Time-resolved X-ray diffraction experiment of dehydration of serpentine at high pressure

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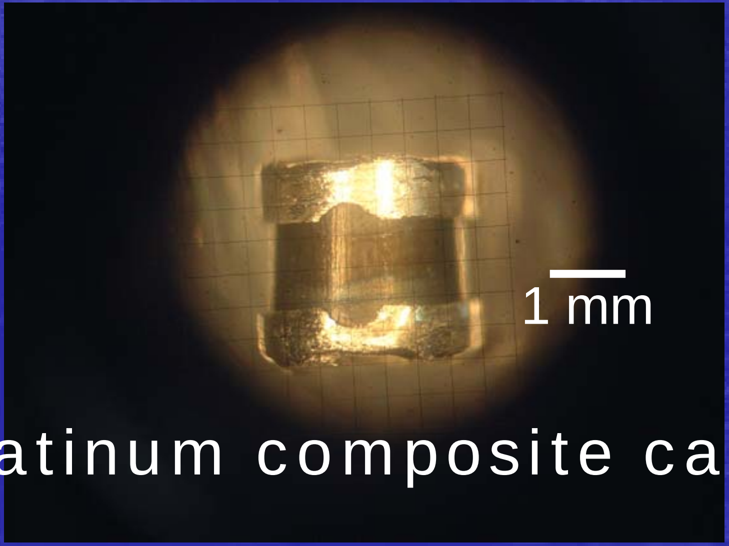
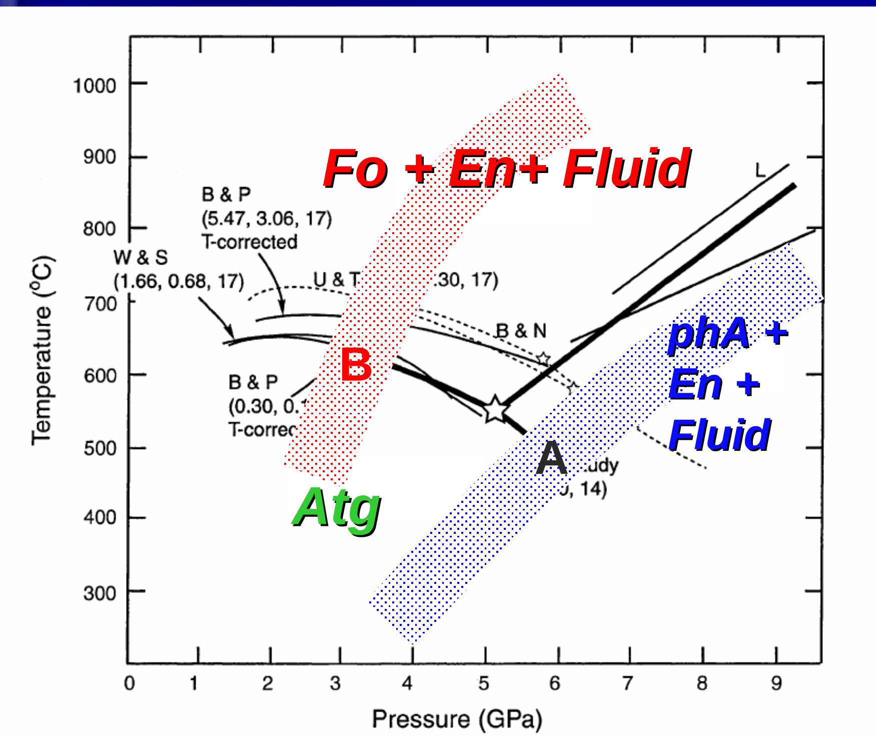


Diamond-platinum composite capsule

2007APS workshop

Phase diagram of antigorite



Modified from Komabayashi et al. (2005)

Atg: Antigorite, Fo: Forsterite

En: Enstatite, phA: Phase A

A

Atg: $5Mg_6Si_4O_{10}(OH)_8$

$\rightarrow 2Mg_7Si_2O_8(OH)_6 + 16MgSiO_3 + 18H_2O$

ph A, En, Fluid

9.1 wt% water released

3.9wt% water transported to deep mantle

B

Atg: $Mg_6Si_4O_{10}(OH)_8$

$\rightarrow 2Mg_2SiO_4 + 2MgSiO_3 + 4H_2O$

Fo, En, Fluid

13 wt% water released

⇒How about the reaction rate in subducting slab (low temperature)?

There are many experimental studies about the stability of antigorite (phase equilibrium study) under pressure.

However, few study about time-resolved study (reaction kinetics study) under pressure.

(Perrillat et al.(2005) etc)

↓

Time-resolved experiment of dehydration of antigorite under pressure

Experiments

High pressure apparatus : MAX80 (AR-NE5C in KEK)

Time-resolved experiment: every 60 sec.

Anvil truncation: 4, 6 mm

X-ray diffraction : Energy dispersive system by Ge-SSD

Sample: Natural antigorite
Ideal formula: $Mg_6Si_4O_{10}(OH)_8$
※Al_2O_3 1.5 wt%, FeO 2.6 wt%

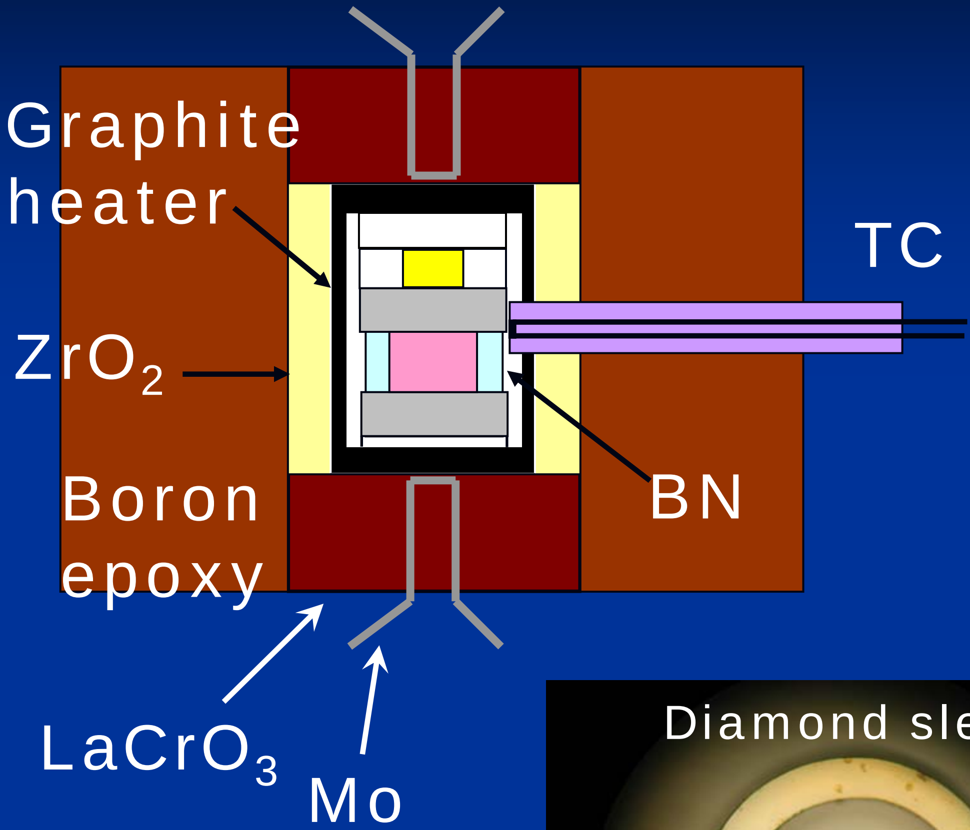
P-T : 3-9 GPa, <1000℃

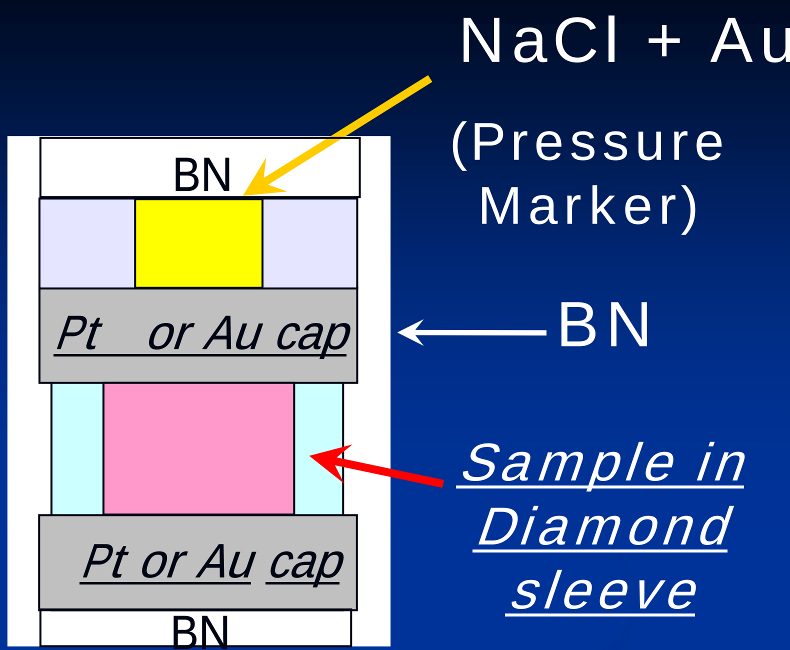
Pressure marker: NaCl (Decker, 1971)

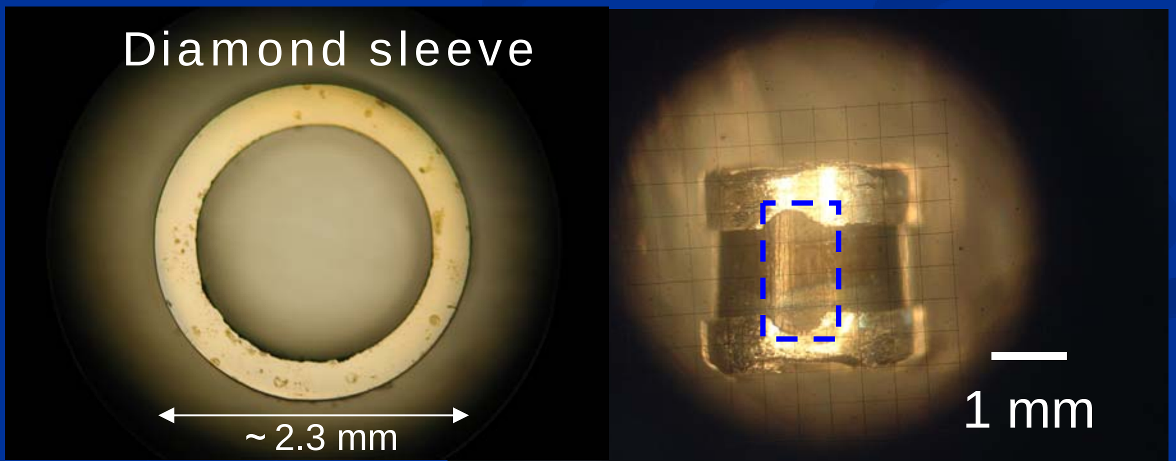
Analyses of recovered sample: SEM-EDS, FE-SEM,XRD

MAX80 cubic-type apparatus (KEK, AR-NE5C)

Cell assembly

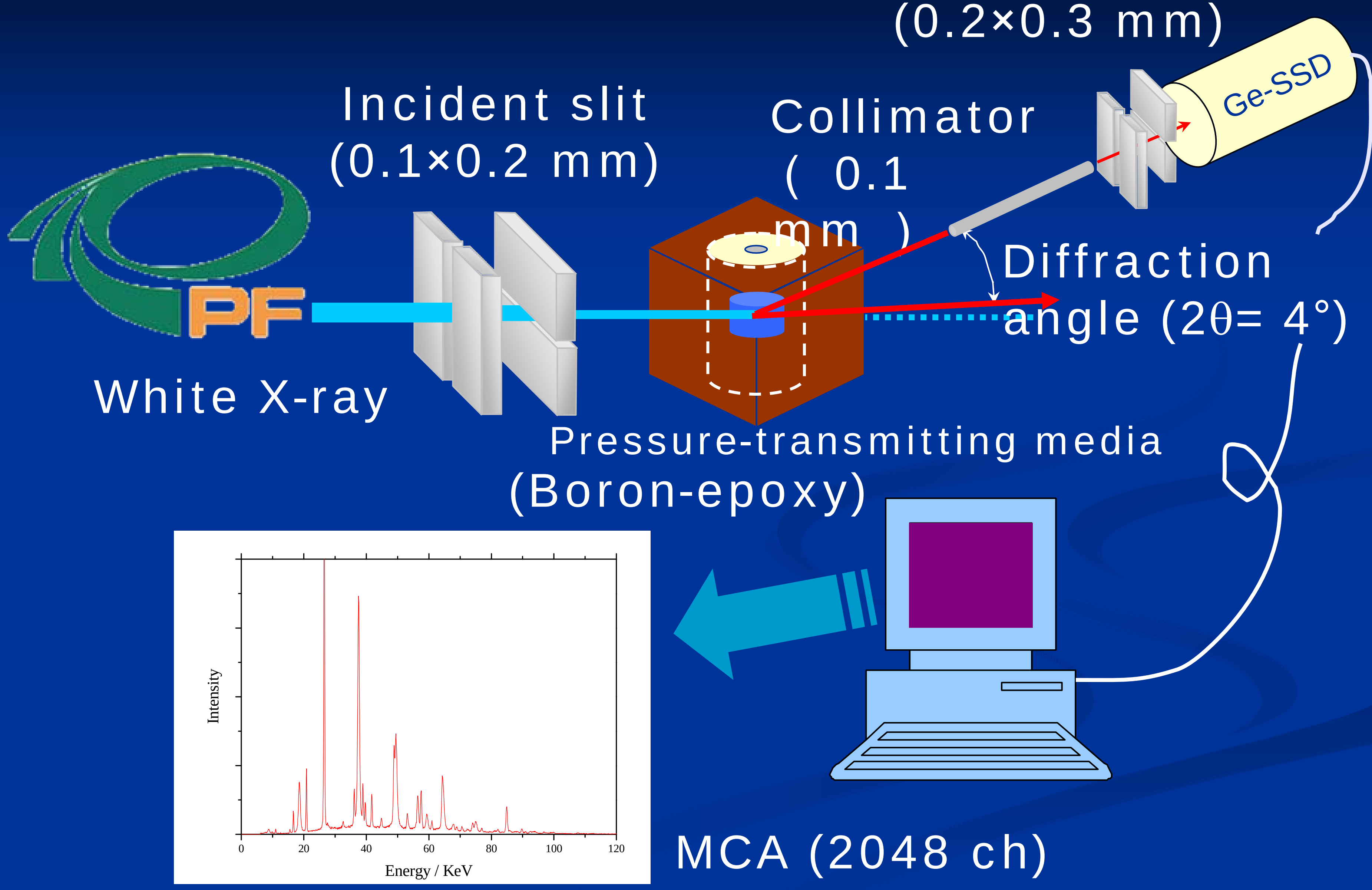




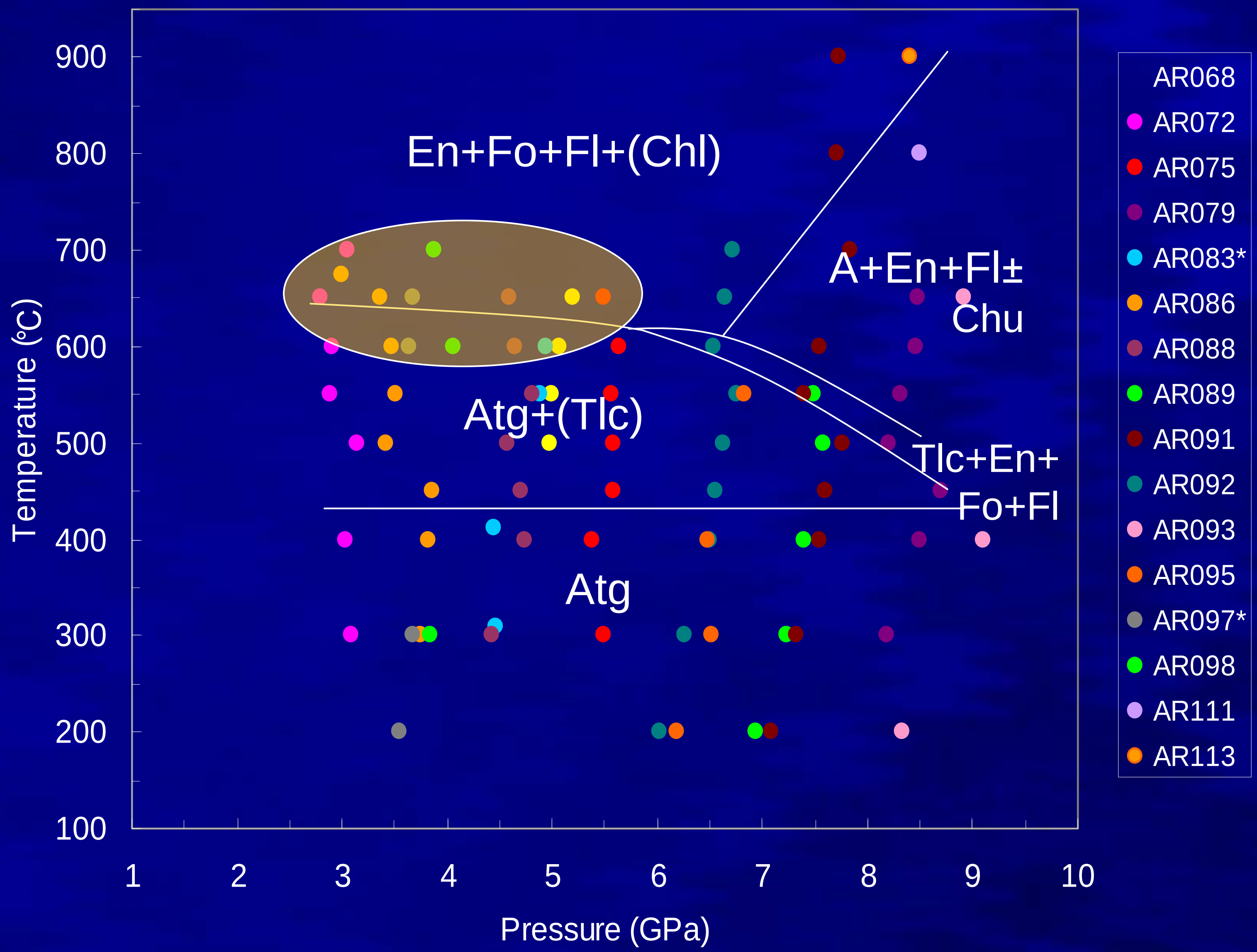


Diamond - Pt or Au composite capsule

Optical system (AR-NE5C)



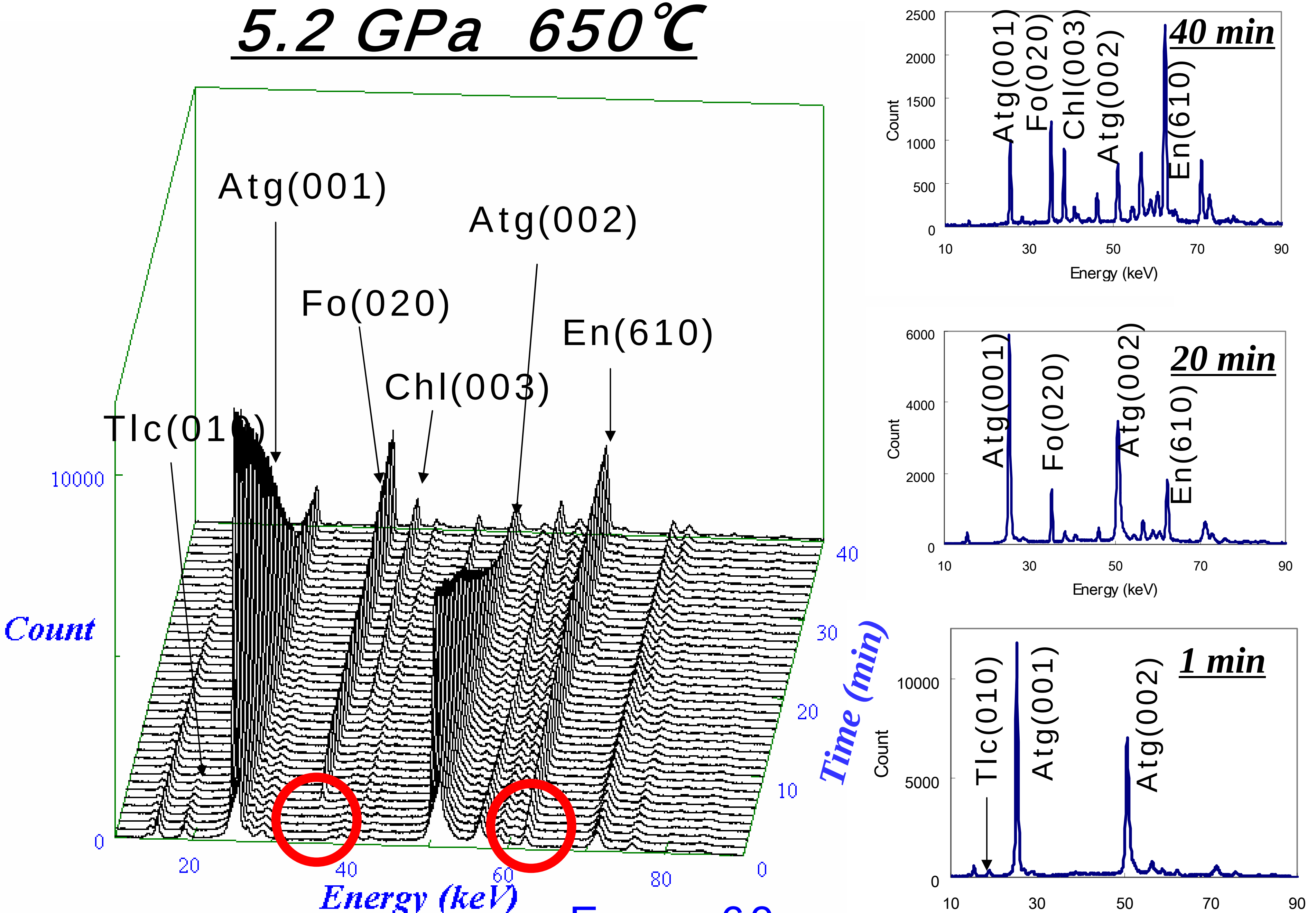
Phase diagram of Antigorite



Atg: Antigorite, Tlc: Talc, Fo: Forsterite, En: Enstatite, Chl: Chlorite, A: Phase A, Chu: Clinohumite

( ):Small amount, *: power estimate

5.2 GPa 650℃



Every 60 sec

Avrami model

$$V = 1 - \exp(-kt^n)$$

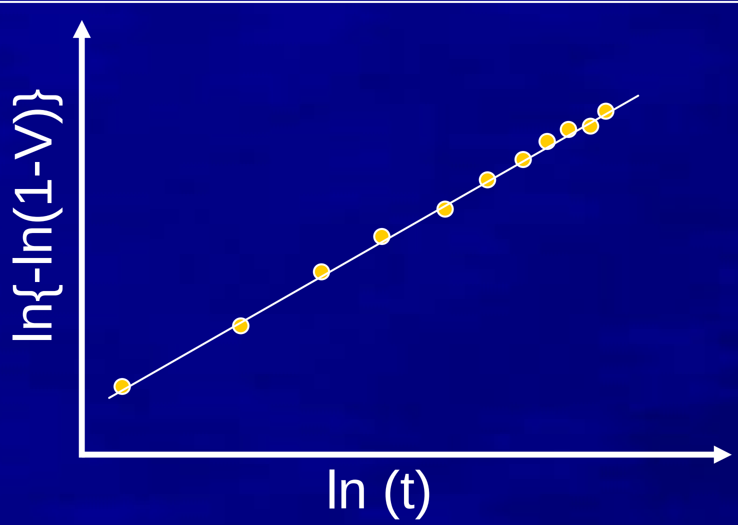
t : time

V: transformed volume fraction ($V=I/I_{max}$)

k: rate constant

n: constant that depends on the reaction mechanism

$$\ln\{-\ln(1-V)\} = \underline{n}\ln(t) + \underline{\ln(k)}$$



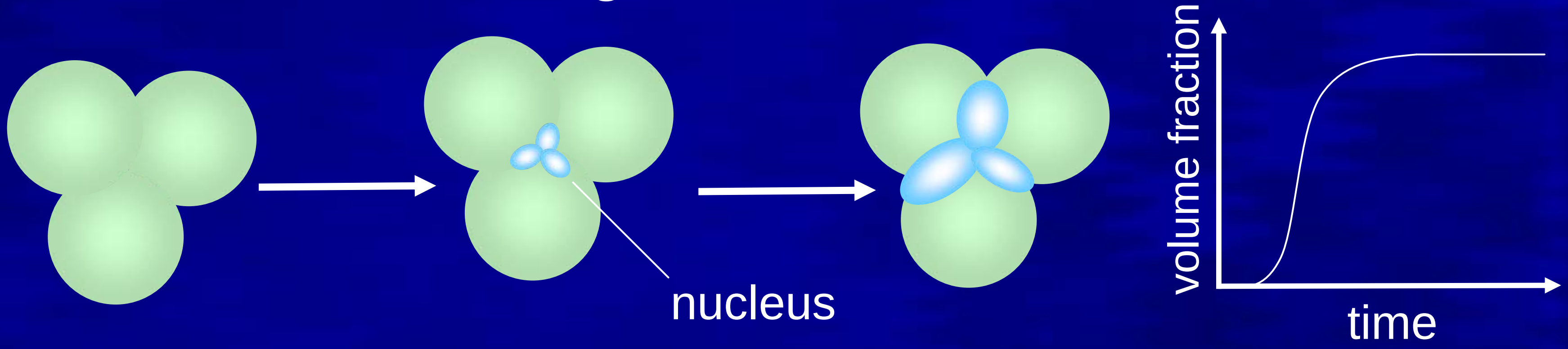
slope ⇒ n

intercept ⇒ ln(k)

Interpretation of n value

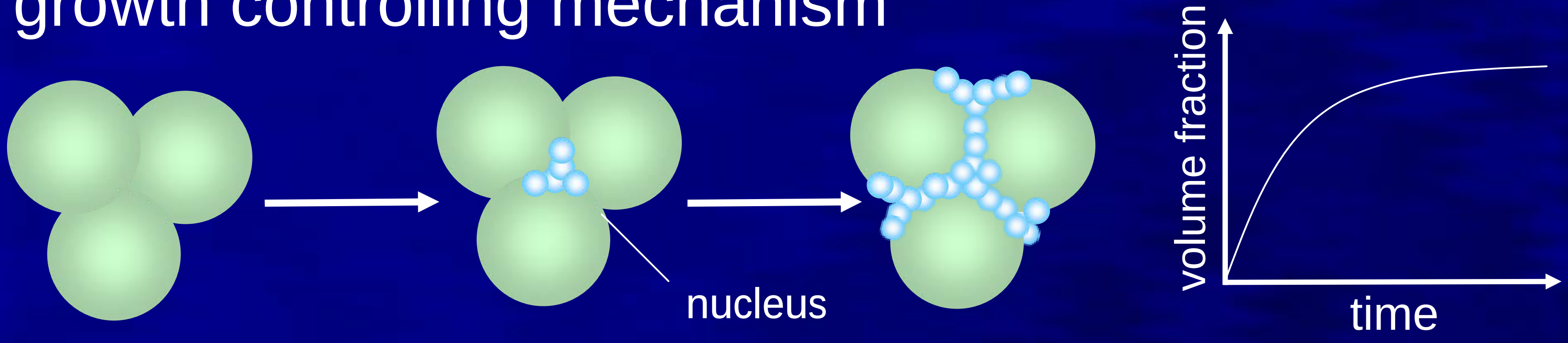
n>1: the growth rate is large relative to nucleation rate

nucleation controlling mechanism

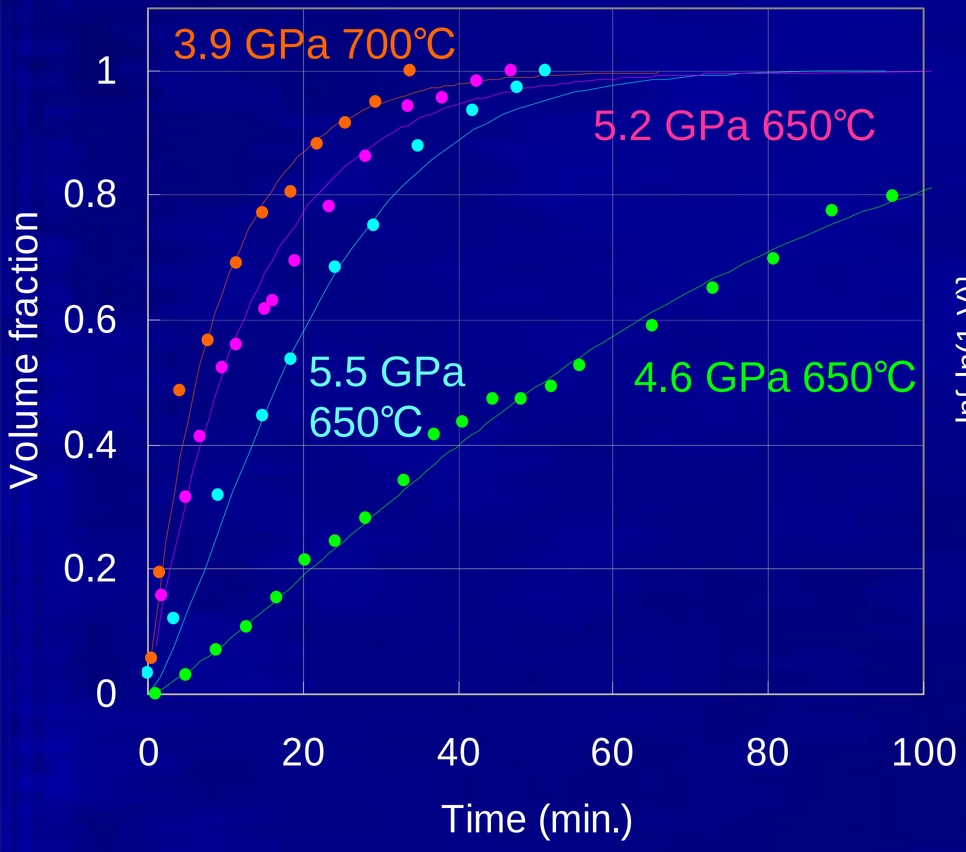


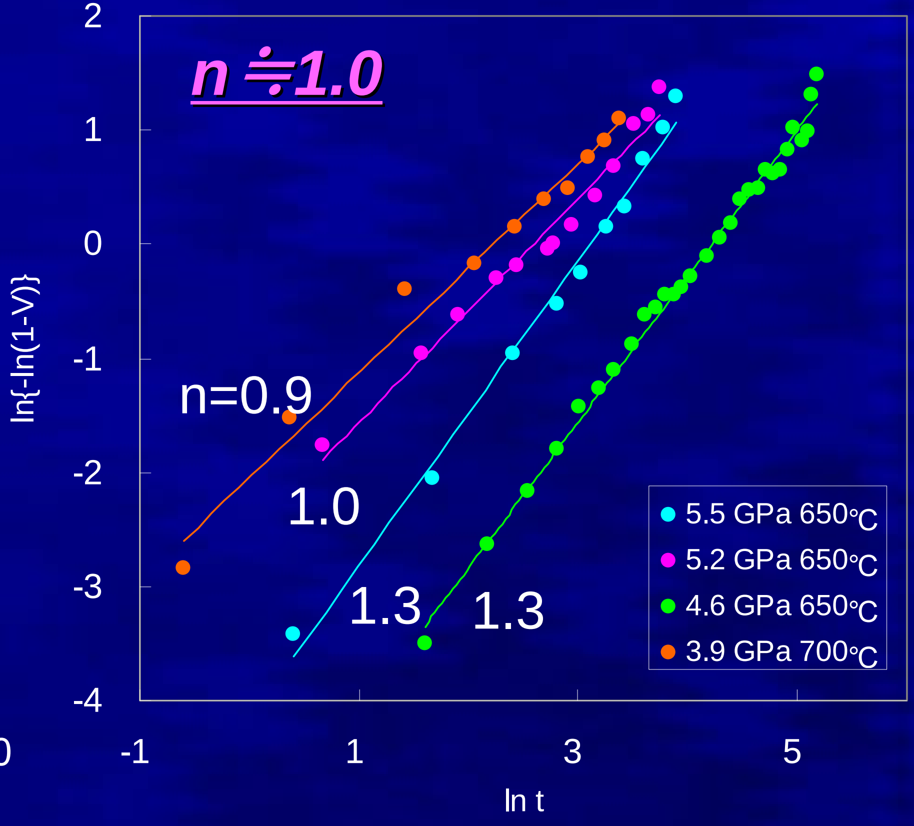
n≦1: the nucleation rate is large relative to growth rate

growth controlling mechanism



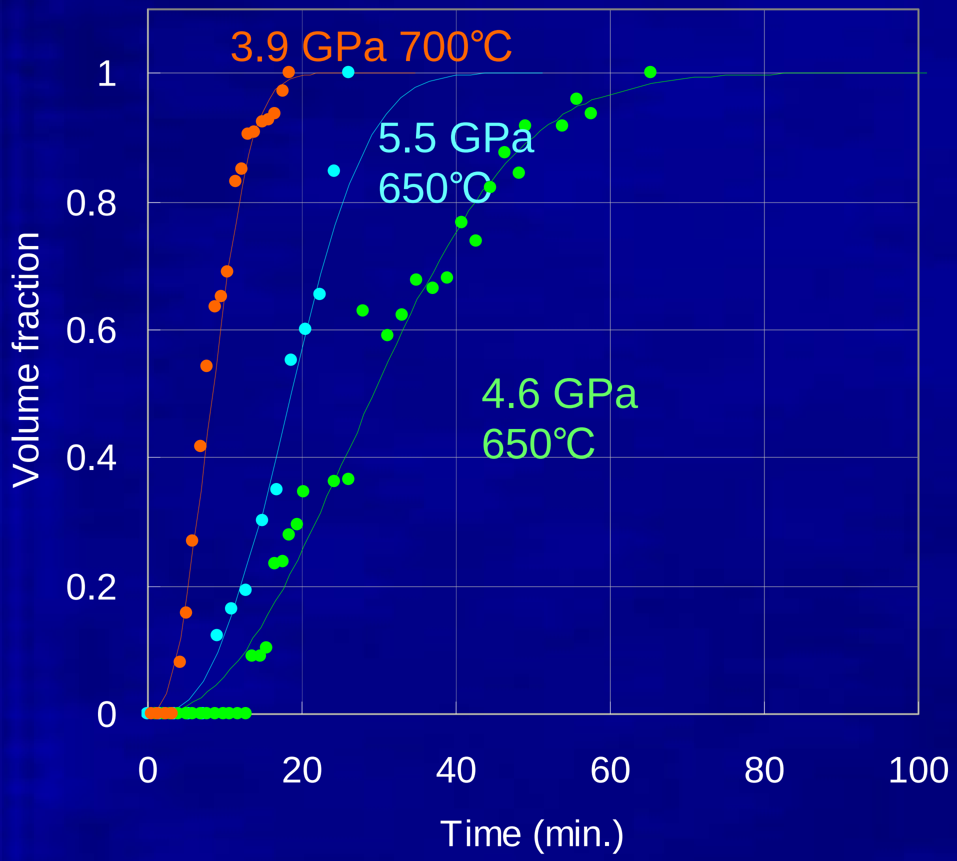
Fitting of Enstatite growth

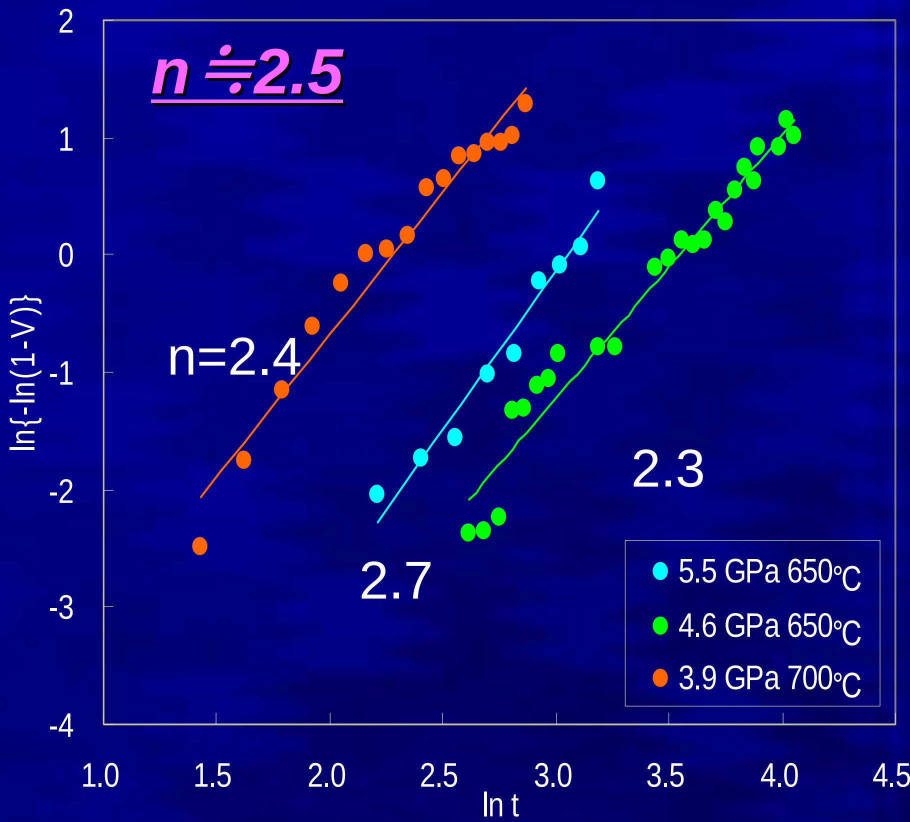




➢ ***n ≒1.0*** growth controlling mechanism

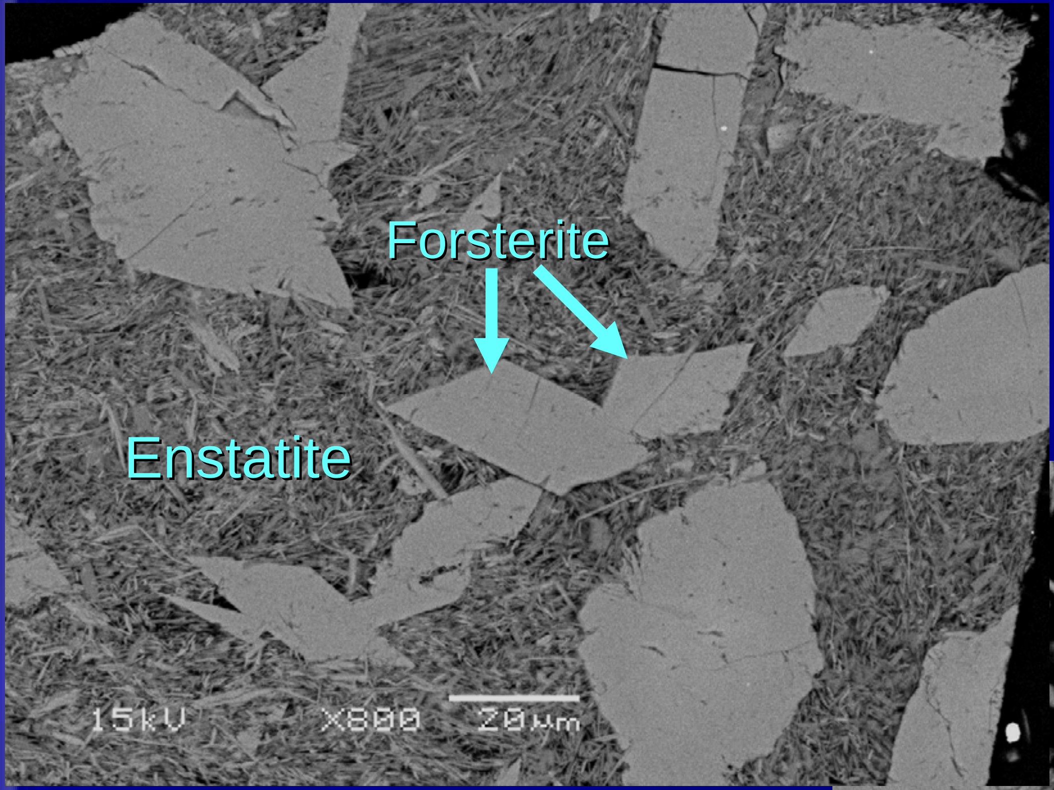
Fitting of Forsterite growth



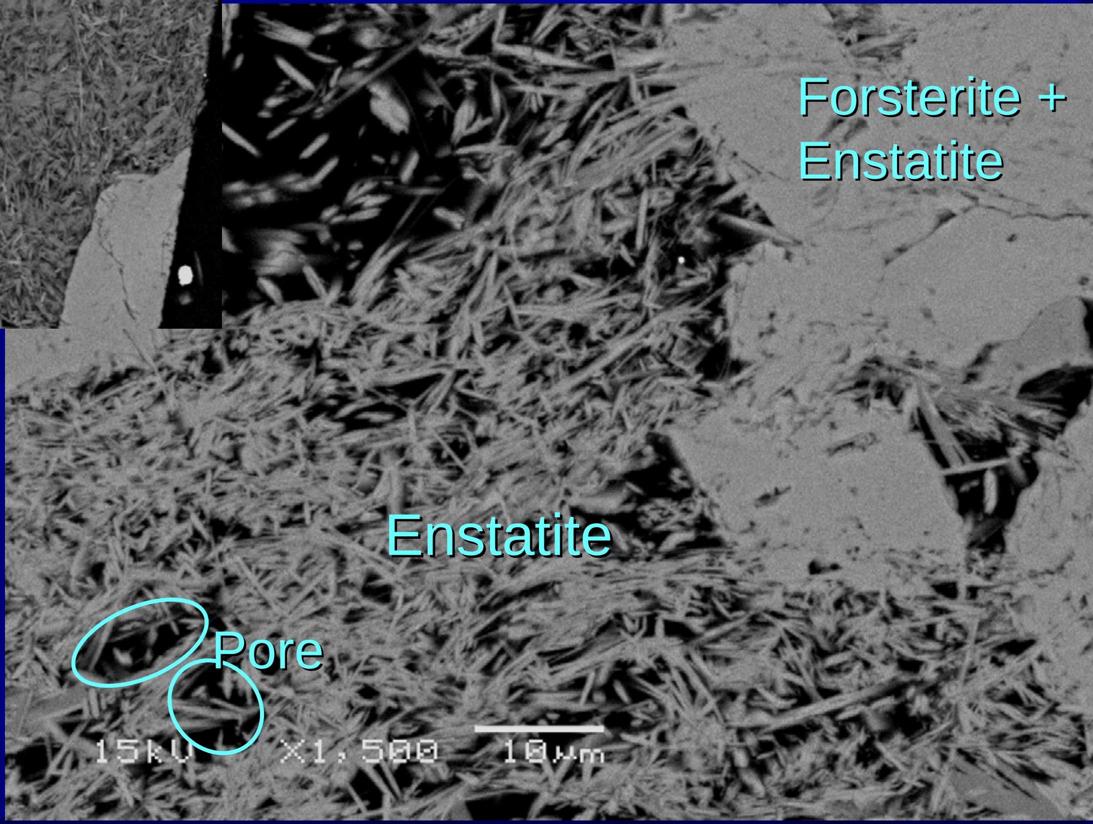


- ***n ≒2.5*** nucleation controlling mechanism

BEI of recovered sample



5.5 GPa 650℃



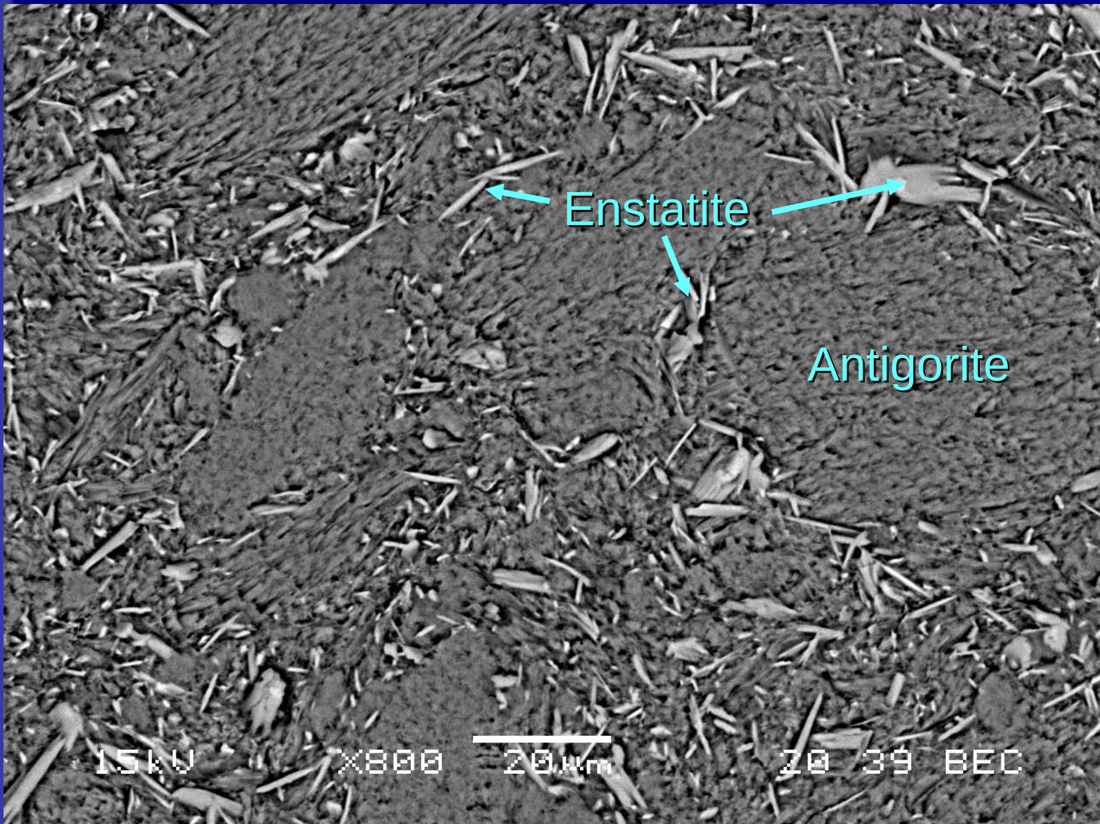
En: nucleation rate → high

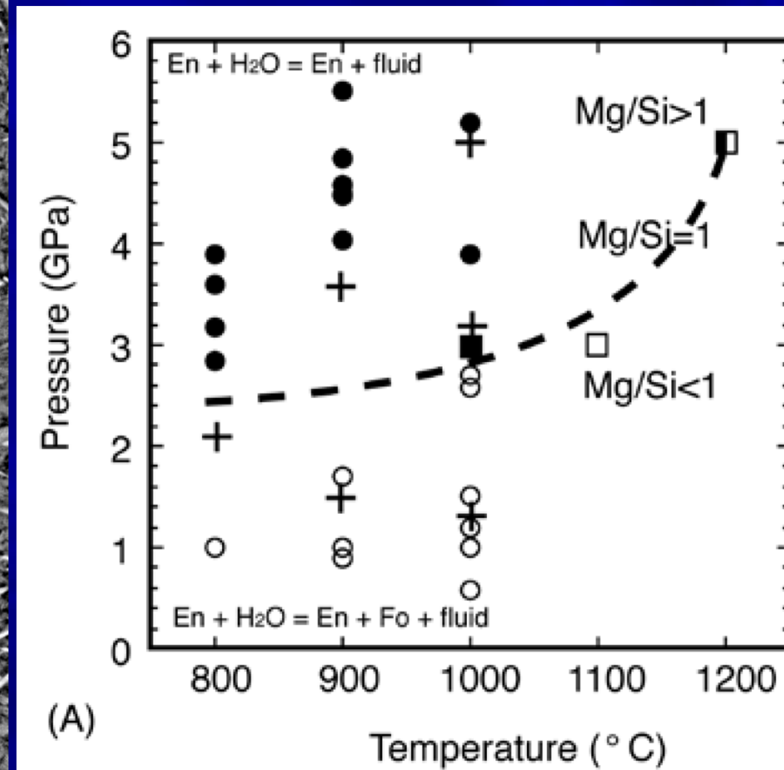
growth controlling

Fo: nucleation rate → low

nucleation controlling

BEI of recovered sample (4 GPa, 700℃, 15min keep)





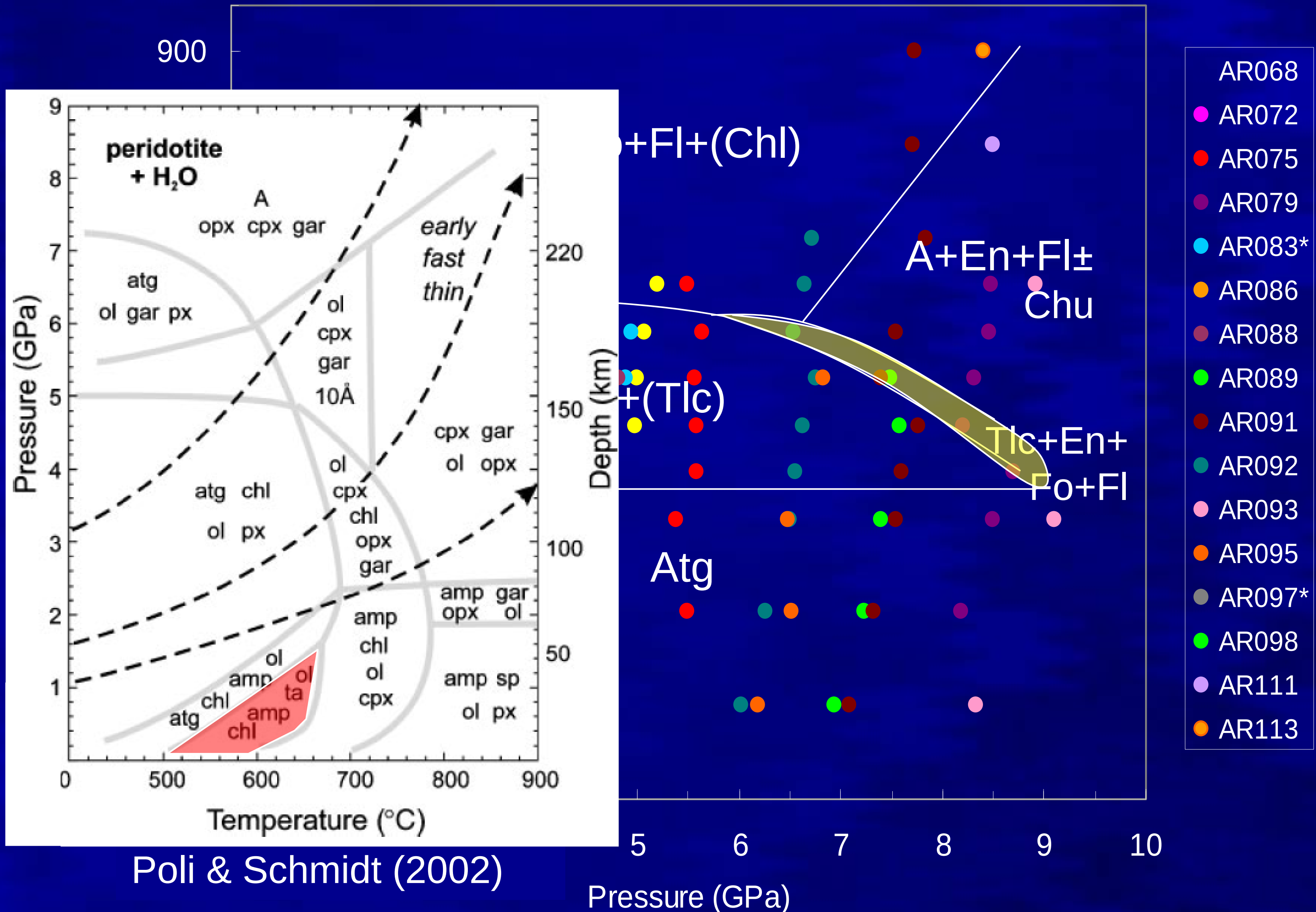
Kawamoto et al. (2004)

Antigorite → Enstatite + Fluid

Mg/Si:1.5 1.0 >1.5

MgO-rich fluid (Mg/Si>1.5) is formed.

Phase diagram of Antigorite



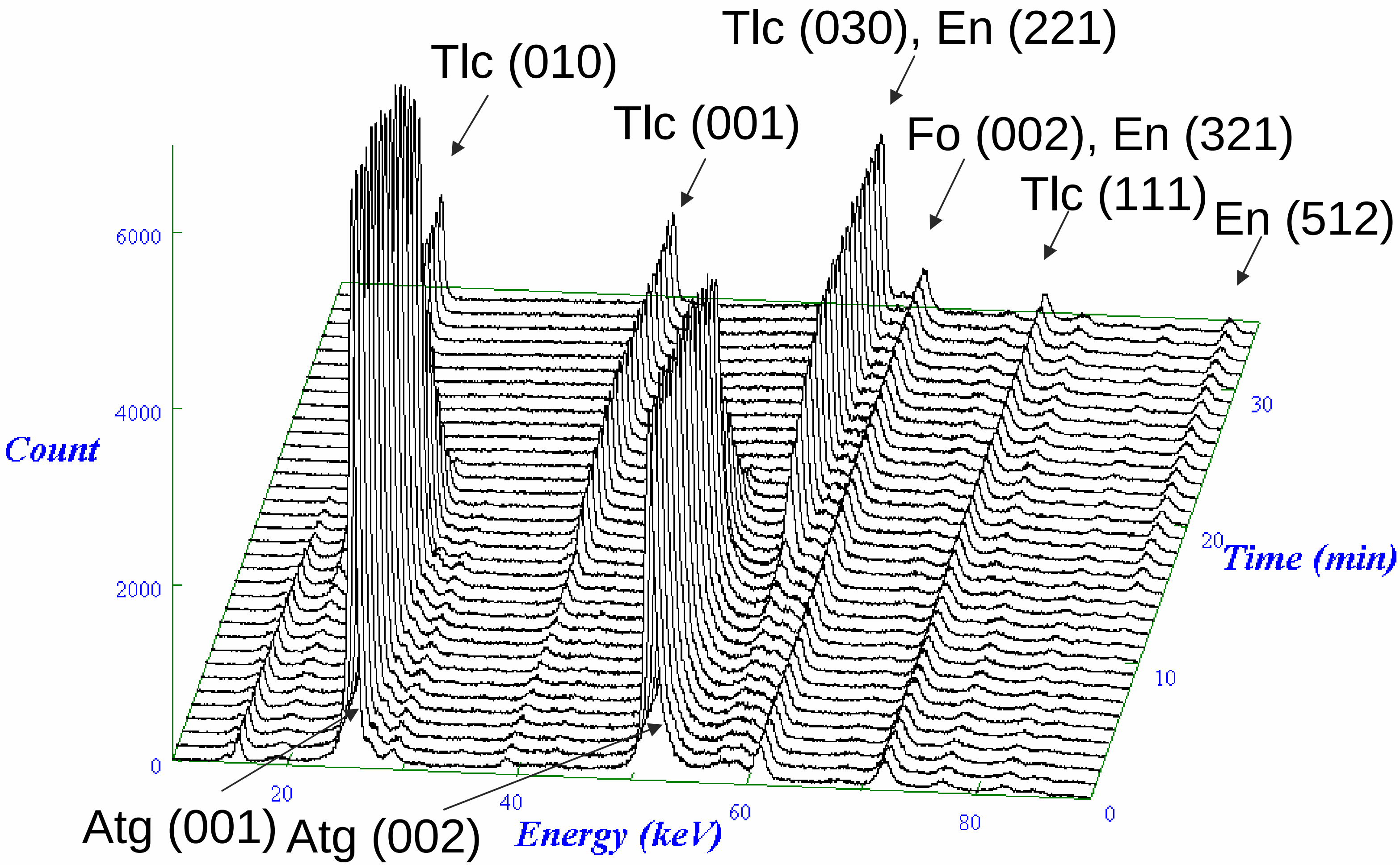
Atg: Antigorite, Tlc: Talc, Fo: Forsterite, En: Enstatite, Chl: Chlorite, A: Phase A, Chu: Clinohumite

( ):Small amount, *: power estimate

Dehydration at 8.0 GPa, 500℃

Antigorite → Talc + Forsterite + Enstatite + Fluid

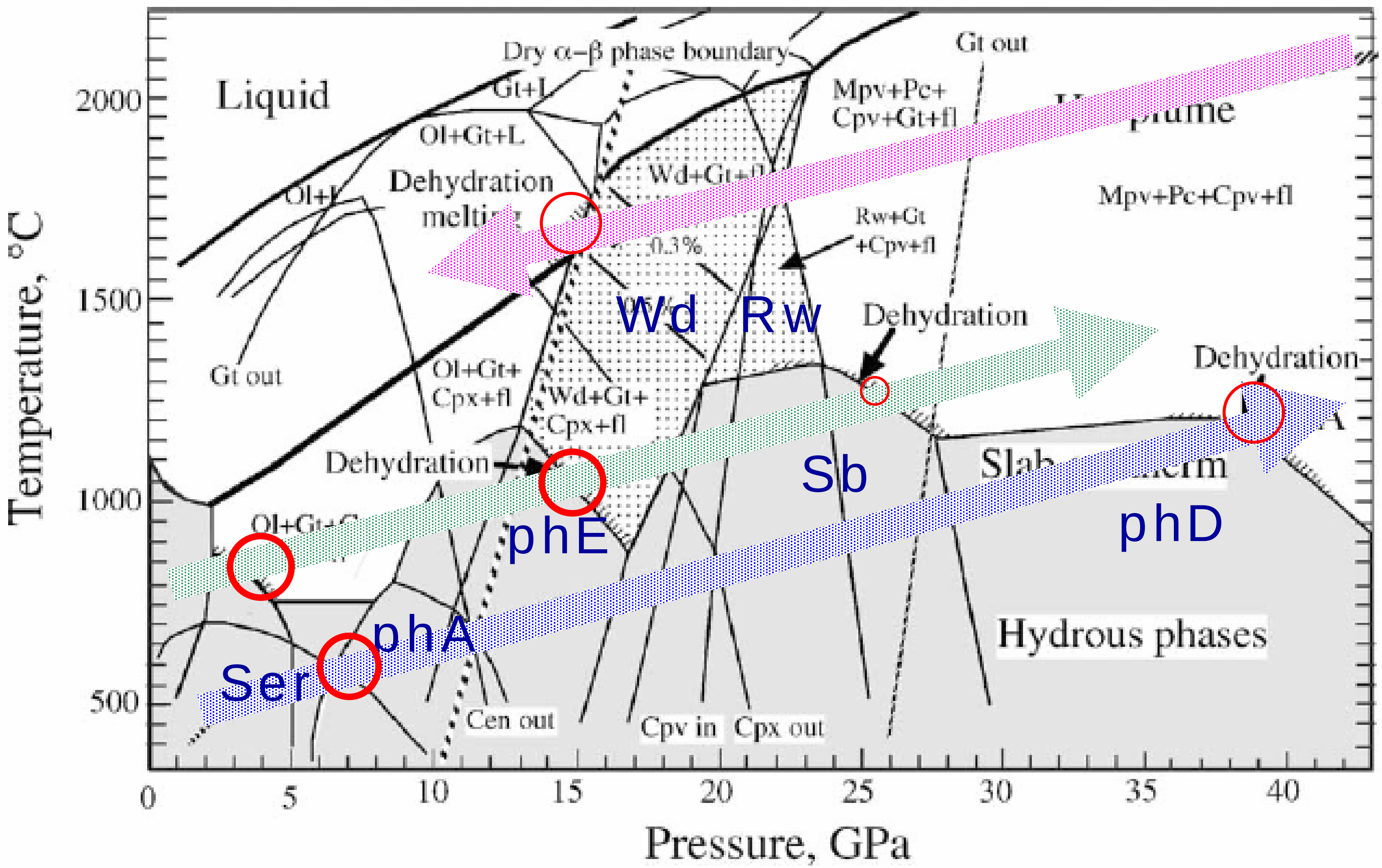
$Mg_3Si_4O_{10}(OH)_2$ 4.7 wt% H_2O



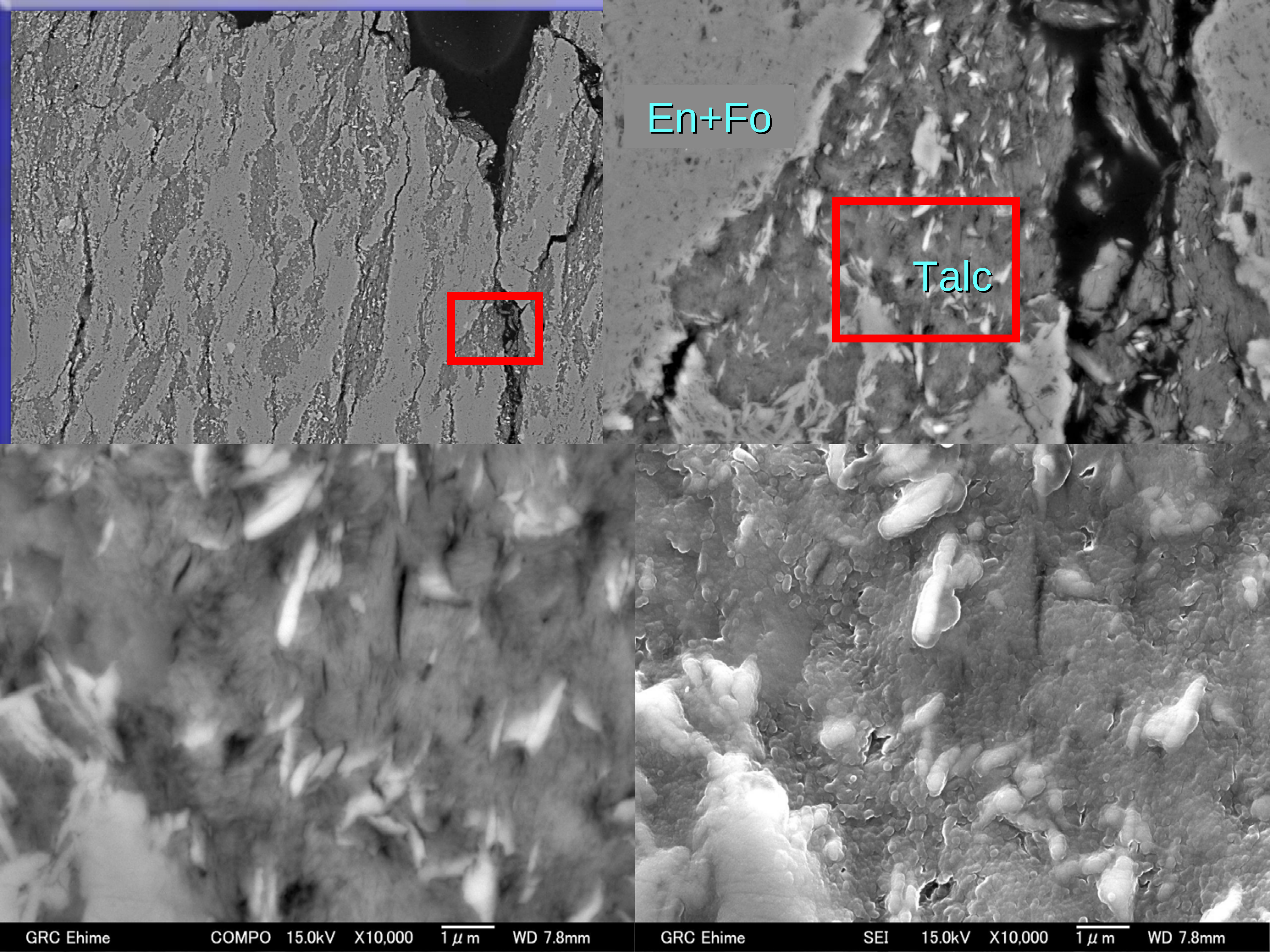
Summary

- We have conducted the time-resolved dehydration experiments of Atg at high pressure and high temperature by in situ X-ray diffraction using diamond capsule.
- Atg in subducted slab should quickly dehydrate when the slab crosses the dehydration boundary of Atg. Thus metastable Atg can not exist in subducted slab at around 650-700 ℃ and 3-5 GPa.
- The nucleation rate was quite high for enstatite, but low for forsterite by dehydration of Atg. This result also can be confirmed from the observation that incubation periods exist for forsterite formation.
- Talc was formed above 6 GPa with dissociation of Atg, and then the formation of phase A was observed in the present experiments. Thus talc formation should be important for dehydration sequence in low temperature subducted slab.

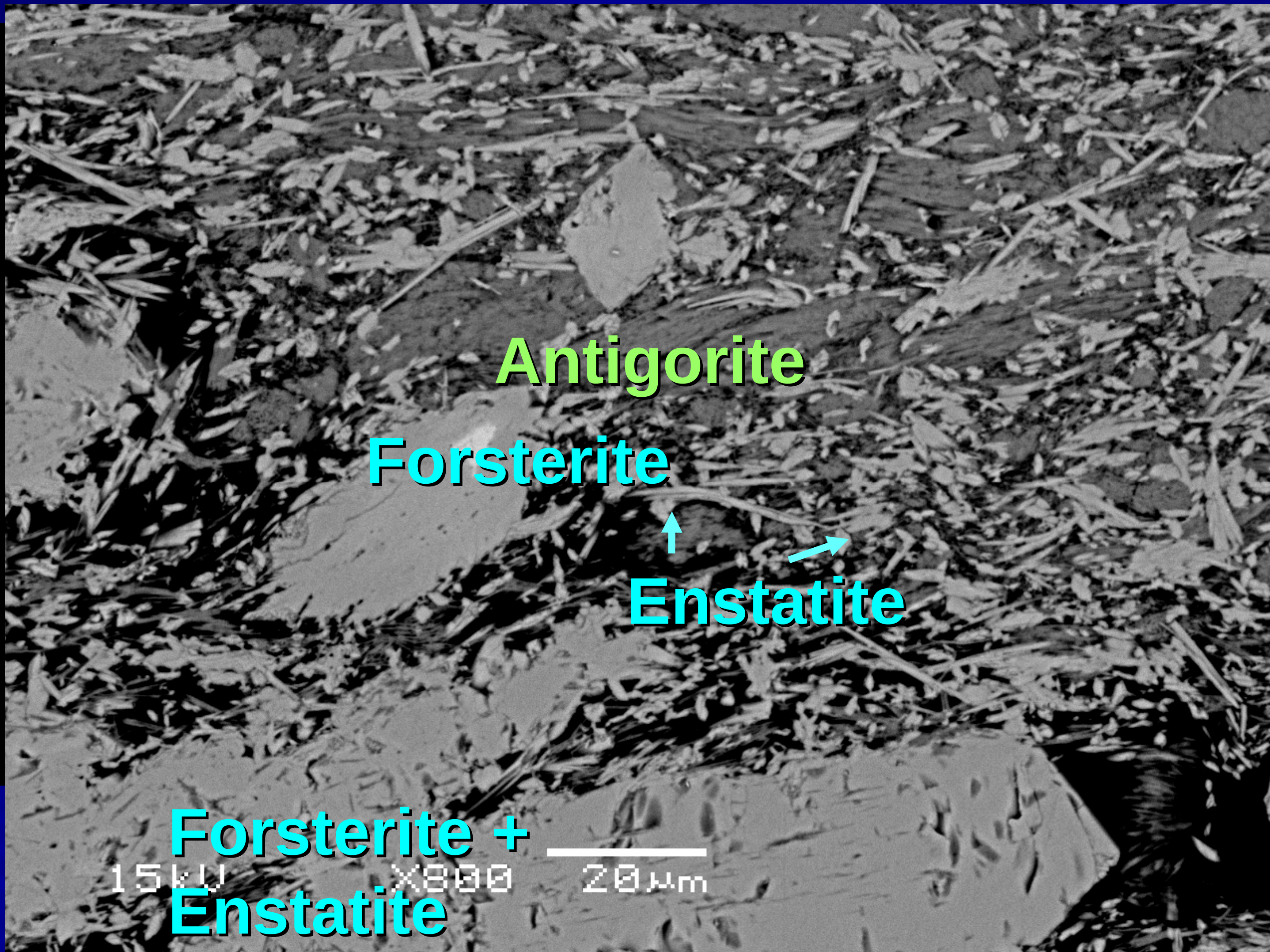
Stability of hydrous phases in hydrous peridotite

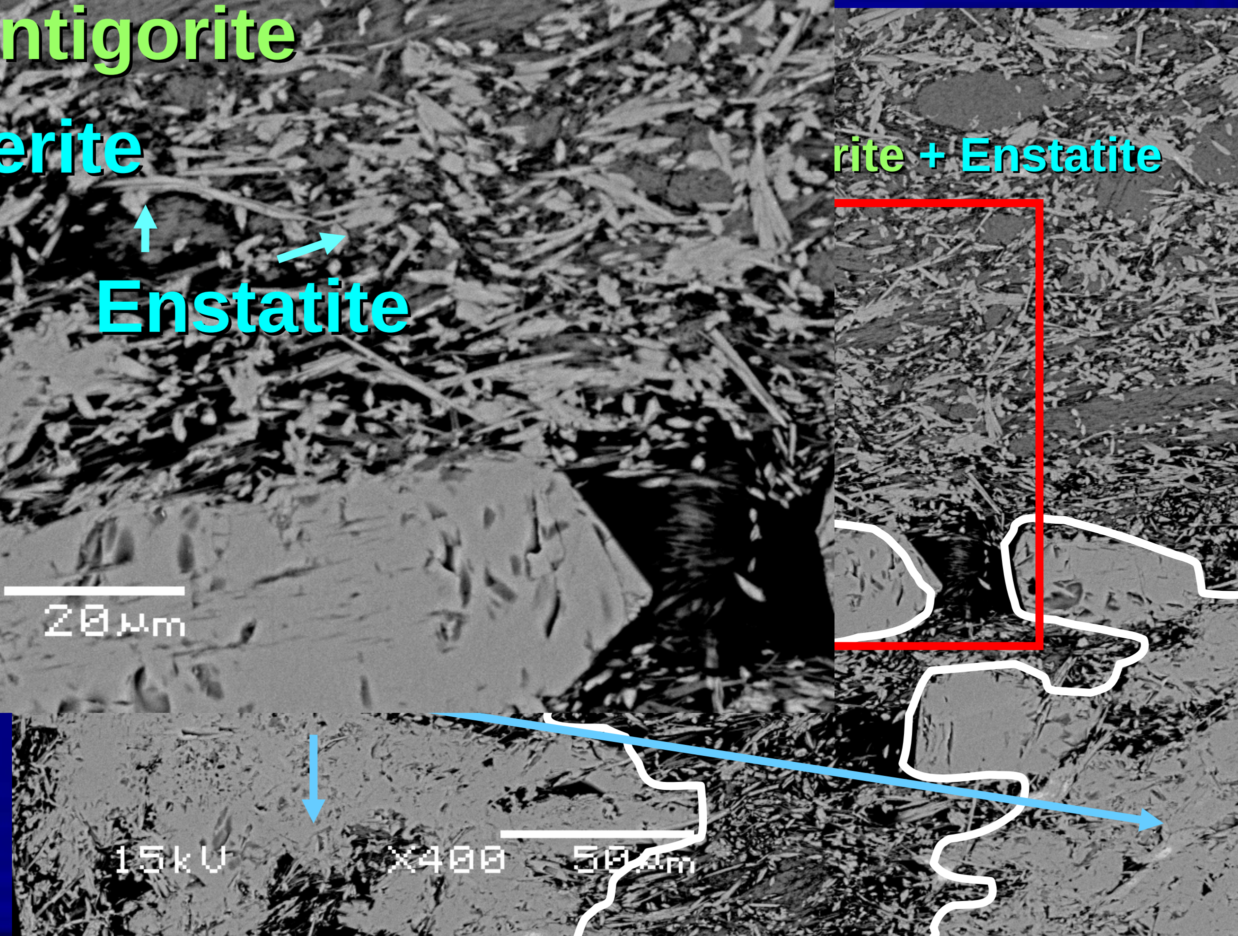


Modified from Ohtani et al. (2004)


En+Fo
Talc
GRC Ehime COMPO 15.0kV X10,000 1 μm WD 7.8mm
GRC Ehime SEI 15.0kV X10,000 1 μm WD 7.8mm

BEI of recovered sample (3.0 GPa, 675℃, 40min. keep)



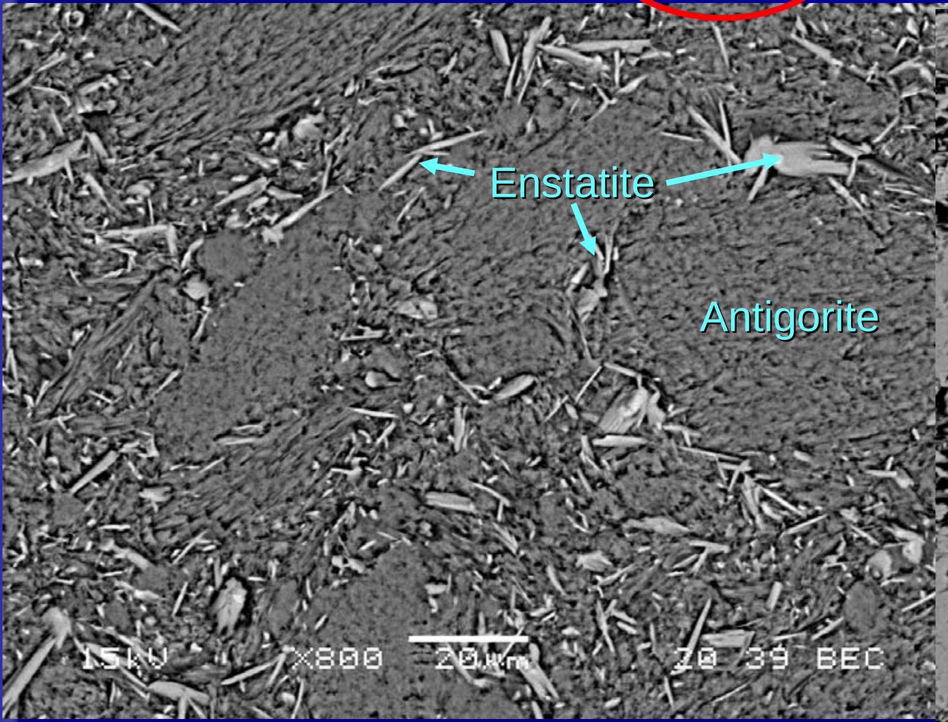


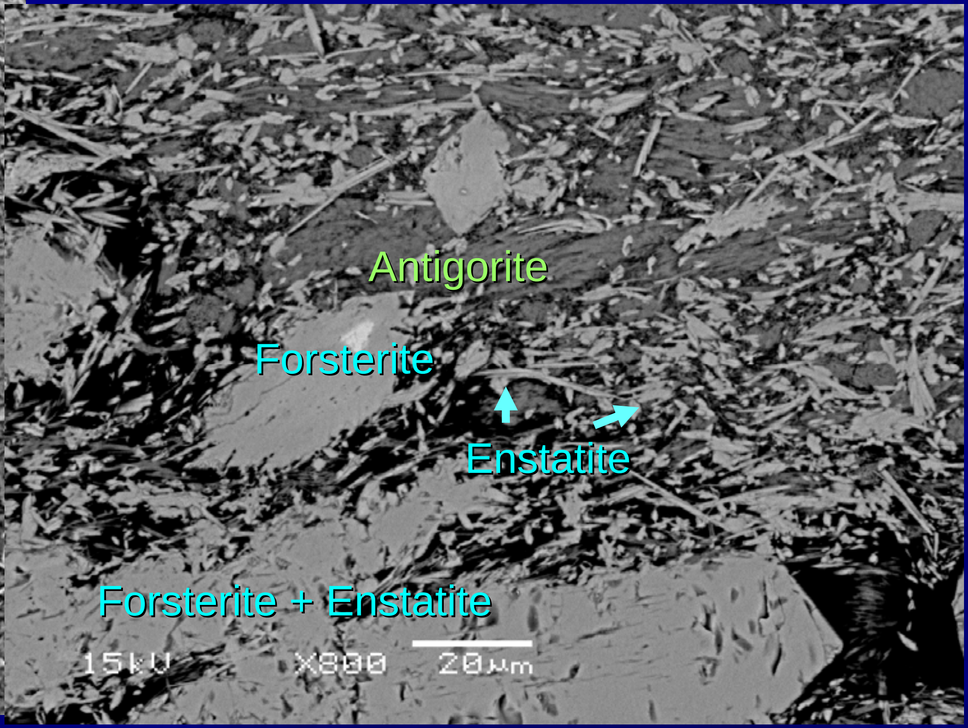
Dehydration reaction at 3-6 GPa

Antigorite → Enstatite + Fluid

Mg/Si: 1.5 1.0 >1.5

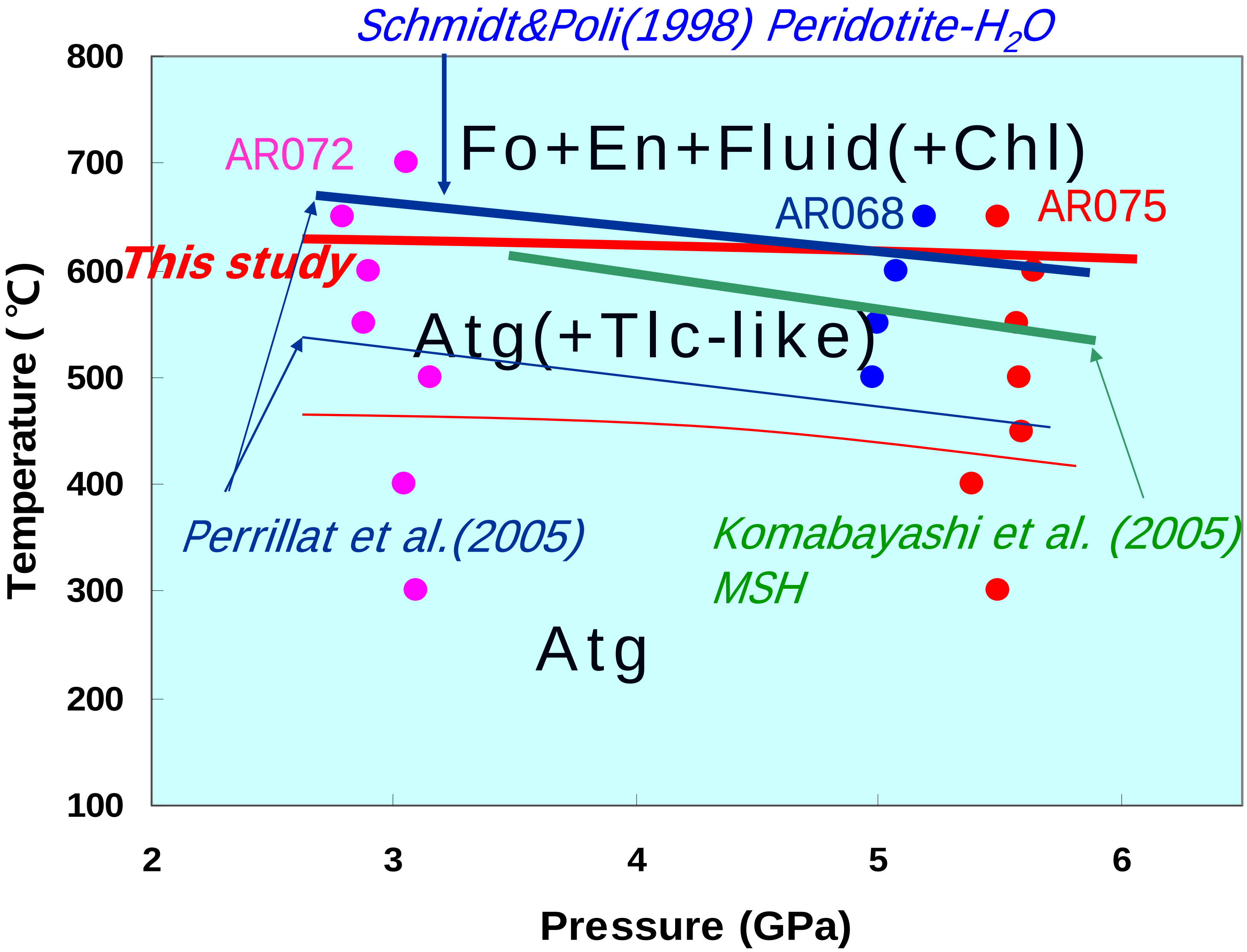
→ MgO-rich supersaturated solution





Forsterite is crystallized from MgO-rich supersaturated solution.

Antigorite phase diagram



実験方法

◇実験試料：京都府宮津市中ノ茶屋産
Antigorite
理想式 $Mg_6Si_4O_{10}(OH)_8$
※Al_2O_3 1.5 wt%, FeO 2.6 wt% を含む
◇実験装置：MAX80@KEK

◇アンビル先端サイズ：4, 6 mm

◇X線回折測定：Ge-SSD を用いたエネルギー分散

測定時間を50秒とし、60秒間隔ごとの時分割測定

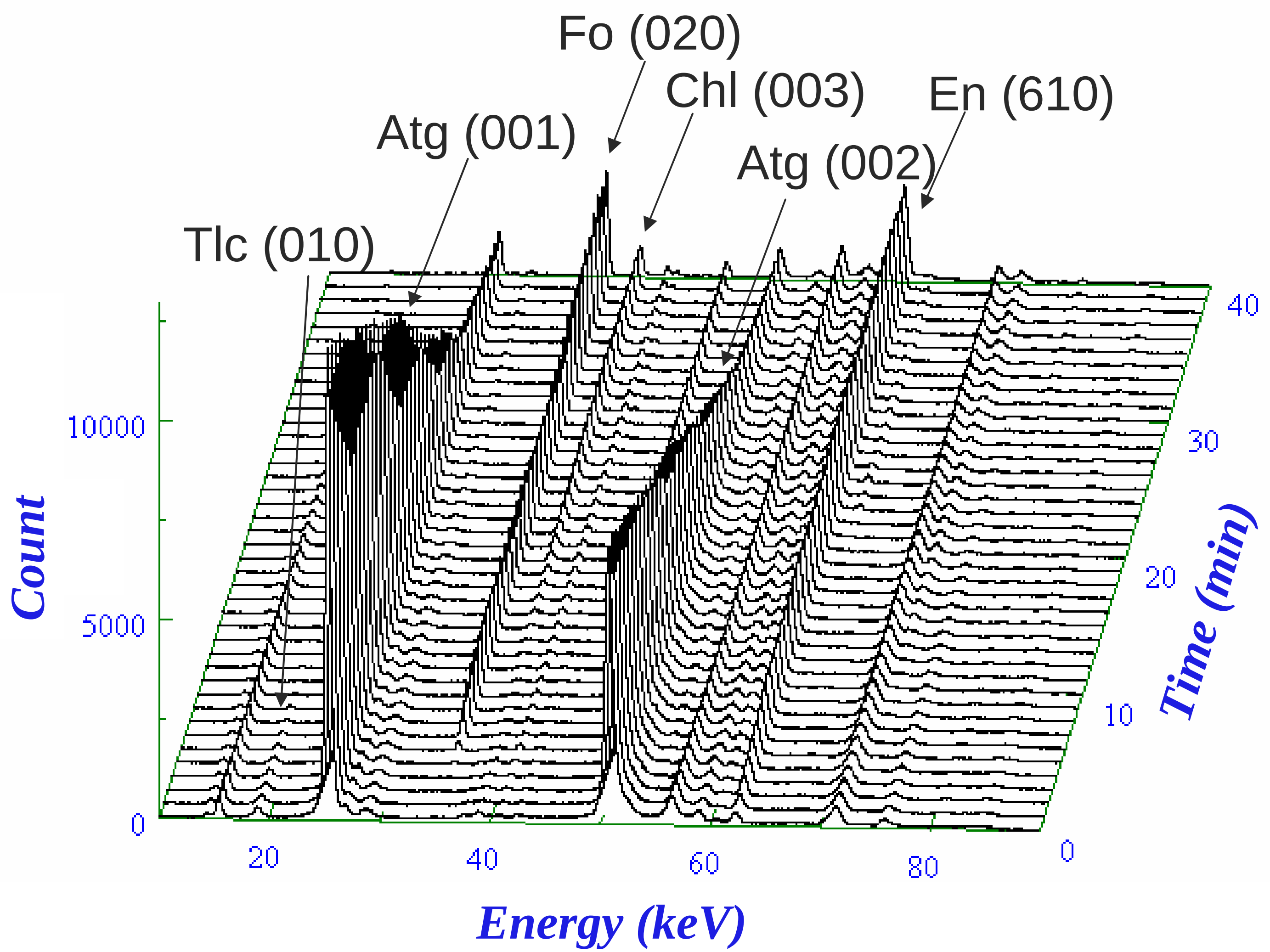
◇圧力温度条件：3-9 GPa, -1000℃

◇圧力決定： NaCl マーカー (Decker, 1971)

◇回収試料の分析：SEM-EDS, FE-SEM,
微小部X線回
折装置

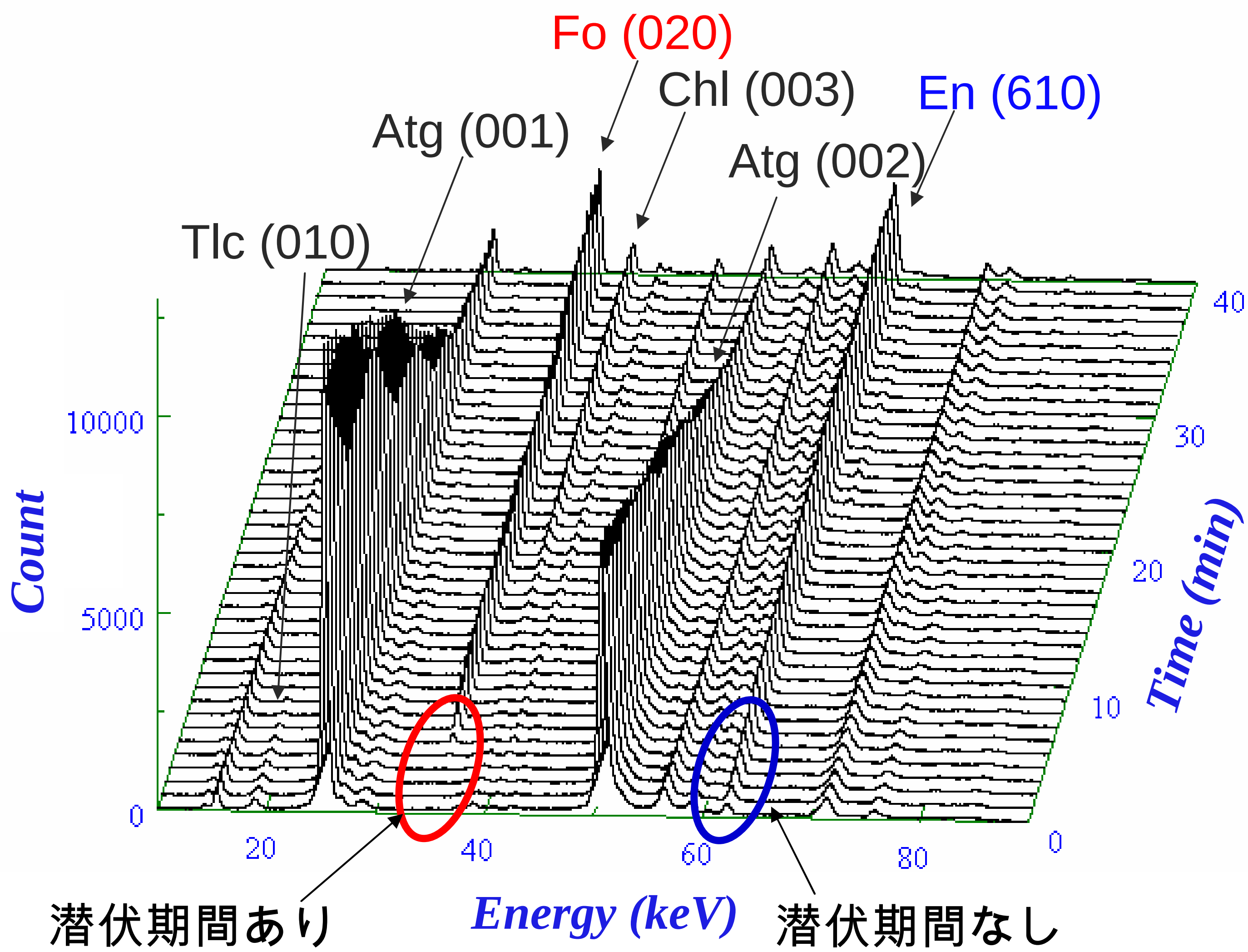
3-6 GPa おける脱水分解反応 *(5.2 GPa, 650℃)*

Antigorite → Forsterite + Enstatite + Fluid

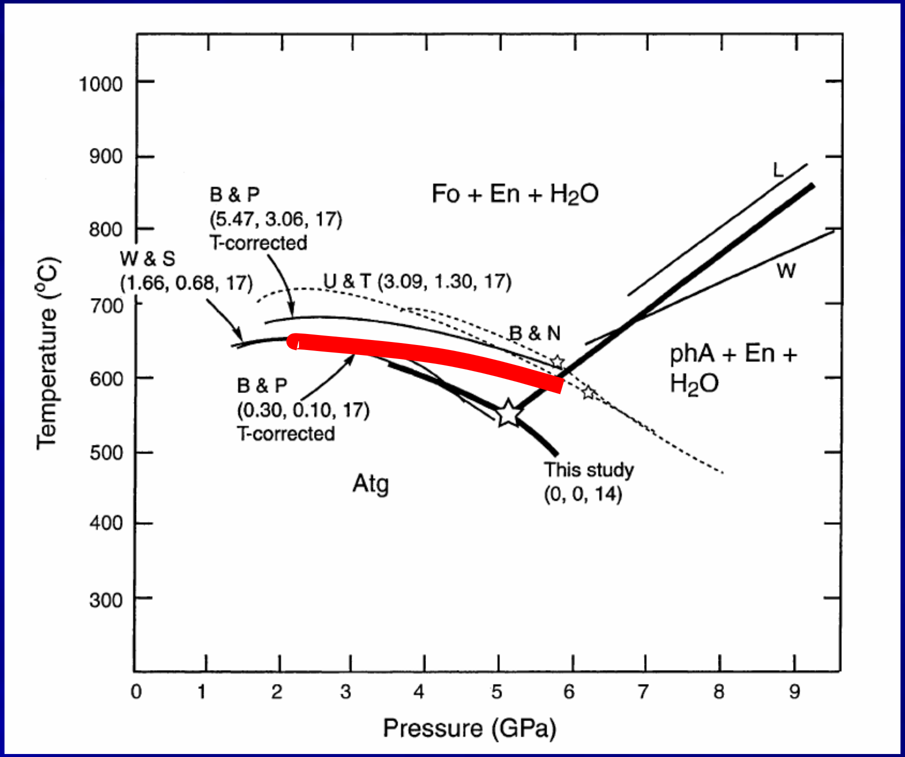


反応初期について

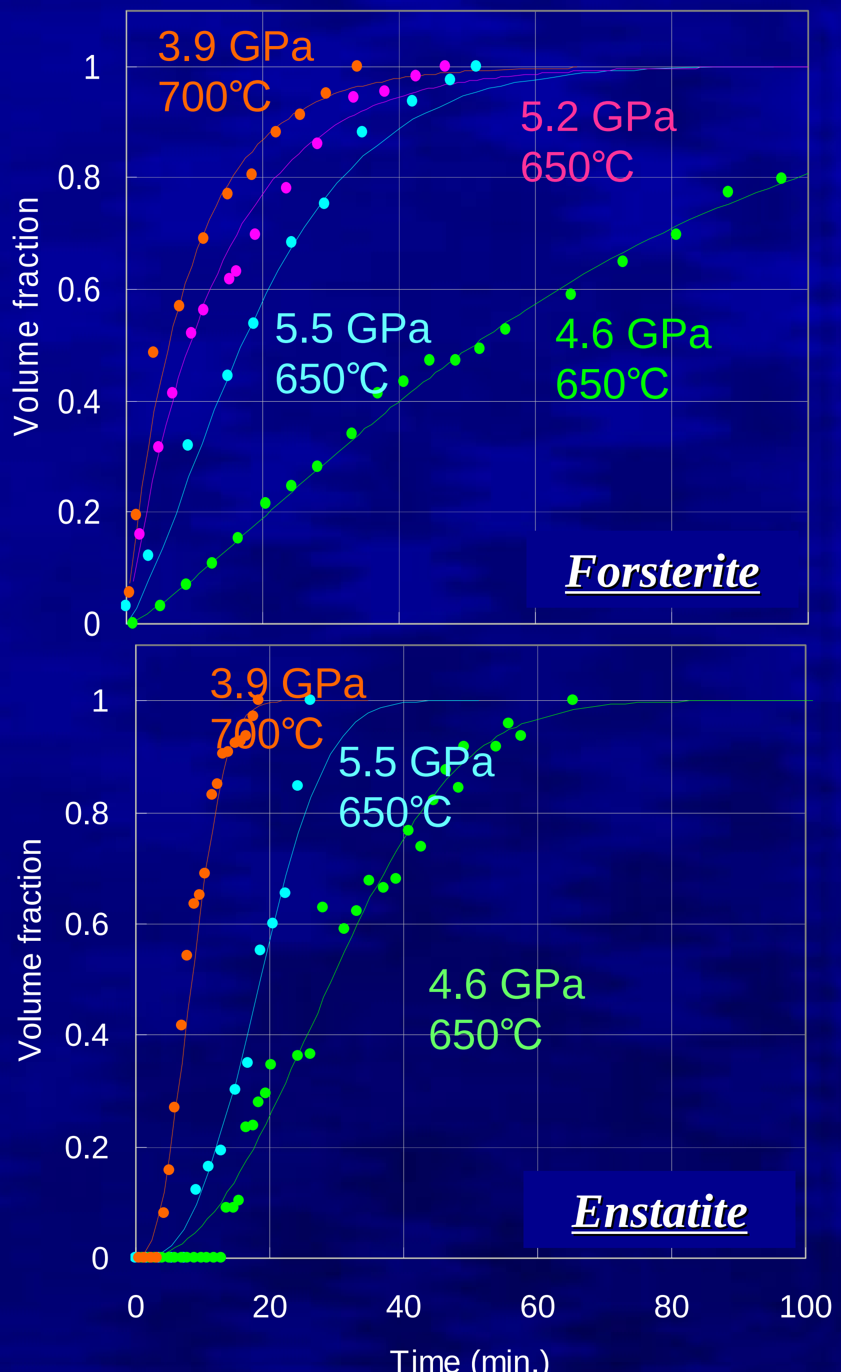
Antigorite → Forsterite + Enstatite + Fluid



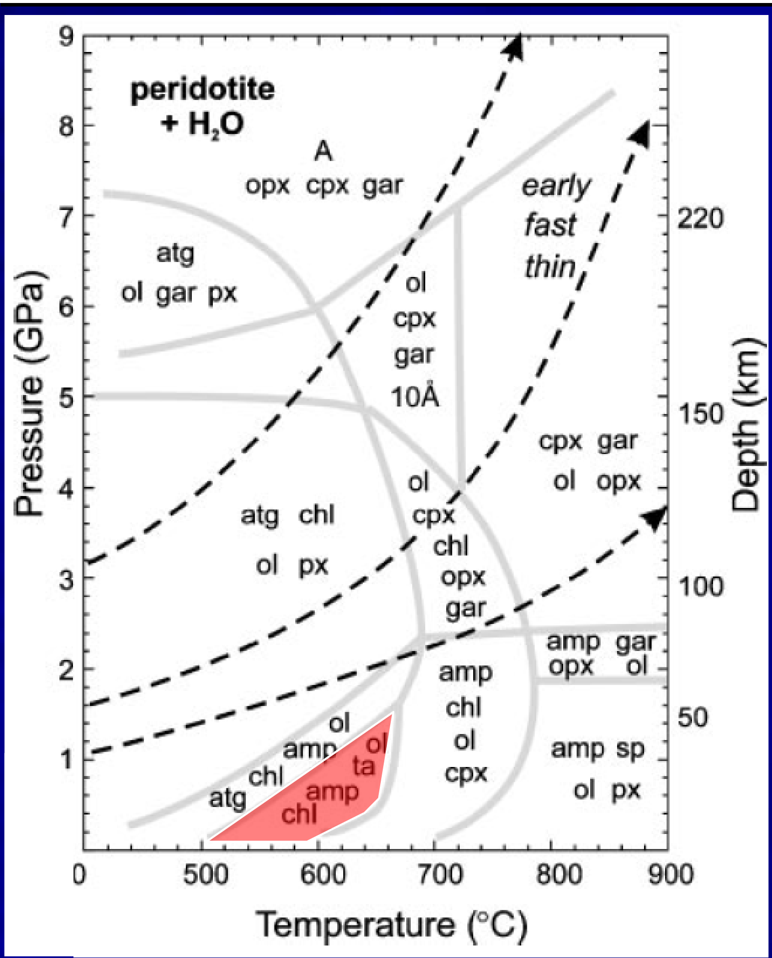
Forsterite+Enstatite+Fluidへの脱水分解



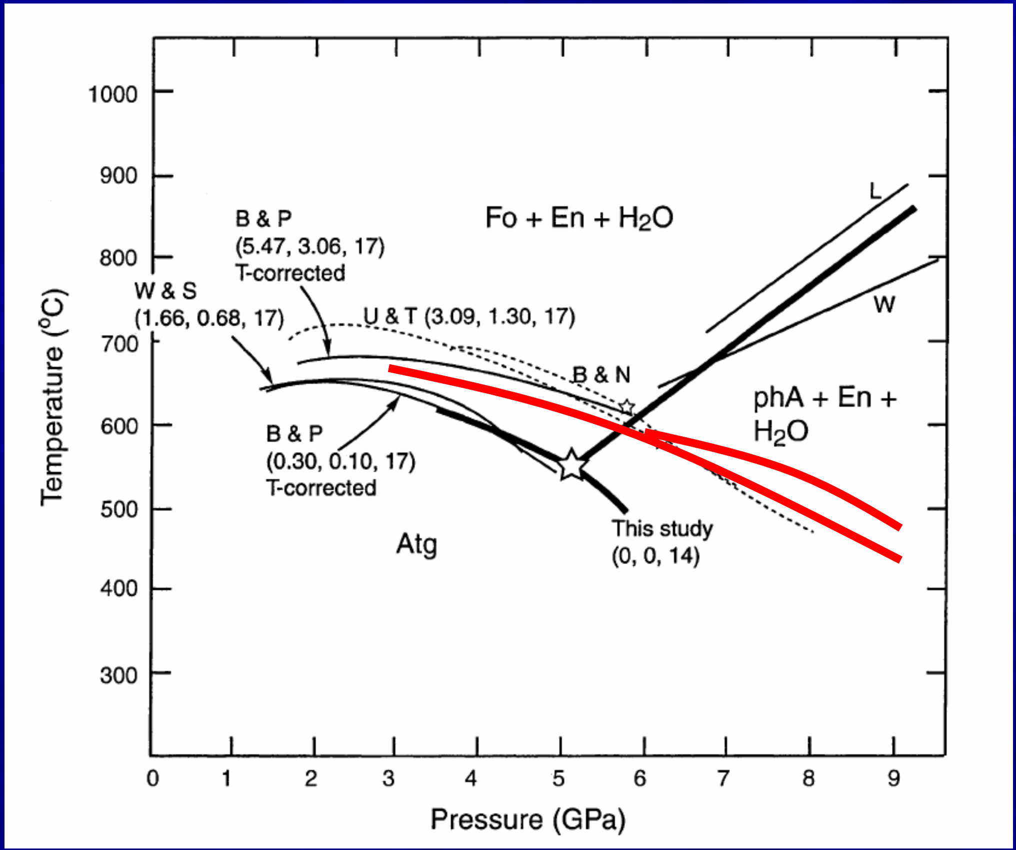
Komabayashi et al. (2005) に加筆



高圧下におけるTalcの生成



Poli & Schmidt (2002)



Komabayashi et al. (2005) に加筆

本研究と類似する脱水分解境界をもつBose & Navrotsky (1998)は, 6.5 GPa 575℃でTalcらしき相を観察している

Stability of antigorite (serpentine)

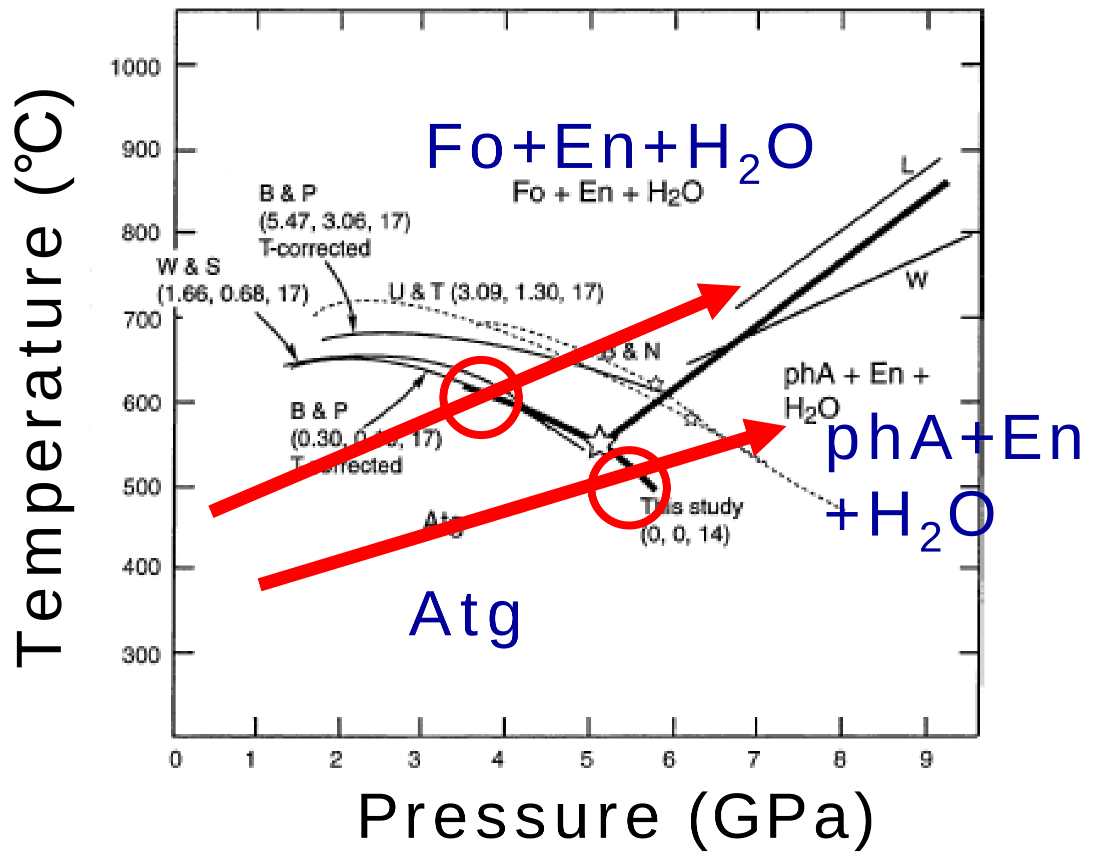
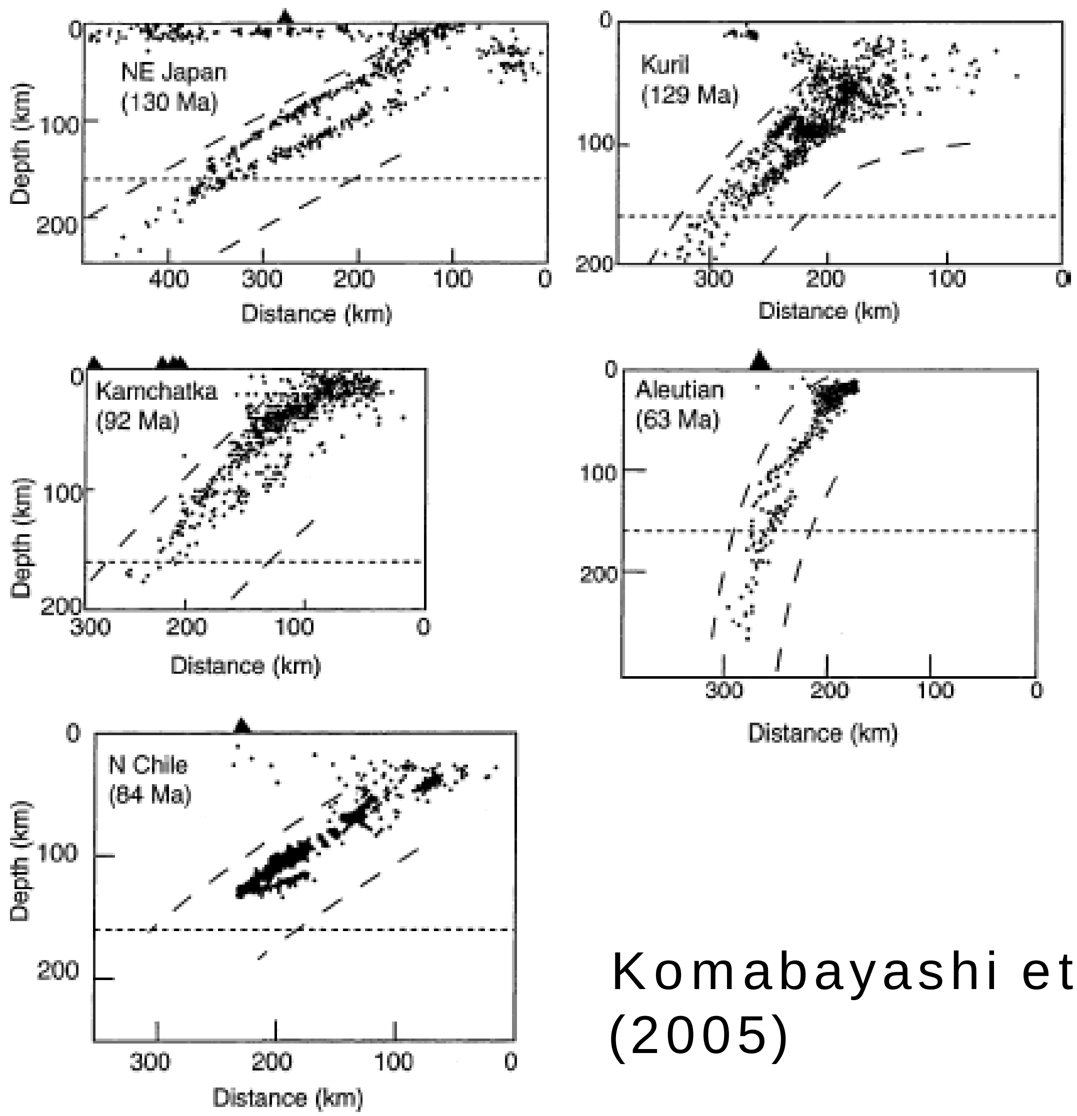


Fig. 8. Comparison of experimental results. Phase boundary of Fo + H_2O = phA + En: L, (Luth, 1995); W, (Wunder, 1998); thick solid straight line, this study. Dehydration curve of antigorite: U & T, (Ulmer and Trommsdorff, 1995); W & S, (Wunder and Schreyer, 1997); B & N, (Bose and Navrotsky, 1998); B & P, (Bromiley and Pawley, 2003); thick solid line, this study. Note B & P, *T*-corrected denotes the results of Bromiley and Pawley (2003) after a correction of temperature (see text for details). The numbers in parenthesis indicate the FeO* (total Fe as FeO), Al_2O_3 contents and *m*-value of starting antigorite, respectively. Large and small stars indicate the invariant point as an intersection of reactions determined in this study in previous studies, respectively.

Modified from Komabayashi et al.(2005)

Hypocenter distributions in subduction zone



Komabayashi et al. (2005)

Fig. 10. Hypocenter distributions in subduction zones. Broken lines show the estimated subducting plate boundary. Dotted line indicates 160 km depth that is critical depth for the formation of hydrous phase A in the subducting slab (see text for details). Data sources are, NE Japan, Hasegawa et al. (1994); Kuril, Ozel and Moriya (1999); Kamchatka, Gorbatov et al. (1994); Aleutian, Engdahl and Scholz (1977); N Chile, Comte et al. (1999).

Dehydration of antigorite (opened system)

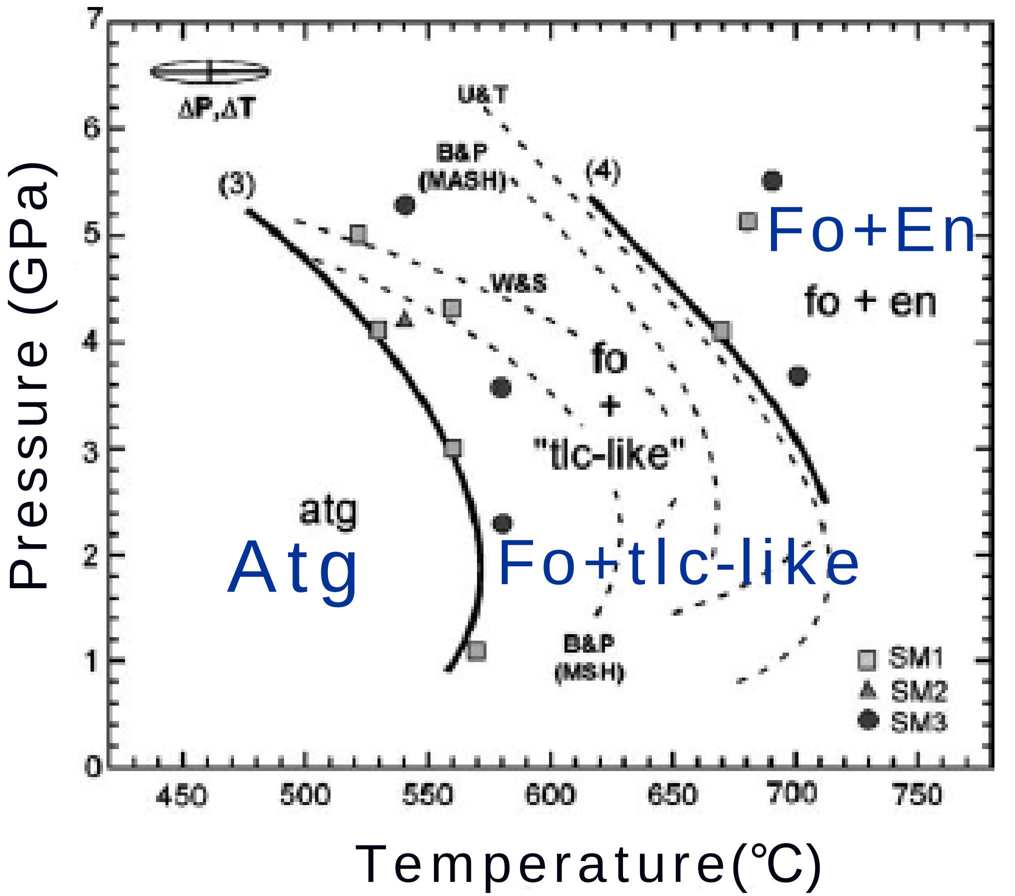


Fig. 2. Experimental P–T diagram for the breakdown reactions of antigorite. The location of reactions (3) and (4) is indicated by bold lines. Dashed lines represent the position of reaction antigorite = forsterite + enstatite + H_2O (2) as determined by U&T [4], W&S [11], B&P [12]. SM1, SM2, SM3 refer to different starting materials (see Section 2.1); ΔP, ΔT to the uncertainty on pressure and temperature.

Appearance of Talc-like phase

Modified from Perrillat et al. (2005)

Dehydration reaction of antigorite (<5 GPa)

$$Mg_6Si_4O_{10}(OH)_8 \rightarrow 2Mg_2SiO_4 + 2MgSiO_3 + 4H_2O$$

Atg Fo En Fluid

13 wt% water released

$$5Mg_6Si_4O_{10}(OH)_8 \rightarrow 2Mg_3Si_4O_{10}(OH)_2 + 12Mg_2SiO_4 + 18H_2O$$

Atg Tlc Fo Fluid

4.8 wt % H_2O

H_2O	13.0 wt%	1.3 wt%	11.7 wt%

11.7 wt% water released

Dehydration reaction of antigorite (>5 GPa)

$$5Mg_6Si_4O_{10}(OH)_8 \rightarrow 2Mg_7Si_2O_8(OH)_6 + 16MgSiO_3 + 18H_2O$$

Atg Phase A En Fluid

11.8 wt % H_2O

H_2O 13.0 wt% 3.9 wt% 9.1 wt%

9.1 wt% water released

With increasing temperature

$$Mg_7Si_2O_8(OH)_6 + 3MgSiO_3 \rightarrow 5Mg_2SiO_4 + 3H_2O$$

Phase A En Fo Fluid

3.9 wt%

Remnant 3.9 wt% water released

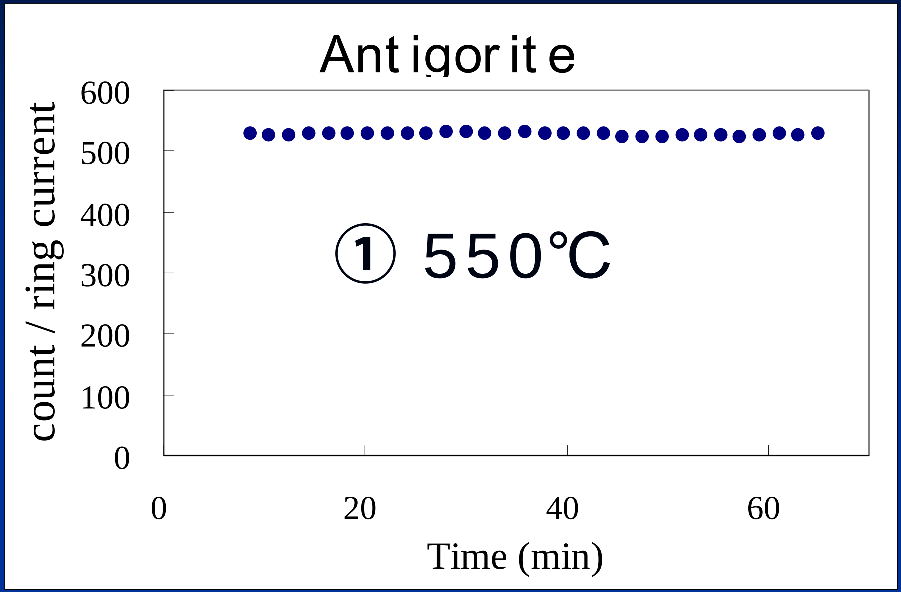
Phase appearance or disappearance and hold time (min)

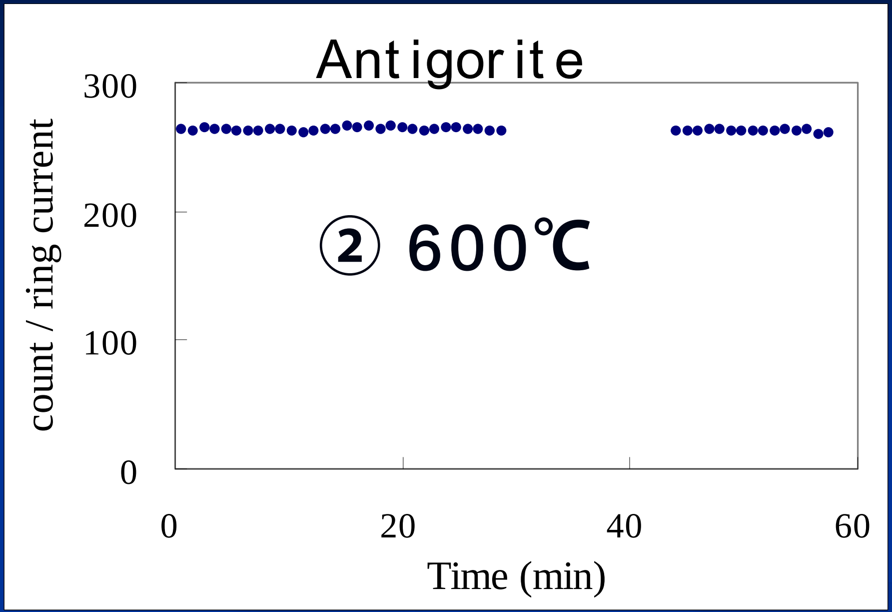
T (℃)	AR072 3.0 GPa	AR068 5.2 GPa	AR075 5.5 GPa	AR079 8.5 GPa
300	no (15)		no (15)	
400	no (20)		no (25)	
450			Tlc-like*: appear (50) Atg: no	no (35)
500	Tlc-like*: appear (30) Atg: no	Tlc-like*: appear (30) Atg: no	no (40)	Atg: disappear (90) Tlc-like: appear
550	no (90)	no (80)	no (40)	Tlc-like: disappear (50) En: appear
600	no (80)	no (60)	no (45)	no (50)
650	Tlc-like: increase (120) Atg: decrease	Atg: disappear (120) Tlc-like*: disappear Chl: appear En: appear Ol: appear	Atg: disappear (90) Tlc-like*: disappear En: appear Ol: appear	no (60)
700	Atg: disappear (90) Tlc-like*: disappear En: appear Ol: appear			

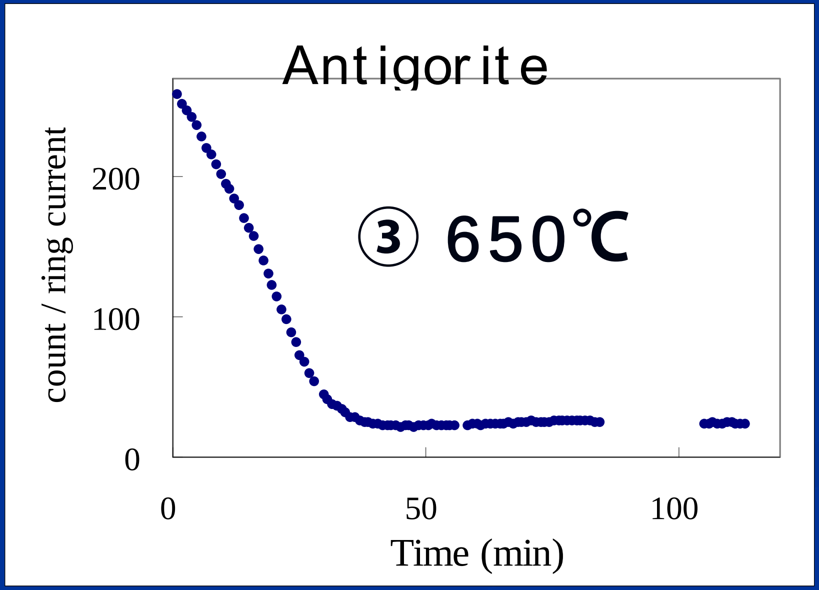
Blue: appear or increase, red: disappear or decrease

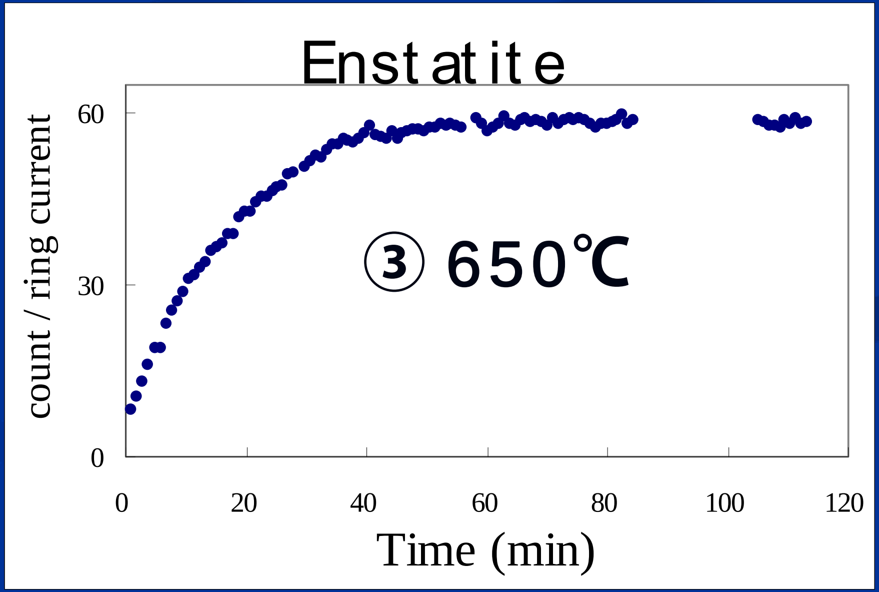
Antigorite dehydration

P=5.2 GPa

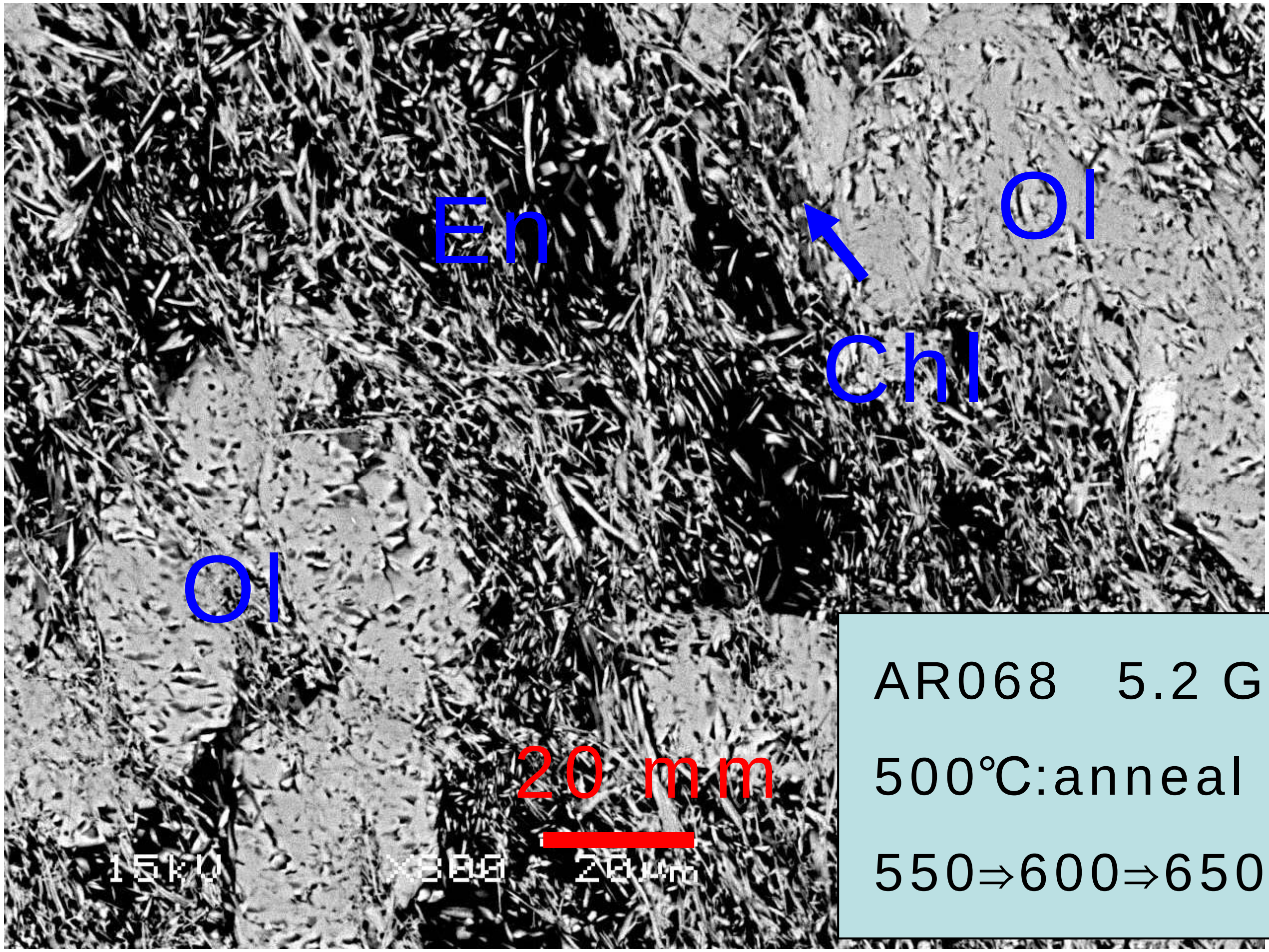








BEI at 5.2 GPa, 650℃ run product



AR068　5.2 GPa

500℃:anneal

550⇒600⇒650⇒quench