Kinetic and rheological properties of Earth and planetary materials studied by time-resolved X-ray diffraction

放射光Ｘ線回折時分割測定を用いた高温高圧下における地球惑星物質の多結晶カイネティクスとレオロジーの研究

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Research interest

極限環境下で様々な時間スケールにおよぶ地球惑星のダイナミックな現象を物質科学（特にカイネティクスとレオロジー）から制約する

Topics

- 衝撃隕石中の高温高圧非平衡反応（15-30GPa, 1000-2500K, ~0.01-1 secスケール）と衝撃のP-T-t条件の制約
- ダイアモンド包有物中の高温高圧非平衡反応（5-15GPa, 1000-1500K, 数時間スケール）とダイアモンド上昇履歴
- 岩石や氷の高圧相転移と塑性流動特性：地球（～15-35GPa, 1000-3000K）や氷天体（～2-3GPa, 200-400K）のマントル対流運動（数百万年スケール）の理解

実験手法

高圧実験：（変形）マルチアンビル型装置、DAC

放射光Ｘ線回折時分割測定：エネルギー分散、角度分散

２topics

（１）Plagioclase breakdown in shocked meteorites
斜長石の非晶質化と高圧相結晶化のカイネティクス
マルチアンビル装置と白色Ｘ線エネルギー分散法によるＸ線回折時分割測定 (Kubo et al., Nature geoscience, in press)

（２）Time-resolved 2D-XRD observations of grain nucleation and growth during high-pressure transformations
個々の結晶粒挙動に着目した高圧相転移の核生成ー成長のカイネティクス研究
マルチアンビル装置と単色Ｘ線角度分散法によるＸ線回折時分割測定 (久保他, 高圧力の科学と技術 2009; Kubo et al., JPCS in press)

（２）Time-resolved 2D-XRD observations of grain nucleation and growth during high-pressure transformations

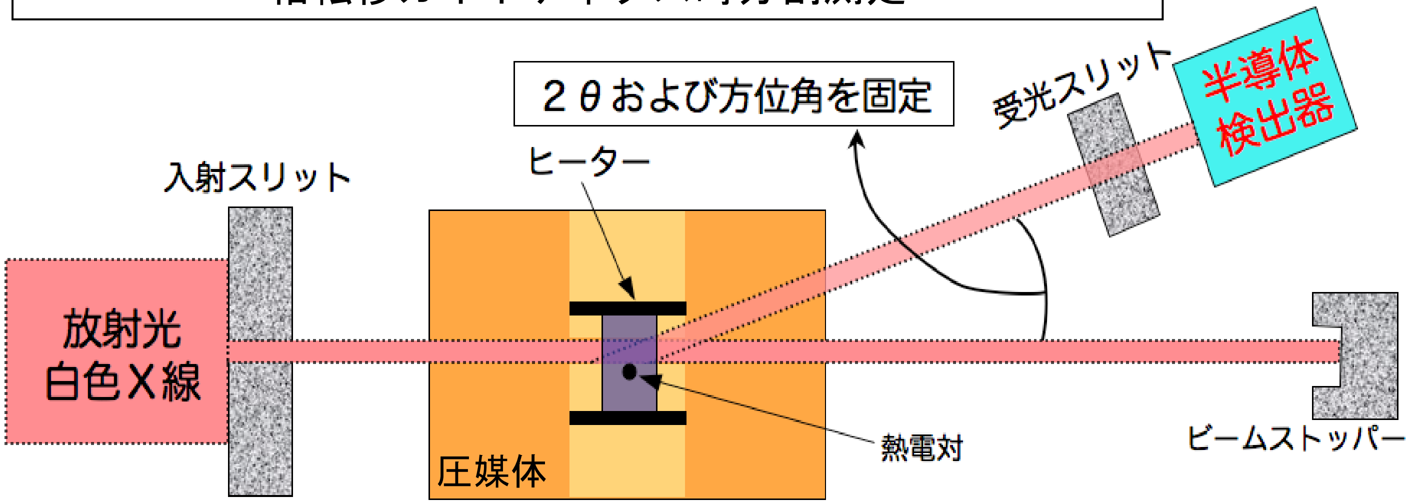
The number and intensity of diffracion spots on 2D detector are used to observe nucleation and growth kinetics of high-pressure transformations.

Preliminary model experiments on

1. Ice VI-VII and VI-VIII transformations using DAC
2. Coesite-stishovite transformation using the KAWAI-type MA apparatus

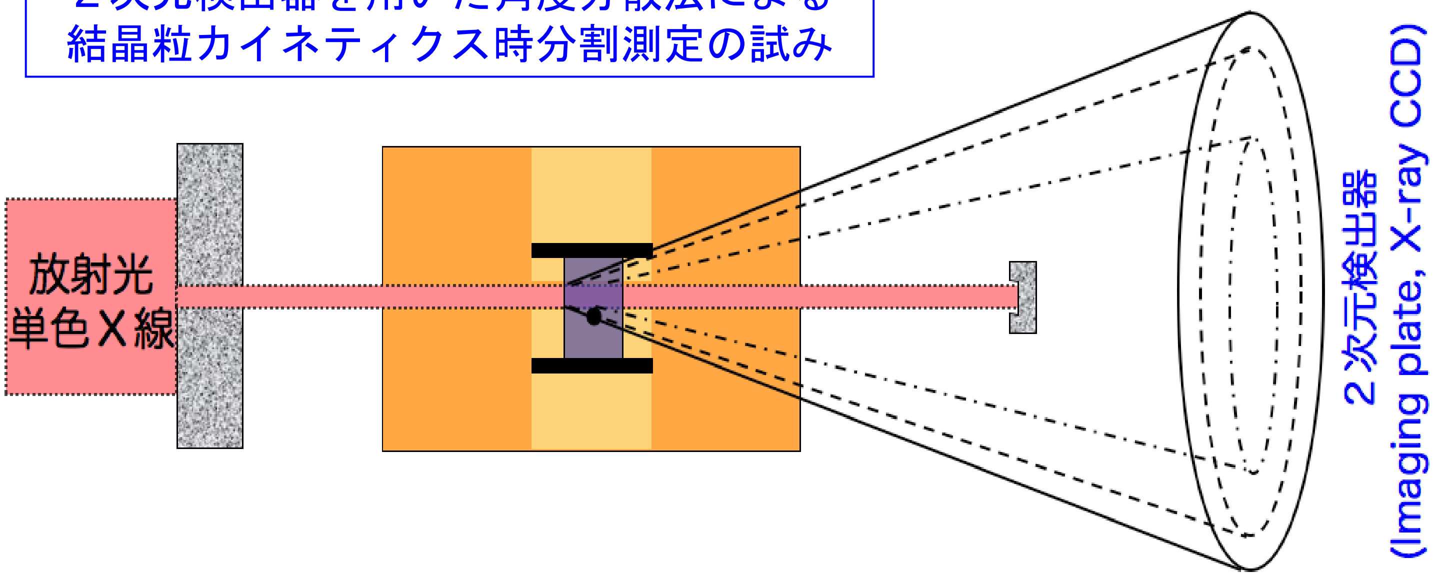
放射光Ｘ線回折時分割測定による高圧カイネティクス研究

これまでの半導体検出器を用いたエネルギー分散法による
相転移カイネティクス時分割測定



- 簡便に時分割観察
- 多結晶体中の非常に限られた結晶粒の平均情報しか得られない
- 細粒多結晶体しか観察できない、高温アニールできない
- 核生成律速の相転移の観察などに不向き

２次元検出器を用いた角度分散法による
結晶粒カイネティクス時分割測定の試み



- 回折に寄与する結晶粒が大幅に増加
- 回折斑点に着目することで個々の結晶粒の情報が得られる
- 相同定の他に、結晶粒数、結晶粒体積、選択配向、方位関係、応力などの情報を得ることも可能

Kinetic study using time-resolved 2D-XRD method

The number of diffraction spots N_s is proportional to the number of grains N_g
(Watching nucleation of new grains)

$$N_s = N_g p \Delta\theta \cos\theta_B / 2$$

$$(\cos\theta_B \approx 1)$$

$$N_s \approx N_g p \Delta\theta / 2$$

(e.g., Hirsch, 1955)

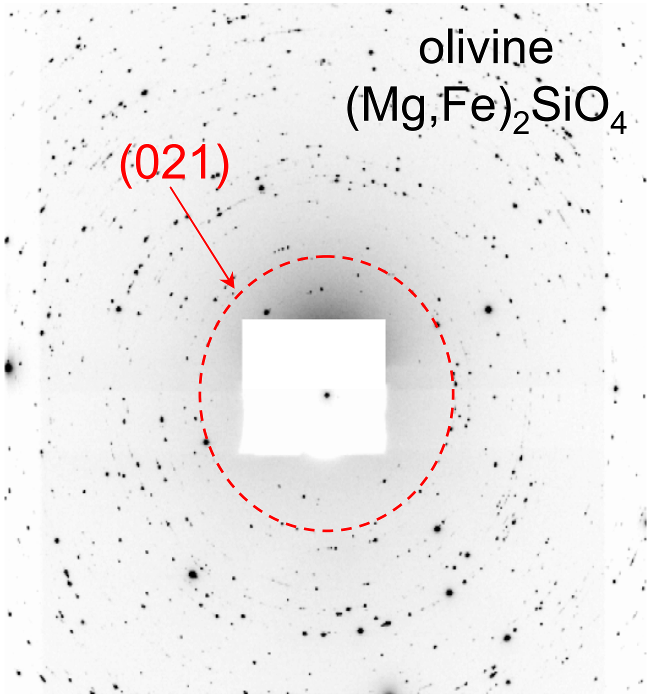
- p multiplicity factor
- $\Delta\theta$ angle over which crystal reflects due to various factors such as divergence of beam
- θ_B Bragg angle

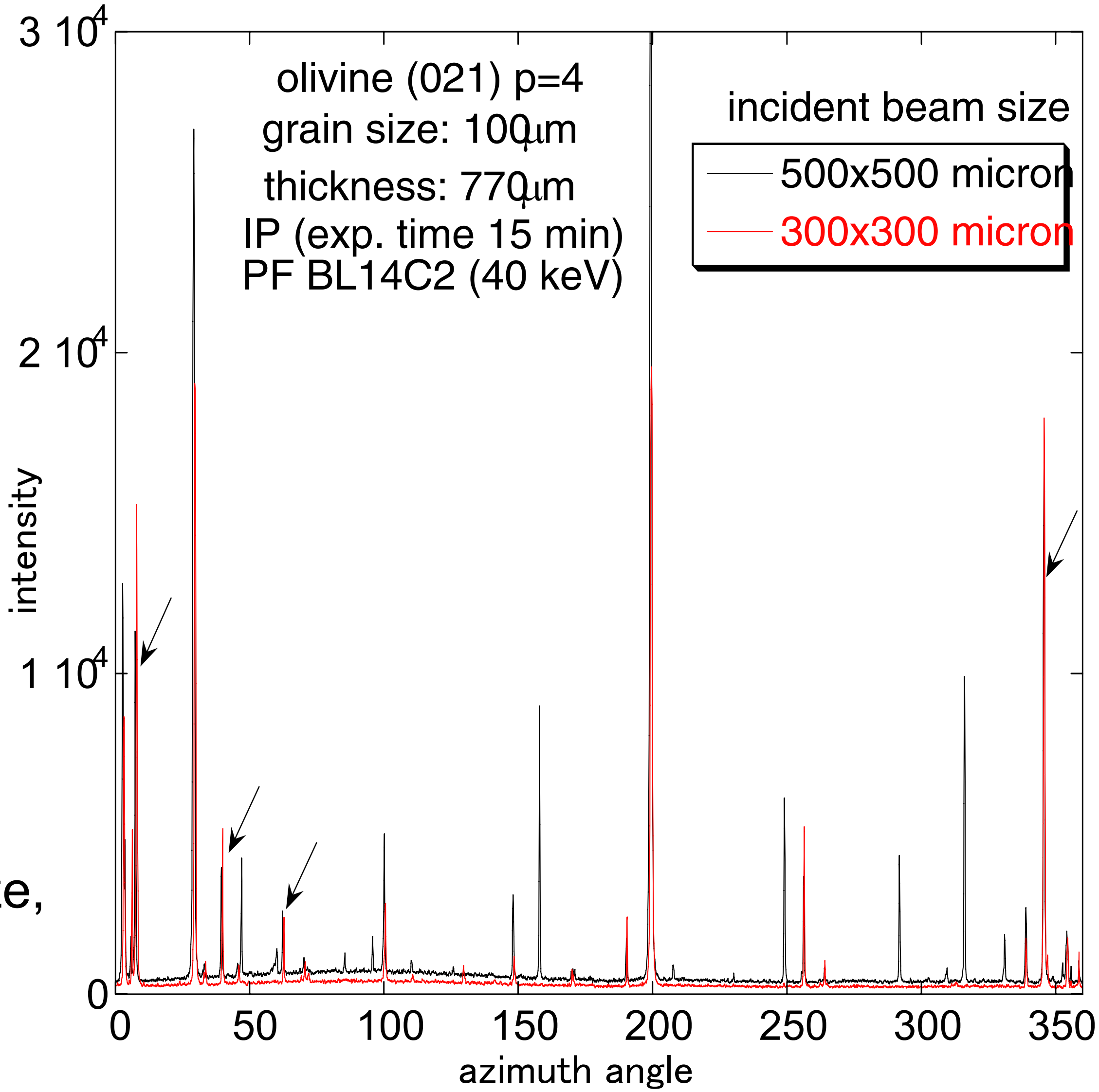
Calibration of the $\Delta\theta$ value $\Rightarrow$ estimates of the number of nucleated grains from the number of newly appeared spot

The intensity of each spot is proportional to the volume of the grain
(Watching growth of individual grains)

Need to make sure "valid reflections"
whether the Bragg reflection is completely recorded on 2D detector

2D-XRD pattern and its azimuthal projection of the intensity along Debye ring





When increasing the beam size,

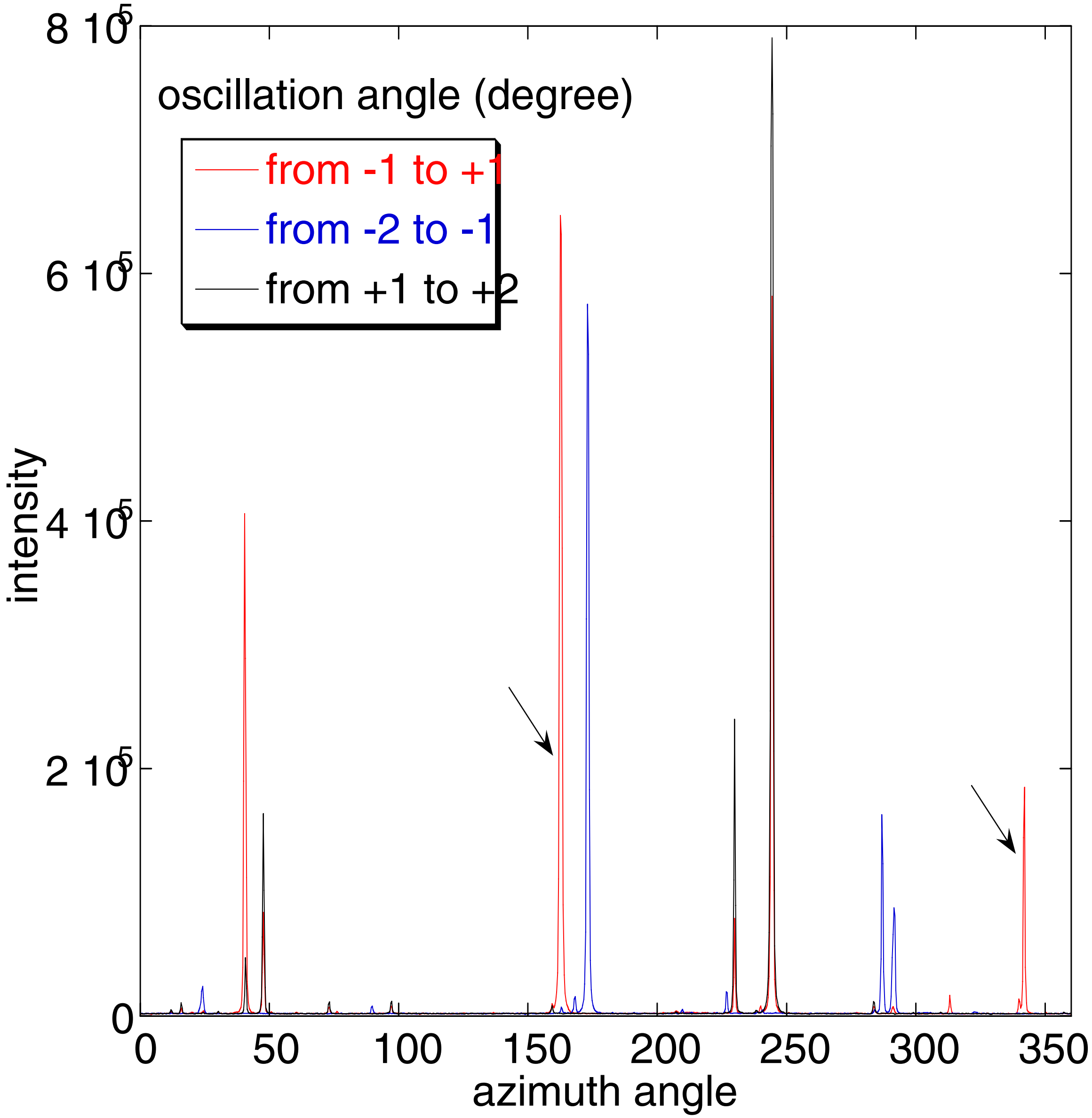
1. Newly appeared spots
2. Increases of the intensity
3. No changes (arrowed)

→ valid reflections

Grains corresponding to the arrowed spots lie completely within the radiated area (300x300).

久保他，高圧力の科学と技術 2009

2D-XRD patterns with the sample oscillation



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central exposure
from -1° to +1°

additional exposure
from -2° to -1°
from +1° to +2°

- The arrowed spots have no intensity left in the additional exposure. ⟶ valid reflections
- The integrated intensity of the arrowed spots is completely recorded in the central exposure.

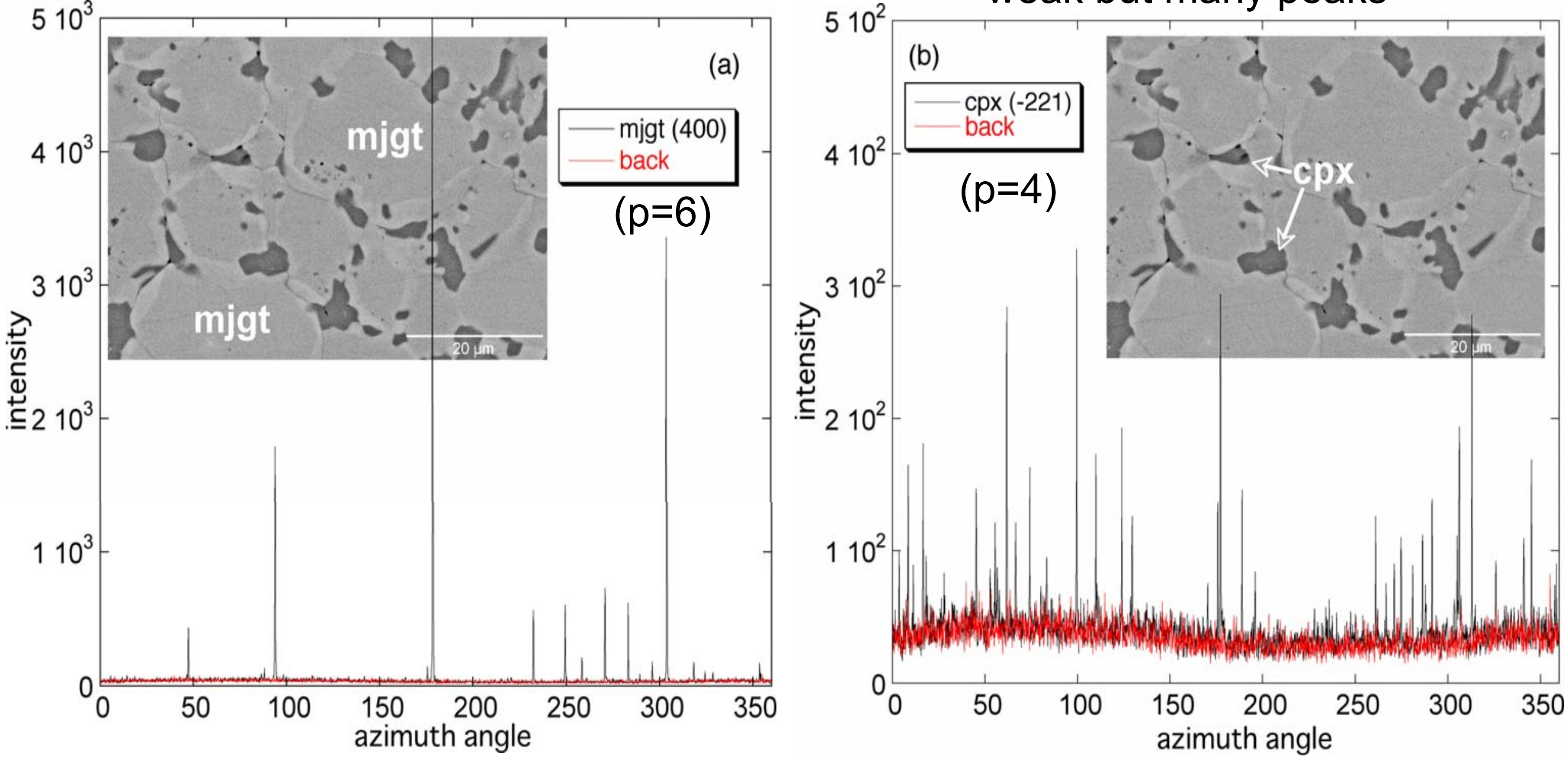
olivine (130)
grain size: ~100 μm
thickness: 770 μm
beam size 100 μm
X-ray CCD (exp. time 100 sec)
SP-8 BL10XU (35 keV)

2D-XRD observations of partially transformed sample

Fine-grained clinopyroxene (cpx) precipitated at grain boundaries of parental majoritic garnet (mjgt). These textures are reflected in the azimuthal intensity profiles.

about 20-μm parental majoritic garnet

a few-micron precipitated clinopyroxene weak but many peaks



Beam size: 100 μm, sample thickness: 120 μm, IP15min@PF-BL14C2 (45 keV)

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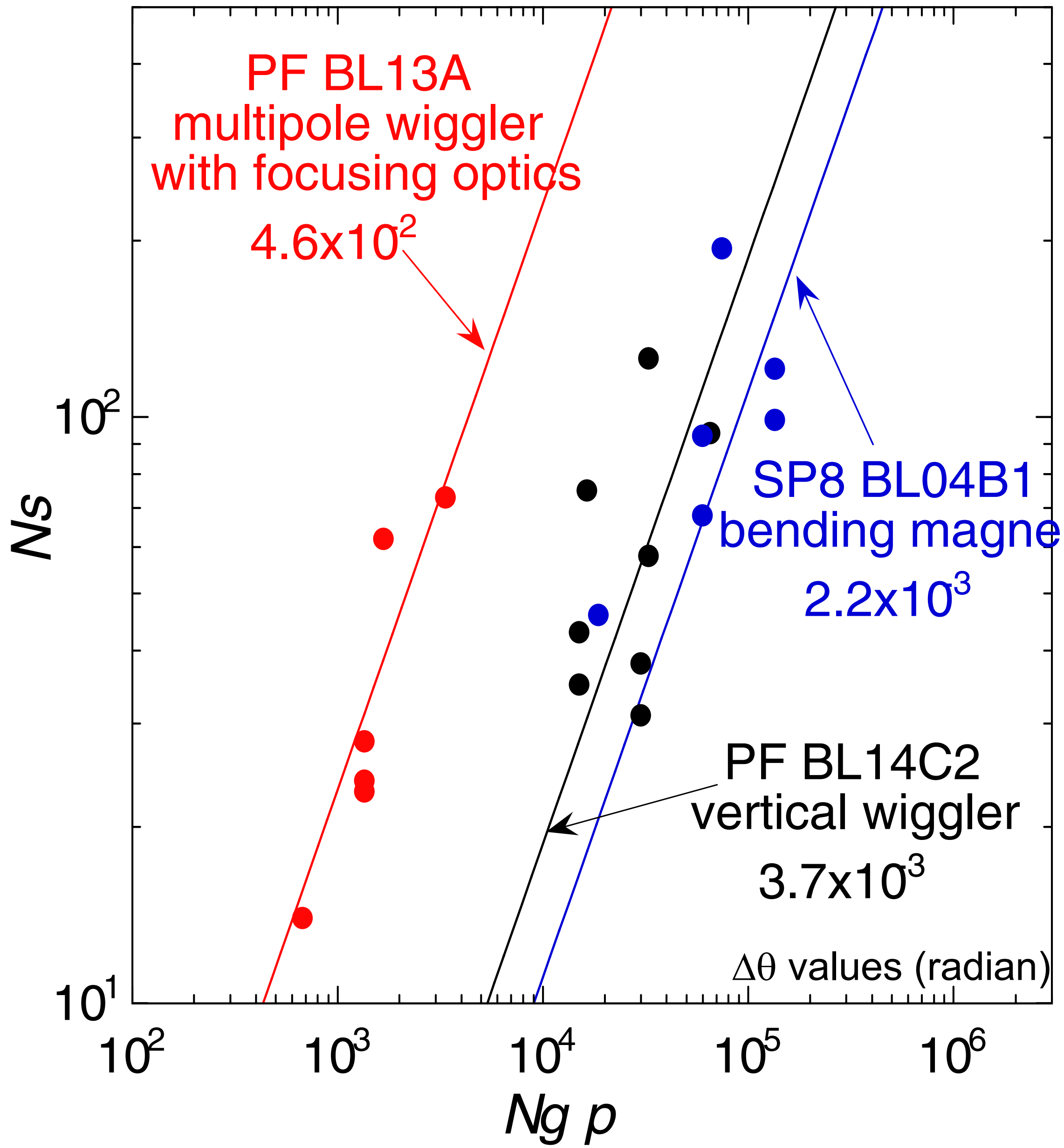
Relationships between the number of spots *Ns* and grains *Ng*

Preliminary calibration of the Δθ value



$$N_s \approx N_g p \Delta\theta / 2$$

- The intercept of each line indicates the Δθ value.
- The Δθ values are different among beamlines probably depending on the light source and focusing optics.

<u>standard samples</u>

wadsleyite (ortho.) and alumina (hex.)
Average grain size: 9 and 16 μm
Thickness: 169 and 255 μm
p: 4-12

<u>Incident X-ray</u>

Beam size: 30-300 μm
Energy: 29-50 keV
IP (exp. time 10-15 min)

久保他，高圧力の科学と技術 2009

Summary (topic 2)

- Time-resolved 2D-XRD method has been applied to observe grain nucleation and growth in high-pressure transformations using MA and DAC.
- The $\Delta\theta$ values for the relationship between *Ng* and *Ns* were preliminarily determined in some beamlines. We should consider "valid diffraction spots" in future study.
- We could directly observe the grain nucleation process in the coesite-stishovite transformation from time evolution of diffraction spots, which is consistent with the analysis of the bulk transformation rate based on the Avrami equation.