dispersive X-ray spectroscopy (EDS) detector at Guilin University of

193   Technology (Guangxi Province, China). Powder XRD patterns were obtained with a

194   Bruker D8 ADVANCE X-ray diffractometer at both the GIGCAS and IGCEA. The

195   analyses were operated using Cu Kα radiation under a 40 kV target voltage and 40 mA

196   target current. Data were collected over the range of 5-70° 2θ with a step size of 0.02°

197   2θ and a count time of 19.2 s per step. For the analyses, the powder diffraction files

198   (PDF) cards of antigorite (monoclinic) from Hess et al. (1952), forsterite

199   (orthorhombic) from Hushur et al. (2009), and talc (triclinic) from Rayner et al. (1973)

200   were employed. For antigorite, the (001) plane at 2θ=12.114, (002) plane at 2θ=24.503,

201   (201) plane at 2θ=35.597, and (211) plane at 2θ=37.121 were used for comparison with

202   the peaks of the starting material and residual antigorite recovered from the high-*PT*

203   experiments. For forsterite, the (112) plane at 2θ=36.538, (021) plane at 2θ=22.898,

204   (130) plane at 2θ=32.346, (122) plane at 2θ=39.715, (140) plane at 2θ=40.096, and

205   (222) plane at 2θ=52.281 were employed for comparison with the peaks of forsterite

206   formed in the process of antigorite dehydration. For talc, planes (001) and (003) at

207   2θ=9.447 and 28.605, respectively, were basically consistent with the peaks of talc in

208   the dehydration products.

209   **Data Processing and Error Evaluation**

210   By calculating the relative area intensities of the strongest diffraction lines in the

211   XRD patterns, subtracting the background, fitting the area intensities of the strongest

212   diffraction peaks with Gaussian curves, and finally normalizing the area intensity to the

213   intensity of the incident beam and acquisition time, we can obtain the transformation

214   degree and relative mass fraction of each solid phase in the experimental product of the

215   antigorite dehydration reaction (e.g., Perrillat et al., 2005). By adding the normalized

216   intensities of the strongest and most obvious diffraction peak areas, a graph of intensity

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217   (*I*) versus time (*t*) can be established for each phase. The relative mass fraction or

218   relative intensity is plotted as a function of time to study its effect on the reaction

219   kinetics.

220   For a dehydration reaction at a given temperature, the degree of departure from

221   the fitted line (with the intercept equivalent to zero) of each data point on the plot of

222   the molar percent of forsterite or talc produced versus that of antigorite decomposed

223   can be considered the uncertainty. In addition, isothermal kinetic model simulations

224   can be used to provide constraints on the error evaluation of decomposed antigorite.

225   Uncertainties in quantitative phase analysis may mainly result from the preferred

226   orientation of phyllosilicate minerals (i.e., antigorite and talc) and the grain

227   morphology and size of the three phases controlled by kinetic mechanisms.

228

229   **RESULTS**

230   **Reaction Progress of Antigorite Dehydration**

231   Table 1 shows the conditions and results of thirty-six experiments, in which

232   systematic time-dependent reaction experiments were carried out under the conditions

233   of a confining pressure of 200 MPa and temperatures of 500-650 °C. XRD analysis of

234   all the experimental products showed that only forsterite and talc were produced in our

235   experiments through the following reaction:

236   Antigorite $\rightarrow$ Forsterite + Talc + H_2O (1)

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237   Figure 3 shows a comparison of XRD patterns of dehydrated products over time

238   for representative samples at a confining pressure of 200 MPa and a temperature of

239   600 °C. From the figure, we can see that there is no obvious dehydration of the

240   antigorite when $t{\leq}15$ h; thus, the XRD patterns are basically consistent with that of the

241   starting material. After the phase identification of the experimental products, water

242   subtraction and normalization of the solid phases, we find that the samples are not

243   dehydrated for durations of 6 h or less and that the degree of dehydration of the sample

244   after 9 h is very small, with only 3 wt.% talc produced. The dehydration degree is also

245   small for the 15-h sample, in which the amount of talc produced is only 8 wt.% (Table

246   1). With increasing duration, the characteristic peaks of forsterite and talc in the XRD

247   diffraction pattern are increasingly obvious, and the intensity of the peak increases. For

248   instance, the amount of talc produced reached 32 wt.% in a 36-h sample. We also

249   carried out experiments under a confining pressure of 200 MPa at 580 °C, 565 °C,

250   550 °C and 500 °C (Table 1). The maximum durations for operation under these target

251   *PT* conditions were 360 h, 360 h, 6 h, and 745.5 h, respectively. The results show that

252   dehydration of antigorite does not occur at 565 °C but occurs significantly at 580 °C,

253   suggesting that a certain temperature between 565 and 580 °C can be regarded as the

254   temperature stability limit of antigorite under 200 MPa pressure.

255   As clearly shown in Figure 4, with increasing duration, the decomposition of

256   antigorite increases rapidly at first and then slowly; correspondingly, the production of

257   talc and forsterite exhibits similar changes. However, the degrees of decomposition of

258   antigorite and crystallization of talc and forsterite are distinct. Under initially

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259   water-unsaturated conditions, the degrees of change in the three phases are more

260   obvious for experiments at 625 and 650 °C (Figures 4b and 4c). Furthermore, the

261   reaction rate at 650 °C is much faster than that at 625 °C, and the reaction rate at

262   625 °C is much faster than that at 600 °C. Accordingly, at 650 °C, the decomposition

263   of antigorite and the crystallization of both forsterite and talc reach near completion

264   within 9 h. In contrast, the reaction progress at 600 °C is ~80% when the duration is up

265   to 84 h and changes very slowly thereafter (Figure 4a), implying that the water activity

266   is close to 1 (i.e., water saturation) beginning at 84 h. The data point scattering reflects

267   the uncertainty in the quantitative phase analysis. Under water-saturated conditions,

268   however, the reaction rate is much slower at 650 °C (Figure 4d).

269   **Kinetic Parameters**

270   In our experiments, antigorite dehydrates to only forsterite + talc + water, and the

271   Avrami model suitable for heterogeneous solid-state reactions (Avrami, 1939) is thus

272   used to simulate the isothermal kinetic data of the experimental products over time at

273   600, 625 and 650 °C. To study the dehydration kinetics, the strongest peak area

274   calculation is performed for all XRD measurements on recovered run products. For

275   instance, for the strongest peak of antigorite, the peak area at a given temperature

276   before the start of the reaction is regarded as the initial intensity I_0, and the intensity at

277   time t for a given PT condition is marked as I_t; then, I_t/I_0 represents the relative

278   intensity. For isothermal reactions, the reaction progress α can be expressed as follows:

279    $$\alpha = 1 - \frac{I_t}{I_0} \qquad (2)$$

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280   where I_t represents the integrated intensity of a peak at time t (e.g., Wang et al., 2015).

281   This reaction progress can be well described by the classic Avrami model, which

282   includes the two processes of nucleation and growth and can be expressed by the

283   following equation:

284 $$\alpha = 1 - \exp\left(-kt^n\right) \quad (3)$$

285   where t is the time in seconds, k is the rate constant and n is the Avrami exponent. As

286   the Avrami constants, the parameters k and n are considered to have great importance

287   in indicating the nucleation and crystallization mechanisms. In terms of a combination

288   of nucleation and growth processes, Cahn (1956) derived the theoretical n value in the

289   Avrami equation, which varies from 1 to 4. The k and n values are considered to

290   depend on both the time and dimensionality or morphology of the nucleation and

291   growth processes. For $n=1$, the nucleation rate is faster than the growth rate, and when

292     $n=4$, the growth rate is faster than the nucleation rate.

293   Figure 5 shows the fitting to the experimental data at 600, 625, and 650 °C, and

294   the results are summarized in Table 2. Fitting of the data under initially

295   water-unsaturated conditions yields $n=1.33\pm0.13$ and $\ln k=-15.92\pm1.49$ at 600 °C,

296     $n=1.40\pm0.02$ and $\ln k=-14.83\pm0.38$ at 625 °C, and $n=1.50\pm0.02$ and $\ln k=-13.50\pm0.38$ at

297   650 °C for the decomposition of antigorite (Figure 5a); $n=1.37\pm0.08$ and

298     $\ln k=-15.84\pm0.90$ at 600 °C, $n=1.24\pm0.01$ and $\ln k=-13.21\pm0.19$ at 625 °C, and

299     $n=1.15\pm0.01$ and $\ln k=-11.19\pm1.67$ at 650 °C for the crystallization of forsterite (Figure

300   5b); and $n=2.68\pm0.20$ and $\ln k=-30.43\pm2.18$ at 600 °C, $n=2.71\pm0.05$ and

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301   ln$k$=-26.88±0.89 at 625 °C, and n=2.67±0.00 and ln$k$=-24.58±0.03 at 650 °C for the

302   crystallization of talc (Figure 5c). Under water-saturated conditions, n=1.16±0.08 and

303   ln$k$=-13.29±0.92 at 650 °C for the decomposition of antigorite (Figure 5d).

304   The reaction rate constant k shown in equation (3) is expressed by the Arrhenius

305   equation:

306 $$k = A\exp\left(-E/\mathrm{R}T\right) \qquad (4)$$

307   where A is the pre-exponential factor, E is the activation energy in kJ/mole, R is the gas

308   constant (8.314 J K/mol), and T is the absolute temperature in K. The fitted line shown

309   in Figure 6 can be obtained by plotting the natural logarithm of the rate constant and

310   the reciprocal of the absolute temperature, which gives the value of E as 353.51 ±

311   23.69 kJ/mol. Uncertainty on activation energy is the uncertainty of the slope of the

312   line fit to the data points, and does not include propagated errors from the uncertainty

313   on each data point.

314

315   **DISCUSSION**

316   The activation energy value obtained in the present study is higher than the two

317   average activation energies (268.1 kJ/mol and 299.2 kJ/mol) obtained by Liu et al.

318   (2019) based on the double Gaussian distribution activation energy model (2-DAEM)

319   but lower than the value (400 kJ/mol) obtained by the same authors using the

320   Flynn–Wall–Ozawa model (Table 3). Furthermore, it is also higher than the activation

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321   energy reported by Sawai et al. (2013) and Gualtieri et al. (2012) but lower than the

322   activation energy given by Weber and Greer (1965) (Table 3). However, Gualtieri et al.

323   (2012) concluded that the activation energy of their sample was much lower than that

324   reported by Weber and Greer (1965) because their sample consisted of only ~79 wt.%

325   antigorite. They speculated that if ~21 wt.% of impurities, i.e., chrysotile, which is one

326   of the main low-temperature serpentine minerals, were removed, the activation energy

327   of the sample consisting of 100% antigorite would be approximately 322 kJ/mol

328   (Gualtieri et al., 2012), which is very close to the value of 353.51 ± 23.69 kJ/mol that

329   we obtained for the nearly pure antigorite sample. As the pre-exponential factor is

330   linearly correlated with the activation energy, the difference in activation energy may

331   result from a large change in the absolute value of the activation energy caused by the

332   pre-exponential factor (Liu et al., 2019). According to equation (4), this difference in

333   activation energy can be used to reflect the change in the reaction rate (kinetic). Thus,

334   the factors (such as particle size, modulation structure, etc.) affecting dehydration

335   kinetics can be considered to have an effect on the activation energy. In addition,

336   chemical and structural differences in the starting material of antigorite (Wunder et al.,

337   1997, 2001) and water activity (Perrillat et al., 2005) may possibly result in slightly

338   different *PT* locations and invariant points for the serpentine dehydration reaction (e.g.,

339   Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997; Figure 7).

340   **Effect Factors for Dehydration Kinetics and Phase Stability**

341   Several high-*PT* experimental studies (Bose and Ganguly, 1995; Bromiley and

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342   Pawley, 2003; Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997) and field

343   observations of eclogite-facies rocks (Auzende et al., 2002; Guillot et al., 2000;

344   Scambelluri et al., 1995) have shown that antigorite is the only serpentine variety that

345   can exist stably under mantle conditions. Additionally, antigorite follows reaction (1) at

346   high temperatures of 600-700 °C and pressures lower than ~2 GPa (Figure 7; Ulmer

347   and Trommsdorff, 1995). Our experiments were performed at a constant pressure of

348   200 MPa, and the XRD analyses of the products indicated that only forsterite and talc

349   were produced in addition to water, which is consistent with the results of previous

350   studies (e.g., Evans et al., 1976; Ulmer and Trommsdorff, 1995; Wunder and Schreyer,

351   1997; Figure 7). As illustrated in Figure 7, our data show that the dehydration

352   temperature (~570 °C) of our antigorite (m=15) is slightly higher than the reaction

353   boundaries (~540±10 °C) at 200 MPa delineated based on the data of Evans et al.

354   (1976) and Wunder and Schreyer (1997), which may be due to the lower m value of

355   our samples than theirs (m=17). This is also one of the main reasons that our sample

356   has a higher stability and activation energy than the antigorite used in previous

357   dehydration kinetics studies (e.g., Liu et al., 2019; Sawai et al., 2013) (Table 3),

358   because for dehydration reaction at the same temperature, a lower dehydration

359   temperature (higher m value) will result in a faster reaction rate and a corresponding

360   lower activation energy. For similar m values, the dehydration temperature of our

361   sample and that of a natural sample from Cerro del Almirez, Spain (Padrón-Navarta et

362   al., 2008), at different pressures can be used to delineate a reaction boundary, which

363   has a trend similar to those of the reaction boundaries determined by Evans et al. (1976)

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364   and Wunder and Schreyer (1997).

365   Previous studies suggested that if the system contains a small amount of

366   aluminum, the entire phase boundary will migrate to a higher temperature by

367   ~50-100 °C (e.g., Bromiley and Pawley, 2003). However, our antigorite contains only

368   0.06 wt.% Al_2O_3, which is much lower than the aluminum contents of the samples used

369   previously [e.g., 3.45 wt.% in Perrillat et al. (2005) and Chollet et al. (2011); 1.51

370   wt.% in Inoue et al. (2009); 1.73 wt.% in Sawai et al. (2013); and 1.03 wt.% in Liu et

371   al. (2019)]. In contrast, the effect of iron on the thermal stability of antigorite is

372   twofold. On the one hand, Fe^{2+} is known to reduce its stability by ~15-20 °C (Ulmer

373   and Trommsdorff, 1999); on the other hand, Fe^{3+}, like Al and Cr, could stabilize

374   antigorite to higher *PT* conditions (e.g., Bromiley and Pawley, 2003; Debret et al.,

375   2015; Padrón-Navarta et al., 2008, 2013). Recently, 10 wt.% FeO was determined to

376   decrease the stability of antigorite by only 25 °C (Merkulova et al., 2016), suggesting

377   that the effect of iron is subordinate to that of Al. The amount of iron contained in our

378   sample is 0.97 wt.% TFeO; thus, the effect of low iron and aluminum contents on the

379   phase boundary of antigorite might be partially offset.

380   The sample powders used in this study (~10-15 μm) are slightly larger than those

381   in some previous experiments [e.g., 5-10 μm in Liu et al. (2019) and 2-3 μm in

382   Perrillat et al. (2005)]. This may be not only another main reason why our sample

383   dehydration temperature is slightly higher than theirs within a certain time frame (e.g.,

384   Llana-Funez et al., 2007) but also one of the main reasons for the higher activation

385   energy of our coarse-grained samples than those of the fine-grained samples used in

18

386   previous studies (Liu et al., 2019; Perrillat et al., 2005) (Table 3). The effect of grain

387   size on dehydration kinetics can also be reflected by the differences in activation

388   energy of various grain sizes, as the lower the activation energy is, the faster the

389   reaction rate is. For example, earlier experiments on the dehydration kinetics of

390   trehalose dihydrate performed by Taylor and York (1998) suggested that the activation

391   energy decreases with decreasing particle size because smaller particles contain more

392   lattice defects, allowing water to be released more easily, and thus have lower

393   activation energy. Similar results were also reflected in the study of lizardite

394   dehydration kinetics by Llana-Fúnez et al. (2007), who determined average activation

395   energies of 429±201 and 528±34 kJ/mol for powdered and intact samples, respectively.

396   Correspondingly, the dehydration rate of powdered samples is 10 times faster than that

397   of intact samples under the same conditions (Llana-Fúnez et al., 2007). Concurrently,

398   Candela et al. (2007) studied the dehydration kinetics of chrysotile at low pressure and

399   found that fine particles with large surface-to-volume ratios dehydrated more rapidly

400   than larger particles. In this regard, the dehydration kinetics of antigorite were

401   proposed to be dominated by the diffusion of hydrogen in the mineral. If this is correct,

402   the kinetics could be a function of the diffusion length of hydrogen, which is

403   proportional to the specific surface of the grains or the square of the inverse of the

404   grain size (Sawai et al., 2013). Thus, doubling the grain size results in four-times

405   slower kinetics. In addition, the diffusion coefficient of hydrogen in the mineral should

406   depend on temperature, probably with an Arrhenius relation, and thus may be a source

407   of the temperature dependence of the dehydration kinetics of antigorite (Sawai et al.,

19

408   2013). Recently, Wang et al. (2015) conducted an experimental study on the

409   dehydration kinetics of natural talc and found that the dehydration rate of talc

410   increased with decreasing particle size, but when the particle size was less than 5 μm,

411   there was almost no effect on the dehydration rate. Therefore, fine-grained antigorite is

412   generally more likely to dehydrate, and the dehydration rate may be faster than that of

413   a coarse-grained sample.

414   In addition, water activity is an important factor affecting the dehydration

415   boundary of antigorite. Previous studies have shown that the stability limit of antigorite

416   (i.e., the highest temperature under water-saturated conditions) shifts toward lower

417   temperatures with decreasing water activity (e.g., Perrillat et al., 2005; Hilairet et al.,

418   2006; Figure 7). As shown in Table 1 and Figure 4d, the water-saturated samples

419   (Atg60 and Atg61) do not completely decompose to form forsterite + talc at longer

420   durations, but the initially water-unsaturated sample Atg23 under the same PT

421   conditions does nearly completely decompose. The powdered samples Atg60 and

422   Atg61 are immersed in water so that the voids within the sample powders are filled

423   with water to form a water-saturated environment, which is supported by the presence

424   of free water in the recovered sample (e.g., Perrillat et al., 2005). In contrast, the voids

425   within sample Atg23 are partially filled with water generated only by the

426   decomposition of the sample itself, the water activity of the sample increases with

427   duration, and the sample becomes water saturated until near completion of the

428   dehydration reaction. Furthermore, we find that the rate of dehydration slows down

429   significantly when the sample is heated at 600 °C for 60-120 h (Figure 4a), which

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430   means that the water activity of the sample increases, making it impossible for our

431   antigorite to completely dehydrate at this temperature. At higher temperatures (625 and

432   650 °C), however, the rate of dehydration decreases significantly when the sample is

433   nearly completely decomposed in much shorter durations (Figures 4b and 4d). This

434   response implies that an increase in temperature can offset the effect of an increase in

435   water activity.

436   In summary, combining our results with those of previous studies, the stability of

437   antigorite is affected by the modulation structure (i.e., m value), aluminum content,

438   iron content, water activity, and deformation within the Earth. Antigorites with low m

439   values can be stabilized at higher temperatures. An increase in aluminum or Fe^{3+}

440   content can cause the stable boundary to move toward higher temperatures, while an

441   increase in Fe^{2+} content has the opposite and smaller effect. Water activity acts as the

442   driver of the reaction and determines the stability of the antigorite under certain PT

443   conditions (e.g., Perrillat et al., 2005). Different from our static experiments,

444   differential stress must be present within the earth where deformation geometry (such

445   as compression, shear, or the direction of the foliation plane with respect to the

446   maximum principal stress) may change the phase stability of antigorite and thus its

447   dehydration kinetics (Okazaki and Katayama, 2015; Shao et al., 2021; Takahashi et al.,

448   2011). A reduction in particle size can increase the reaction rate (Candela et al., 2007;

449   Llana-Funez et al., 2007; Taylor and York, 1998).

450   **Kinetic Mechanism**

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451   For the decomposition of antigorite, higher n values are found at high

452   temperatures than at low temperatures (Figure 5 and Table 2). The mean n value for

453   antigorite decomposition at the three examined temperatures is 1.41±0.09, indicating

454   an instantaneous nucleation mechanism followed by a growth process governed by

455   chemical species diffusing to the crystal surface (Christian, 1975). Such a mechanism

456   was reported by Perrillat et al. (2005) for the crystallization of forsterite and talc-like

457   phases in the process of antigorite dehydration. The n value (n=1.37) for the

458   crystallization of forsterite is close to that (n=1.33) for the decomposition of antigorite

459   at 600 °C in the same reaction process. However, the value of n for the crystallization

460   of forsterite decreases to 1.15 when the temperature increases to 650 °C (Figure 5),

461   indicating that the crystallization of forsterite is mainly controlled by the growth

462   process with increasing temperature and is accompanied by rapid nucleation saturation.

463   In contrast, the crystallization of talc shows little change in the n value at 600, 625 and

464   650 °C (average n=2.69±0.02), suggesting that the formation mechanism of talc is the

465   same at the three temperatures and is dominated by nucleation. In other words, the

466   nucleation rate of forsterite becomes quite high with increasing temperature, while at

467   the initial stage of the reaction, the nucleation of talc is no longer instantaneous but

468   slow and then increases with time. In addition, the k values of the three minerals

469   increase with increasing temperature, which is similar to the results of a study on talc

470   dehydration kinetics (Wang et al., 2015). Using various methods, however, previous

471   studies determined different kinetic mechanisms for antigorite dehydration. Based on

472   XRD, for example, Perrillat et al. (2005) obtained n=2 for the dehydration of antigorite,

473   indicating a mechanism of surface growth at the grain edge. In contrast, also using

474   XRD, Gualtieri et al. (2012) found that antigorite dehydration is controlled by a

475   one-dimensional diffusion process, which is similar to the finding obtained by Sawai et

476   al. (2013) using in situ high-temperature infrared spectroscopy analysis. In terms of

477   thermogravimetric analysis and in situ XRD, Balucan et al. (2011) found that the

478   dehydration kinetics of antigorite can be well modeled by a three-dimensional phase

479   boundary reaction model. Most recently, also employing thermogravimetric analysis,

480   Liu et al. (2019) determined that the antigorite dehydration kinetics follow 2-DAEM.

481   However, most of these studies did not perform microstructural observations of

482   products to support their analyses of the kinetic mechanism of antigorite dehydration.

483   To confirm our kinetic results, we conducted two complementary experiments

484   (Atg103 and Atg112) and further analysis of the run products. Figure 8 shows

485   backscattered electron (BSE) images of the recovered products produced at 600 and

486   650 °C. Under 600 °C and initially water-unsaturated conditions, the experiment

487   conducted for 48 h generated abundant fine grains of forsterite (Figure 8a), suggesting

488   that the formation of forsterite is controlled by the growth process, followed by rapid

489   nucleation saturation. Furthermore, large crystals of talc were generated in this

490   experiment, indicating that the formation of talc is mainly controlled by nucleation.

491   These observations based on the BSE images of the recovered samples were consistent

492   with the kinetic results that $n=\sim1.3$ for the formation of forsterite and ~2.7 for the

493   formation of talc. Under 650 °C and water-saturated conditions, in contrast, the

494   amounts of forsterite and talc produced were much lower in the experiment conducted

495   for only 3 h (Figure 8b), which is basically consistent with the results of the powder

496   XRD analyses.

497   **Isothermal Kinetic Model and Fluid Production Rates**

498   Previous studies have shown that the hypocenters of the lower-plane seismicity in

499   a DSZ are roughly distributed along the estimated location of the 600-650 °C

500   isotherms (e.g., Peacock, 2001). According to the abovementioned dehydration kinetics

501   data of antigorite at 600 and 650 °C, we can calculate the fluid production rate during

502   the antigorite dehydration process at the two endmember temperatures corresponding

503   to the isotherms bounding the hypocenters. On the basis of the fitting to the

504   decomposition of antigorite at the two temperatures, as shown in Figures 5a and 5d, we

505   can obtain the following relationships indicating the variation in the progress of the

506   dehydration reaction with time at 600 and 650 °C:

507    $$\alpha(T = 600\ ^{\circ}C \text{ and initially water-unsaturated}) = 1 - \exp\left(-\frac{t^{1.33\pm0.13}}{8178342.01\pm0.23}\right) \quad (5)$$

508    $$\alpha(T = 650\ ^{\circ}C \text{ and initially water-unsaturated}) = 1 - \exp\left(-\frac{t^{1.50\pm0.02}}{716404.33\pm0.68}\right) \quad (6)$$

509    $$\alpha(T = 650\ ^{\circ}C \text{ and water-saturated}) = 1 - \exp\left(-\frac{t^{1.16\pm0.08}}{588893.13\pm0.40}\right) \quad (7)$$

510   Figure 9 shows the curves indicating variations in the progress of the reaction

511   with time at 600 and 650 °C calculated according to the above three equations. Some

512   data points at 600 °C seriously depart from the curve because these data have large

513   errors and thus were not included in fitting to obtain n and k used for modelling the

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514   curve. Despite the large errors of some data points, most of the data are consistent with

515   the simulated dehydration kinetics curve. The rate of antigorite dehydration clearly

516   increases with increasing temperature under initially water-unsaturated conditions. At

517   t=800 min, for instance, the antigorite dehydration progress is only ~18.96% at 600 °C

518   and almost 100% at 650 °C under initially water-unsaturated conditions, while it is

519   only ~37.96% at 650 °C under water-saturated conditions. When half of the antigorite

520   is consumed during the breakdown reaction, the dehydration rate can be obtained

521   according to the half-life of the reaction (e.g., Chollet et al., 2011),

522
$$V_{1/2} = \frac{C_{H_2O}}{t_{1/2}} \times \frac{\rho}{\rho_{H_2O}} \qquad (8)$$

523   where $t_{1/2}$ is the half-life of the reaction when the reaction progress is 50% and C_{H_2O}

524   represents the water content of the mineral. ρ and ρ_{H_2O} are the densities of the

525   mineral and water, respectively. In this study, antigorite has a density of 2.593 g/cm^3

526   and a water content of ~12.19 wt.%. At a pressure of 1.5 GPa, the water density is

527   ~1.057, ~1.048, and ~1.038 g/cm^3 at 600, 625, and 650 °C, respectively (Zhang and

528   Duan, 2005). As shown in Figure 9, the half-lives of the antigorite dehydration reaction

529   at 600, 625 and 650 °C under initially water-unsaturated conditions are 32.65, 8.48 and

530   1.77 h, respectively. In contrast, the half-life of antigorite breakdown at 650 °C under

531   water-saturated conditions is 18.37 h. Therefore, the calculated fluid production rates

532   in the process of antigorite dehydration at 600, 625, and 650 °C under initially

533   water-unsaturated conditions are 2.54×10^{-6}, 9.80×10^{-6}, and 4.69×10^{-5} $m_{fluid}^{3}m_{rock}^{-3}s^{-1}$,

534   respectively. Under initially water-saturated conditions, the calculated fluid production

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535   rate is 4.52×10^{-6} $m_{fluid}^3 m_{rock}^{-3} s^{-1}$ at 650 °C, which is ~10 times slower than that under

536   initially water-unsaturated conditions at the same temperature, similar to the result of

537   Perrillat et al. (2005). These values are comparable to those reported previously for

538   antigorite dehydration [3×10^{-5} – 3×10^{-4} $m_{fluid}^3 m_{rock}^{-3} s^{-1}$ at 625-700 °C in Sawai et al.

539   (2013), 8×10^{-5} $m_{fluid}^3 m_{rock}^{-3} s^{-1}$ at 620 °C and 4.4×10^{-4} $m_{fluid}^3 m_{rock}^{-3} s^{-1}$ at 660 °C in Liu et

540   al. (2019), 10^{-4} $m_{fluid}^3 m_{rock}^{-3} s^{-1}$ in Chollet et al. (2011), and 3×10^{-8} – 3×10^{-6}

541    $m_{fluid}^3 m_{rock}^{-3} s^{-1}$ in Perrillat et al. (2005)]. Likewise, the rate at which antigorite

542   dehydration releases fluids in this study is far greater than the viscous relaxation rate of

543   antigorite (3.0×10^{-12} – 3.0×10^{-7} s^{-1}, i.e., the reciprocal of Maxwell's relaxation time)

544   under subduction zone conditions reported by Hilairet et al. (2007). Previous studies

545   have shown that pressure has no obvious effect on the dehydration kinetics of

546   antigorite (e.g., Perrillat et al., 2005; Rubie and Thompson, 1985). Thus, the fluid

547   production rate calculated above can be applied to shallow intermediate-depth

548   earthquake layers in hot subduction zones (e.g., Kii, Tokai, and Cascadia), where

549   antigorite breakdown into forsterite + talc + water is possible (Figure 7).

550   **IMPLICATIONS**

551   For decades, intermediate-depth earthquakes have commonly been considered to

552   result from the dehydration of antigorite (e.g., Chollet et al., 2011; Ferrand et al., 2017;

553   Hilairet et al., 2017; Liu et al., 2019; Miller et al., 2003; Raleigh and Paterson, 1965;

554   Reynard, 2013; Sawai et al., 2013). In their pioneering work on dehydration

555   embrittlement, Raleigh and Paterson (1965) deformed natural serpentinites which

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556   contained other phases such as olivine, and explained that embrittlement occurred

557   within the dehydrating antigorite due to fluid overpressure. However, many later

558   experiments have indicated that embrittlement occurs in adjacent more brittle

559   peridotite or the piston, rather than in the dehydrating antigorite itself (e.g., Dobson et

560   al., 2002; Ferrand et al., 2017; Jung et al., 2004; Xia, 2013). In fact, antigorite shows

561   semibrittle behavior under mantle conditions and no dehydration embrittlement occurs

562   (e.g., Chernak and Hirth, 2011; Gasc et al., 2011; Shao et al., 2021). In lithospheric

563   mantle, only partial serpentinization (17-31%) occurs (Garth and Rietbrock, 2014) and

564   the distribution of serpentine is heterogeneous (Dunkel et al., 2017). Some researchers

565   have proposed that the fluid produced by antigorite dehydration at intermediate depths

566   in a subduction zone likely migrates into the surrounding brittle peridotite region

567   (Barcheck et al., 2012; Rutter et al., 2009) so as to generate not only high pore fluid

568   pressure but also instantaneous over stress due to the lateral transfer of the stress

569   previously supported by the dehydrating antigorite, thereby inducing earthquakes. This

570   inference is partially similar to the sudden stress transfer model proposed by Ferrand et

571   al. (2017), but it is probably true at P<2 GPa. Whether or not the embrittlement of

572   peridotite around the dehydrating antigorite occurs was considered to depend on the

573   competition between the rate of fluid production and migration into the peridotite and

574   the deformation rate of the peridotite (e.g., Chollet et al., 2011; Liu et al., 2019;

575   Perrillat et al., 2005). In the case when fluid migration from dehydrating antigorite to

576   adjacent peridotite is negligible, if fluid is produced at a faster rate than deformation, a

577   seismic rupture may be nucleated. However, several studies have shown that fast

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578   dehydration kinetics may not lead to dehydration embrittlement (e.g., Chernak and

579   Hirth, 2011; Gasc et al., 2011).

580   Under the conditions of syndeformational antigorite dehydration reaction, there

581   must be another heterogeneous system, namely, antigorite and its dehydration products

582   (e.g., Takahashi et al., 2011). As stated by Gasc et al. (2011), we should emphasize the

583   role of reaction products whose size is in turn controlled by reaction kinetics (Rutter

584   and Brodie, 1988). In a recent study by Proctor and Hirth (2015), forsterite produced

585   by the dehydration of antigorite has a finer grain size in drained samples than in

586   undrained samples. This means that in the interior of the earth, the dehydration of

587   antigorite may produce finer-grained forsterite (<1 μm) than that observed in our

588   undrained experiments (Figure 8). Such fine-grained forsterites may facilitate faulting

589   by their superplasticity (Rutter and Brodie, 1988; Schubnel et al., 2013). However,

590   several studies suggest that stick-slip occurs under the conditions where dehydration of

591   antigorite happens (Okazaki and Katayama, 2015; Takahashi et al., 2011). SEM

592   observations also indicate heterogeneous dehydration products (Takahashi et al., 2011),

593   in which forsterite displays velocity weakening (Boettcher et al., 2007; King and

594   Marone, 2012) while antigorite shows velocity strengthening and thus inhibits normal

595   stick-slip behavior (Chernak and Hirth, 2011; Shao et al., 2021). Consequently, when

596   significant dehydration occurs in the core of a serpentinized fault zone at 650 °C,

597   normal stick-slip behavior can be expected as the velocity-weakening behavior of

598   forsterite dominates the frictional properties of the entire fault gouge (Boettcher et al.,

599   2007; King and Marone, 2012; Okazaki and Katayama, 2015). Once triggered, an

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600   earthquake will propagate into the more brittle surrounding rocks. At 600 °C, slow

601   stick-slip could be induced by interaction between the velocity strengthening behavior

602   of antigorite and the velocity-weakening behavior of forsterite (Okazaki and Katayama,

603   2015). In addition, unstable slip can also be induced by water or talc because such

604   phases may reduce the rate dependence of antigorite (e.g., Moore and Lockner, 2011;

605   Okazaki and Katayama, 2015), thereby facilitating faulting. In a heterogeneous system,

606   the sizes of the dehydration products are crucial, which in turn depend on the kinetic

607   mechanism of dehydration. In this study, the reaction of antigorite dehydration to

608   fine-grained forsterite and large talc crystals is controlled by a heterogeneous

609   nucleation and growth mechanism. As the temperature increases from 600 to 650 °C,

610   the influence of forsterite by growth control increases (n decreases to close to 1, Figure

611   5b), resulting in the formation of finer-grained forsterite. This change indicates that the

612   increase in the dehydration degree in the core of a serpentinized fault zone will

613   facilitate faulting, triggering earthquakes and extending to the more brittle peridotite.

614   Therefore, the reaction of antigorite dehydration to talc, one of the weakest

615   phyllosilicates (Moore and Lockner, 2011), and fine-grained forsterite may be

616   responsible for shallow intermediate-depth seismicity in hot subduction zones (Figure

617   7).

618

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920 **Figure and table captions**

921

922 **Figure 1.** High-resolution TEM image of the starting material (a) and histogram of *m*

923   values showing the distribution of periodicities (b)

924

925 **Figure 2.** Schematics of a Tuttle-type autoclave (cold-seal hydrothermal vessel)

926   employed for the high-*PT* experiments in this study

927

928 **Figure 3.** Comparison of XRD patterns of experimental products over time for

929   representative samples under the initially water-unsaturated conditions of 200 MPa

930   confining pressure and 600 °C temperature. Below the graph are the PDF cards of talc

931   (Rayner and Brown, 1973), forsterite (Hushur et al., 2009) and antigorite (Hess et al.,

932   1952). Atg = antigorite, Fo = forsterite, and Tlc = talc.

933

934 **Figure 4.** Variations in decomposition of antigorite and crystallization of forsterite and

935   talc (wt.%) with time (min) for the dehydration reaction of antigorite to forsterite + talc

936   at 600 (a), 625 (b), and 650 °C (c and d). Panels a-c display data under initially

937   water-unsaturated conditions, while panel d shows data under water-saturated

938   conditions. Vertical line represents error.

939

940 **Figure 5**. Plots of $\ln[-\ln(1-\alpha)]$ versus $\ln(t)$ for each solid phase involved in reaction (1)

941   at 600, 625, and 650 °C. Decomposition of antigorite (a, d) and crystallization of

942   forsterite (b) and talc (c) occur in reaction (1). Reactions shown in panels a-c are under

943   initially water-unsaturated conditions, while those shown in panel d are under

944   water-saturated conditions. The slopes of the lines fit to the data points marked by

945   hollow circles represent the *n* values that best describe the reaction mechanisms. Data

946   points marked by solid circles have not been included for the fitting due to large errors.

947

948   **Figure 6**. Arrhenius diagram of the dehydration of antigorite. As shown in this figure,

949   the activation energy, *E*, can be calculated from the slope of the solid line.

950

951   **Figure 7**. *PT* conditions of the present experiments (red stars) and a MgO-SiO$_2$-H$_2$O

952   (MSH) phase diagram constructed with a blue line, black line, pink line and red dashed

953   line representing the phase boundaries defined by the data of Evans et al. (1976),

954   Ulmer and Trommsdorff (1995), Wunder and Schreyer (1997) and Perrillat et al.

955   (2005), respectively. The phase boundary represented by the red dashed line

956   corresponds to low water activity. Magenta dotted lines delimit *PT* ranges for different

957   *m*-isolines of synthetic antigorite, which are labeled by magenta italic numbers, in the

958   MSH system determined by Wunder et al. (2001). The yellow vertical bar with

959   *m*=14-15 represents natural antigorite from Cerro del Almirez, Spain (Padrón-Navarta

960   et al., 2008). The blue horizontal bar with *m*=15-16 is shown for natural antigorite

961   from central Cuba (Auzende et al., 2002). Circles show the *PT* conditions at

962   hypocenters calculated by Abers et al. (2013) for seismicity in the subducting mantle

45

963   beneath southwestern Japan [Kii (pink circle), Tokai (green circle)] and Cascadia (blue

964   circle). Hollow stars indicate the starting material (i.e., antigorite) with the most

965   frequently observed m=15 (Figure 1), which is stable and undecomposed under the

966   corresponding PT conditions, and solid stars indicate the occurrence of dehydration of

967   the starting material to produce forsterite + talc under the corresponding PT conditions.

968   Atg = antigorite, Fo = forsterite, Tlc = talc, and En = enstatite.

969

970   **Figure 8.** BSE images of recovered run products. (a) Atg103 under 600 °C and initially

971   water-unsaturated conditions for 48 h. (b) Atg112 under 650 °C and water-saturated

972   conditions for 3 h.

973

974   **Figure 9**. Dehydration kinetic models for antigorite at 600 and 650 °C, corresponding

975   to the endmember isotherms bounding the hypocenters of the lower-plane seismicity of

976   a DSZ, derived from the parameters of isothermal experiments. Models for antigorite

977   dehydration kinetics at 625 °C and initially water-unsaturated conditions and at 650 °C

978   and water-saturated conditions are also included for comparisons. A solid line

979   represents an initially water-unsaturated model, while a dashed line shows a

980   water-saturated model. The hollow circles represent the experimental data used for

981   fitting n and k that are used to stimulate the kinetic curves, while the data marked by

982   solid circles are not included for fitting. Vertical line represents the degree of deviation

983   of data from the curve, which can be used to constrain the error of the data.

46

Table 1. Experimental conditions and results for dehydration kinetics of antigorite at a constant pressure of 20 type autoclave

Sample #	Temperature (°C)	Duration (h)	Dehydration	Recovered products (wt.%)*			
				Antigorite	Error[&]	Forsterite	Error
Atg3	650	18	Yes	0.00	0.00	50.30	(31.10)
Atg4	650	3	Yes	41.40	(19.76)	7.60	3.75
Atg5	650	1	Yes	94.20	(19.78)	1.70	(0.58)
Atg7	550	6	No	100.00	0.00	0.00	0.00
Atg8	500	240	No	100.00	0.00	0.00	0.00
Atg10	650	15	Yes	0.00	0.00	14.20	(5.02)
Atg11	500	745.5	No	100.00	0.00	0.00	0.00
Atg12	650	9	Yes	2.00	(1.96)	18.20	0.78
Atg21	650	4.5	Yes	4.10	1.93	19.20	(0.62)
Atg22	650	6	Yes	3.00	(1.67)	21.20	(2.41)
Atg23	650	12	Yes	0.10	(0.10)	55.60	(36.40)
Atg26	600	9	Yes	91.00	(2.71)	7.00	(2.86)
Atg27	600	15	Yes	81.00	(2.81)	11.00	0.03
Atg28	600	36	Yes	39.00	6.41	29.00	4.37
Atg29	600	48	Yes	54.90	(23.49)	15.60	23.56
Atg31	600	6	No	100.00	(7.00)	0.00	0.00
Atg32	600	24	Yes	79.92	(16.79)	6.70	11.76
Atg33	600	60	Yes	21.00	0.04	49.00	(7.50)
Atg35	600	84	Yes	17.00	(8.29)	54.00	(11.26)
Atg36	650	10.5	Yes	0.00	0.00	46.09	(26.90)
Atg41	600	72	Yes	25.00	(11.30)	45.00	(2.81)
Atg50	600	120	Yes	26.00	(24.03)	38.00	5.29
Atg52	650	20	Yes	0.00	0.00	51.49	(32.30)
Atg54	580	360	Yes	67.06	4.20	14.91	0.22
Atg55	565	360	No	100.00	0.00	0.00	0.00
[$]Atg57	650	3	Yes	94.70	(2.77)	5.30	(2.10)
[$]Atg58	650	6	Yes	86.70	(3.88)	6.30	1.73
[$]Atg59	650	9	Yes	81.10	(7.18)	8.60	2.82
[$]Atg60	650	15	Yes	69.70	(11.87)	15.30	3.00
[$]Atg61	650	48	Yes	14.80	(2.80)	53.30	(1.83)
Atg88	625	36	Yes	0.00	0.53	55.10	2.31
Atg89	625	24	Yes	9.90	(4.76)	51.70	0.03
Atg90	625	15	Yes	16.40	5.09	50.10	(2.11)
Atg91	625	6	Yes	71.10	(5.84)	16.90	(0.31)
Atg92	625	3	Yes	82.60	2.45	12.40	(2.41)
Atg93	625	1	Yes	95.50	1.08	4.00	(1.42)

*Uncertainties in quantitative phase analysis may mainly result from the preferred orientation of both antigorit grain morphology and size of three phases in the run products.

[&]Error is constrained by the degree of deviation of decomposed antigorite data from the isothermal kinetic curv[$]Water-saturated conditions.

0 MPa using a Tuttle-

Talc	Error
49.70	31.08
51.00	(3.75)
4.10	0.58
0.00	0.00
0.00	0.00
85.80	(5.02)
0.00	0.00
79.80	(0.79)
76.70	0.62
75.80	2.41
44.30	36.38
3.00	0.00
8.00	0.00
32.00	(7.80)
29.40	(1.00)
0.00	0.00
13.39	0.00
30.00	0.10
29.00	2.00
53.91	26.87
30.00	0.60
37.00	(5.60)
48.51	32.28
18.00	(4.42)
0.00	0.00
0.00	2.10
7.00	(1.73)
10.30	(2.82)
15.00	(3.00)
31.90	1.83
44.90	(2.38)
38.40	(0.09)
33.50	2.05
11.40	0.89
5.00	2.40
0.50	1.41

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Table 2. Information on kinetic mechanism parameters for dehydration of antigorite and crystallization

Phase	T (°C)	n	$\ln k$	R^2
Antigorite	600	1.33 ± 0.13	-15.92 ± 1.49	0.97
	625	1.40 ± 0.02	-14.83 ± 0.38	0.93
	650	1.50 ± 0.02	-13.50 ± 0.38	0.79
	650[*]	1.16 ± 0.08	-13.29 ± 0.92	0.98
Forsterite	600	1.37 ± 0.08	-15.84 ± 0.90	0.99
	625	1.24 ± 0.01	-13.21 ± 0.19	0.97
	650	1.15 ± 0.18	-11.19 ± 1.67	0.95
Talc	600	2.68 ± 0.20	-30.43 ± 2.18	0.99
	625	2.71 ± 0.05	-26.88 ± 0.89	0.81
	650	2.67 ± 0.00	-24.58 ± 0.03	1.00

[*]Water-saturated conditions

of forsterite and talc

Table 3. Activation energies of the dehydration of antigorite from the literature

Activation energy (kJ/mol)	Comment	Methods
268.1	slow dehydration	thermogravimetric analysis and 2-DAEM
299.2	fast dehydration	
400		thermogravimetric analysis and Flynn-Wall-Oza
219	water band 1	
243	water band 2	in situ high-temperature infrared spectroscopy
256	water band 3	
255	612-708 ºC	in situ powder XRD and TEM
444-728	689-766 ºC	thermogravimetric analysis and XRD

References

Liu et al. (2019)

Sawai et al. (2013)

Gualtier et al. (2012)
Weber and Greer (1965)

Figure 1

Pressure gauge

to pressure pump

Cold sealing cone   High-pressure needle valve

Filler rod

Nickel-based alloy autoclave

Thermocouple wire

Tube heating furnace

Temperature controller

Sample capsule
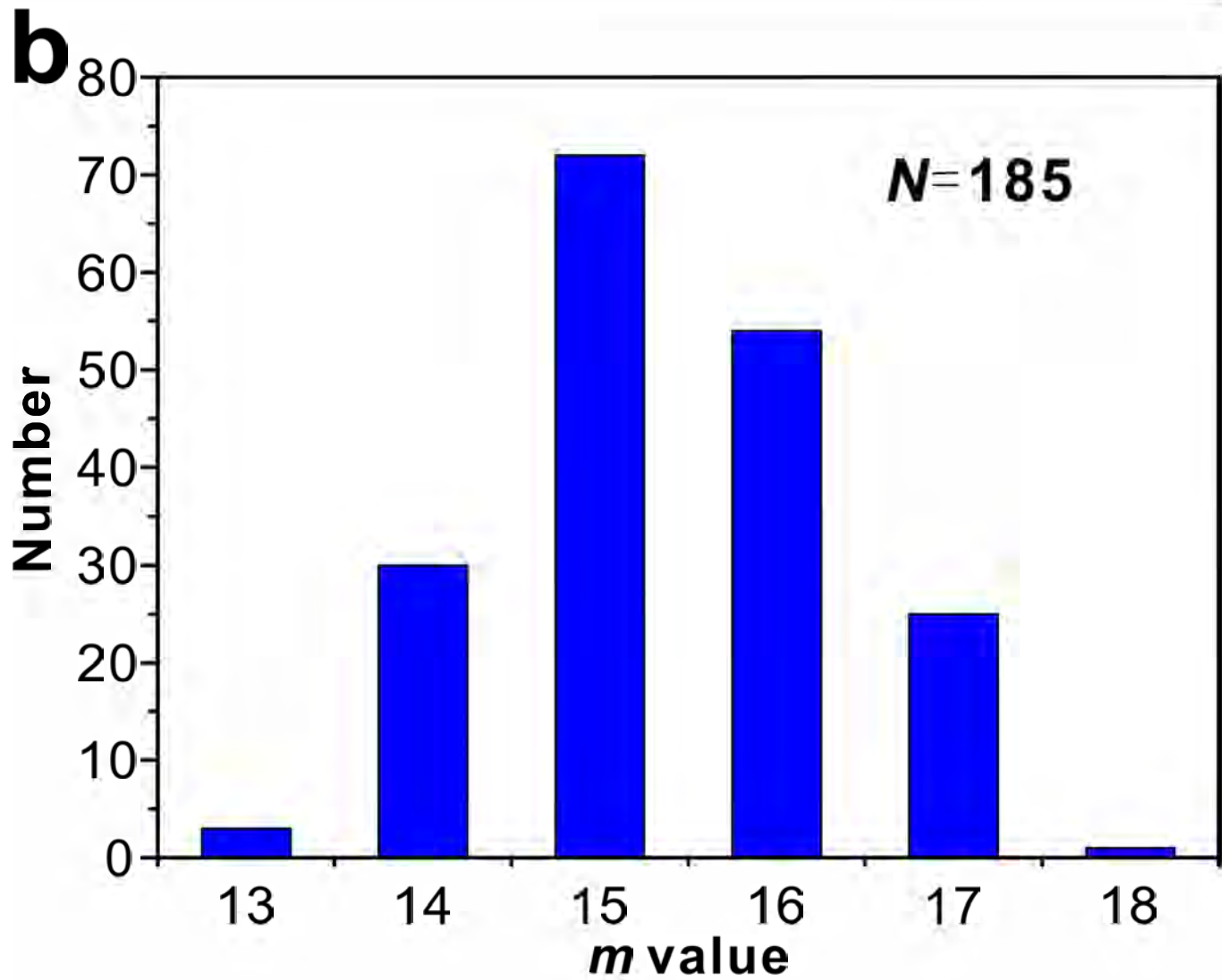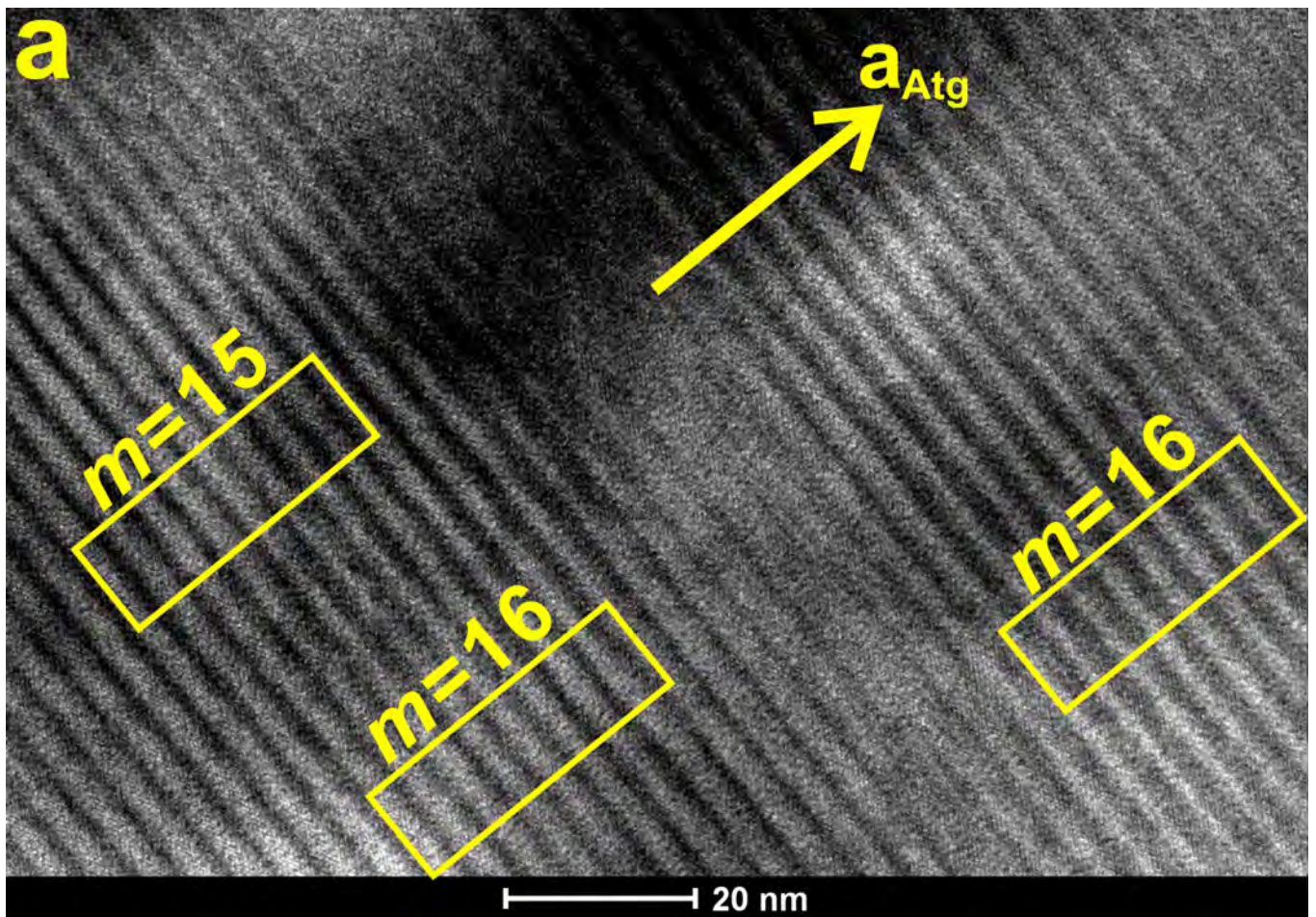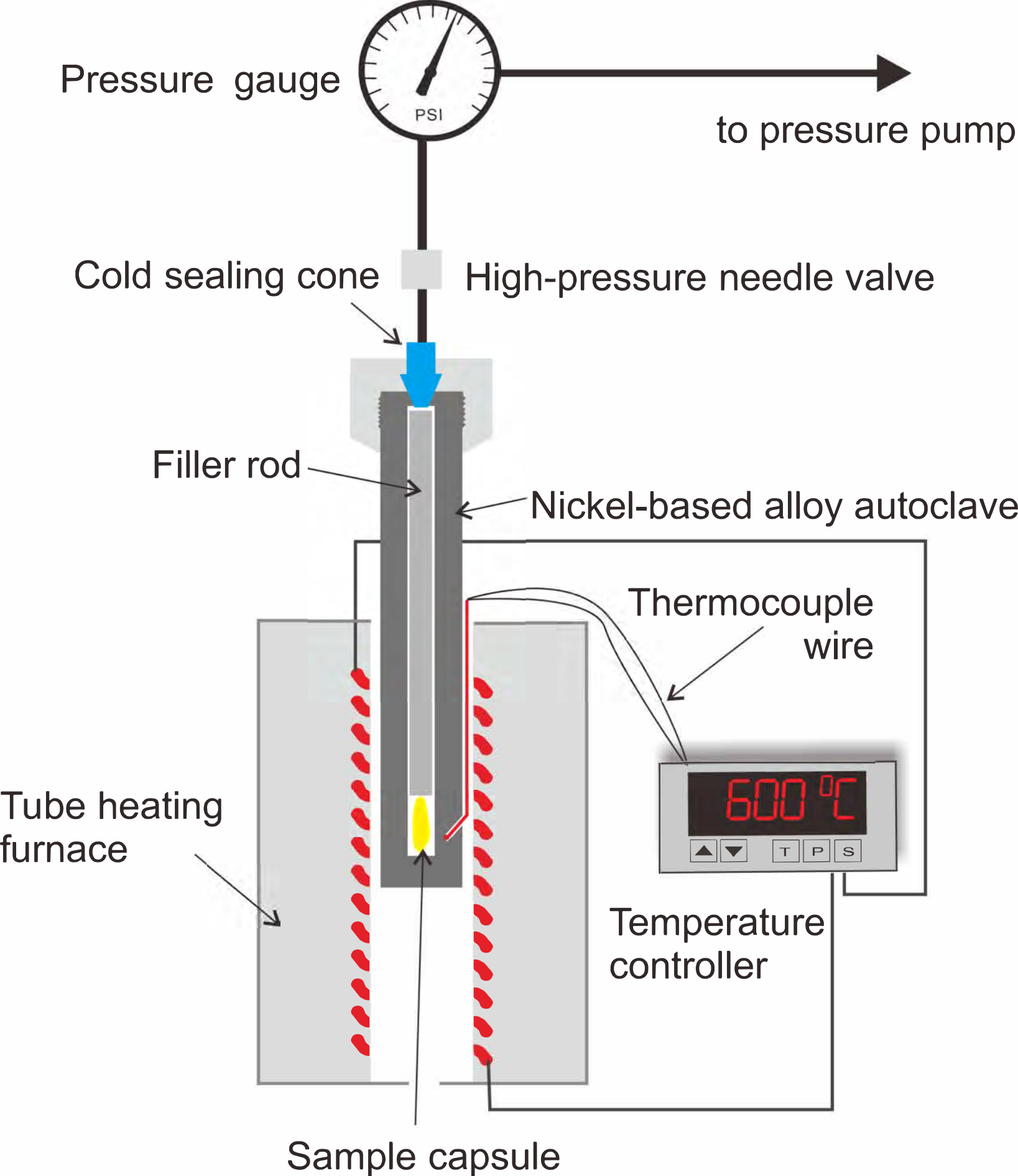
Figure 2

Figure 3

Figure 4

a Initially water-unsaturated

$n=1.40\pm0.02$
$\ln k=-14.83\pm0.38$
$R^2=0.93$ (625 °C)

$n=1.50\pm0.02$
$\ln k=-13.50\pm0.38$
$R^2=0.79$ (650 °C)

$n=1.33\pm0.13$
$\ln k=-15.92\pm1.49$
$R^2=0.97$ (600 °C)

Decomposition of antigorite

b Initially water-unsaturated

$n=1.15\pm0.01$
$\ln k=-11.19\pm1.67$
$R^2=0.95$ (650 °C)

$n=1.37\pm0.08$
$\ln k=-15.84\pm0.90$
$R^2=0.99$ (600 °C)

$n=1.24\pm0.01$
$\ln k=-13.21\pm0.19$
$R^2=0.97$ (625 °C)

Crystallization of forsterite

c Initially water-unsaturated

$n=2.67\pm0.00$
$\ln k=-24.58\pm0.03$
$R^2=1$
(650 °C)

$n=2.68\pm0.20$
$\ln k=-30.43\pm2.18$
$R^2=0.99$ (600 °C)

$n=2.71\pm0.05$
$\ln k=-26.88\pm0.89$
$R^2=0.81$ (625 °C)

Crystallization of talc

d Water-saturated

$n=1.16\pm0.08$
$\ln k=-13.29\pm0.92$
$R^2=0.98$ (650 °C)

Decomposition of antigorite

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9