

# Calcium-Aluminum-rich Inclusions & Chondrules

Guy Libourel

CRPG-CNRS, Nancy, France

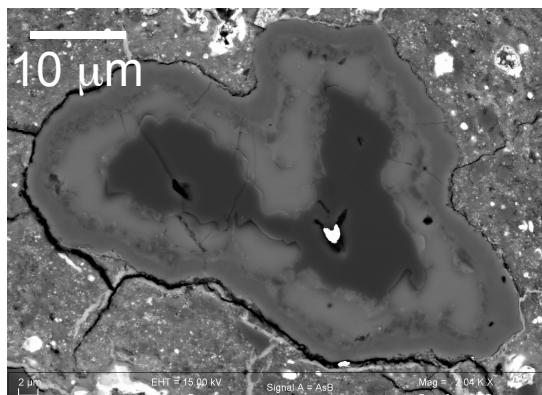


UNIVERSITÉ  
DE LORRAINE



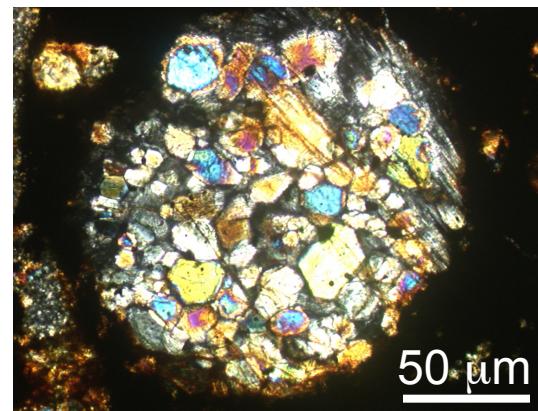
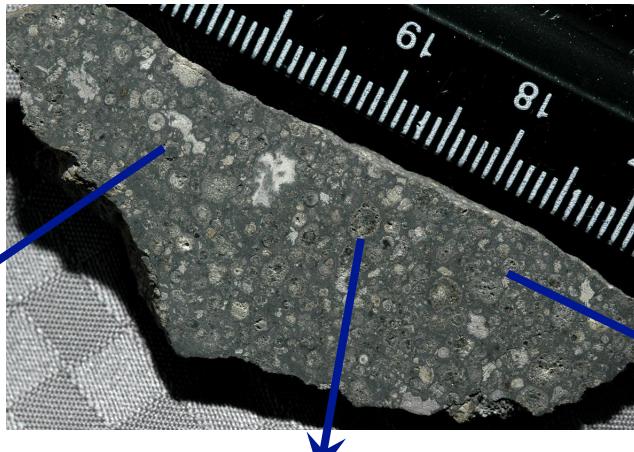
CRPG

# Constituents of primitive meteorites



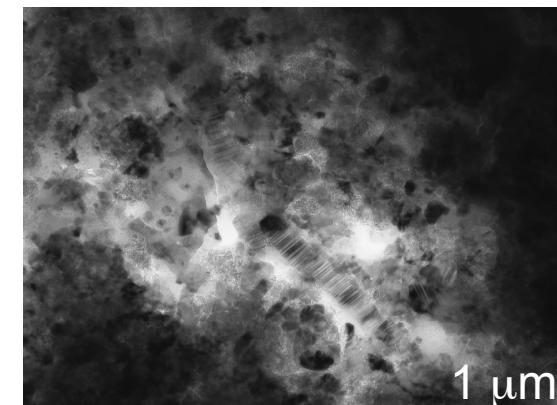
Ca - Al-rich inclusions (CAI)  
(10  $\mu\text{m}$  - 2 cm)

Oldest solids  
in the solar system (t=0)  
4,567 MA



Chondrules  
(10  $\mu\text{m}$  - 0.2 cm)

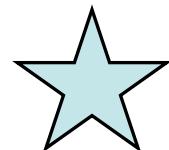
Allende CV3  
(Mexico, fall, February 8, 1969)



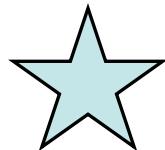
Matrix  
(nm - 10s  $\mu\text{m}$ )

20-80 % by volume of primitive meteorites (chondrites)

# Constituents of primitive meteorites



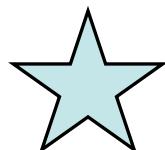
Chronology & isotope chemistry



Mineralogy & petrology



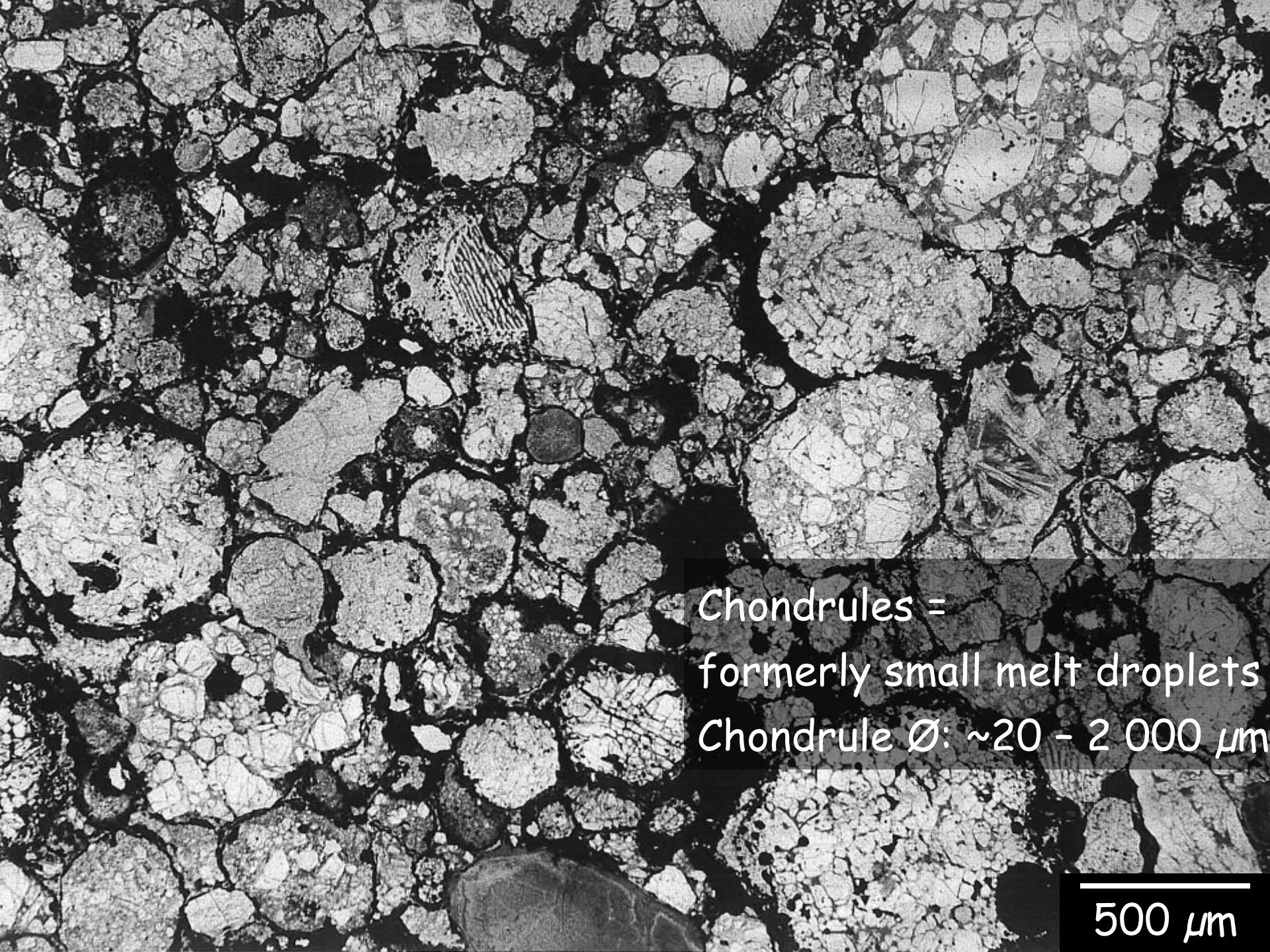
Chemistry



Thermodynamic

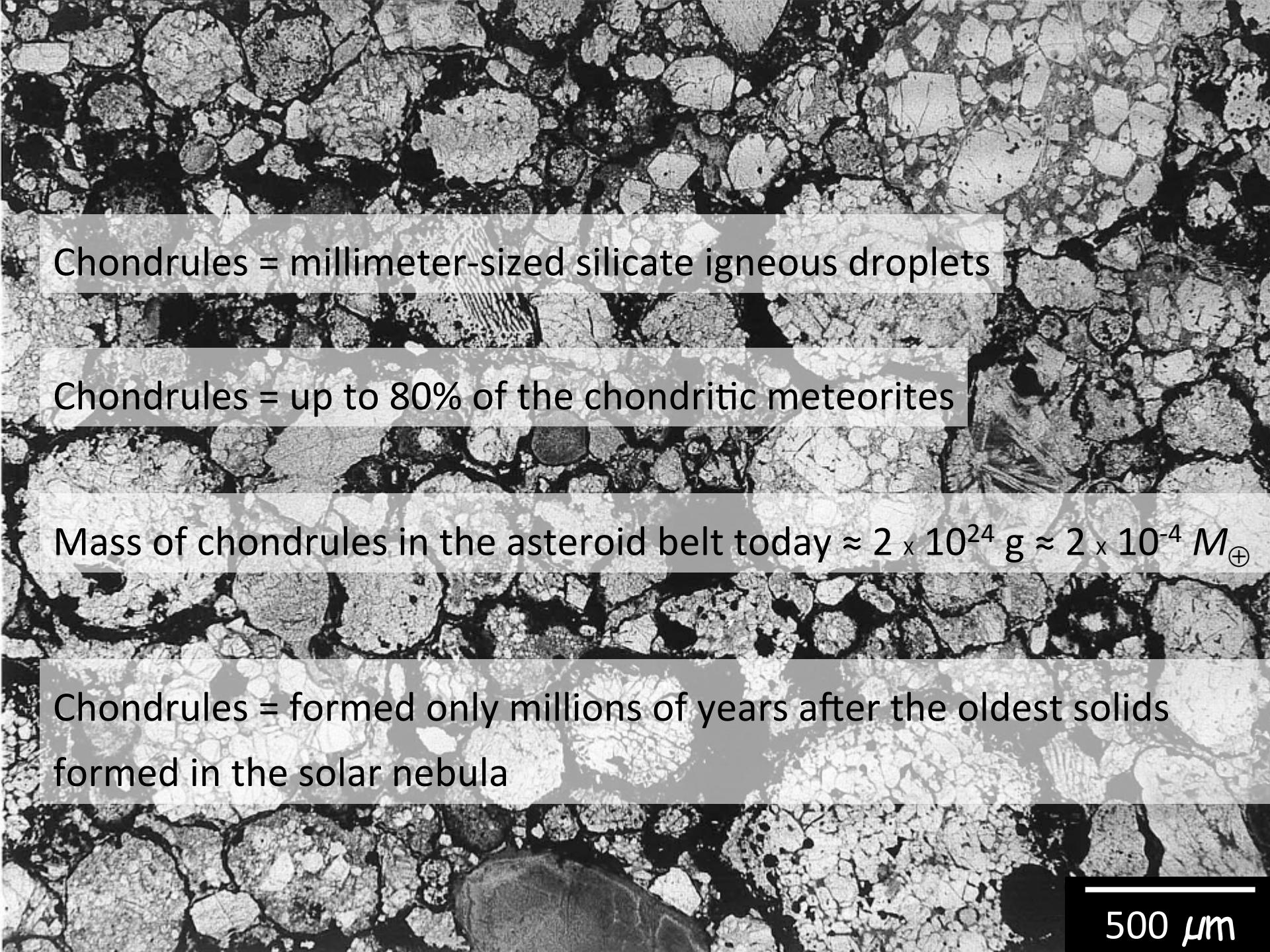


Experiments



Chondrules =  
formerly small melt droplets  
Chondrule Ø: ~20 - 2 000  $\mu\text{m}$

500  $\mu\text{m}$



Chondrules = millimeter-sized silicate igneous droplets



Chondrules = up to 80% of the chondritic meteorites



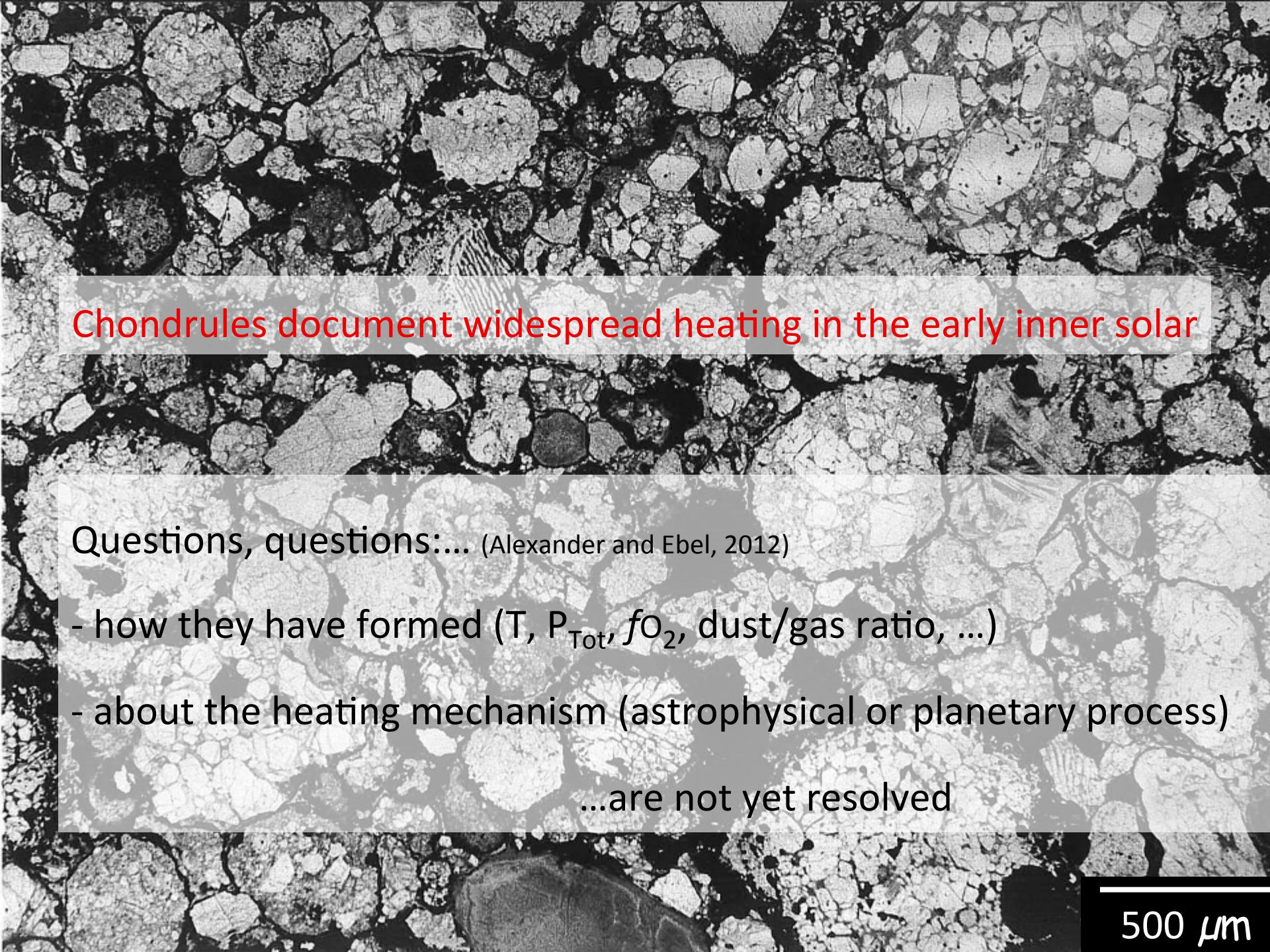
Mass of chondrules in the asteroid belt today  $\approx 2 \times 10^{24}$  g  $\approx 2 \times 10^{-4} M_{\oplus}$



Chondrules = formed only millions of years after the oldest solids formed in the solar nebula



500  $\mu\text{m}$



Chondrules document widespread heating in the early inner solar

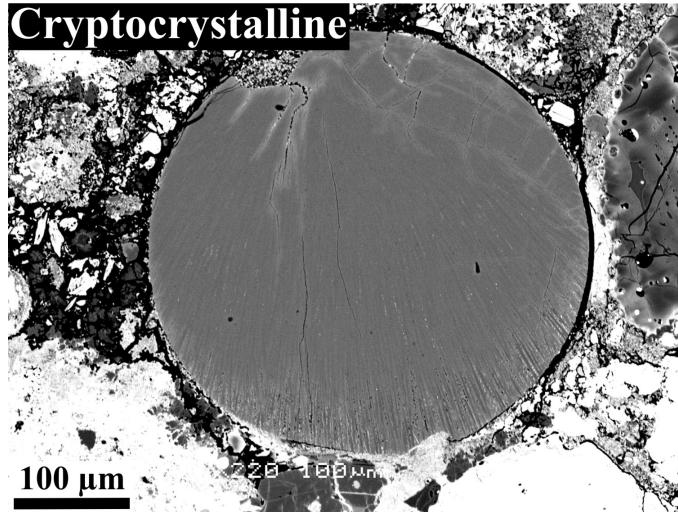
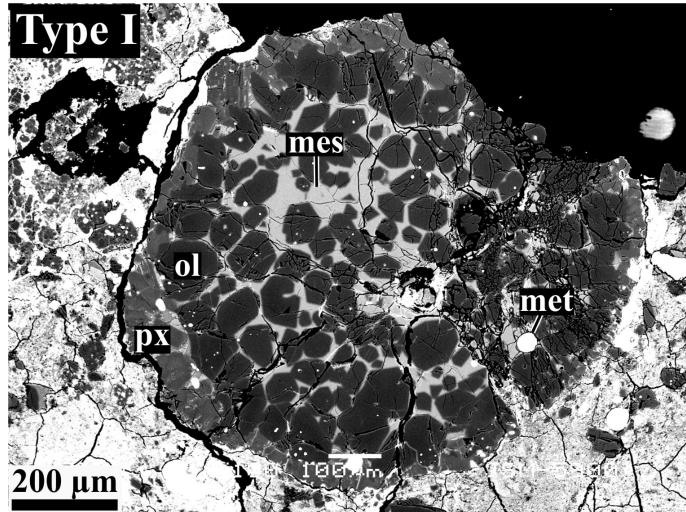
Questions, questions:... (Alexander and Ebel, 2012)

- how they have formed ( $T$ ,  $P_{\text{Tot}}$ ,  $f\text{O}_2$ , dust/gas ratio, ...)
- about the heating mechanism (astrophysical or planetary process)

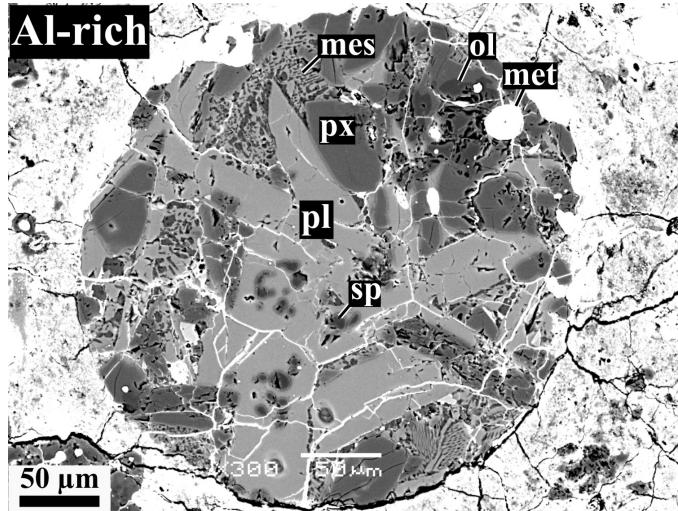
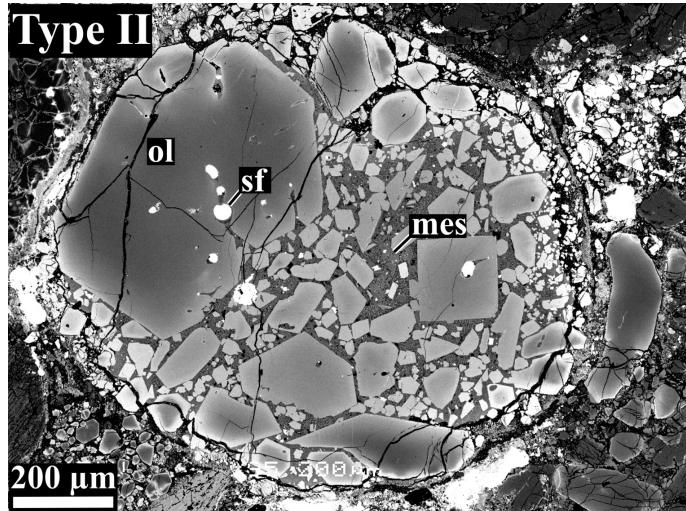
...are not yet resolved

500  $\mu\text{m}$

# Diversity of chondrule textures & chemistry



- large variations in sizes, textures, mineralogy, chemistry



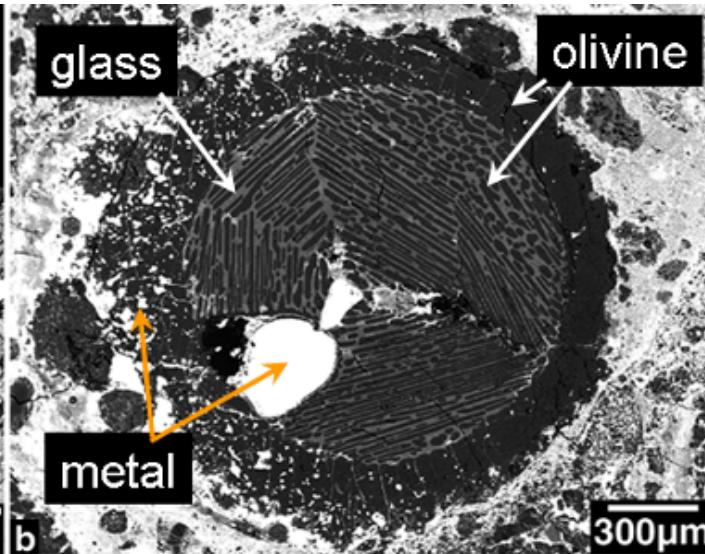
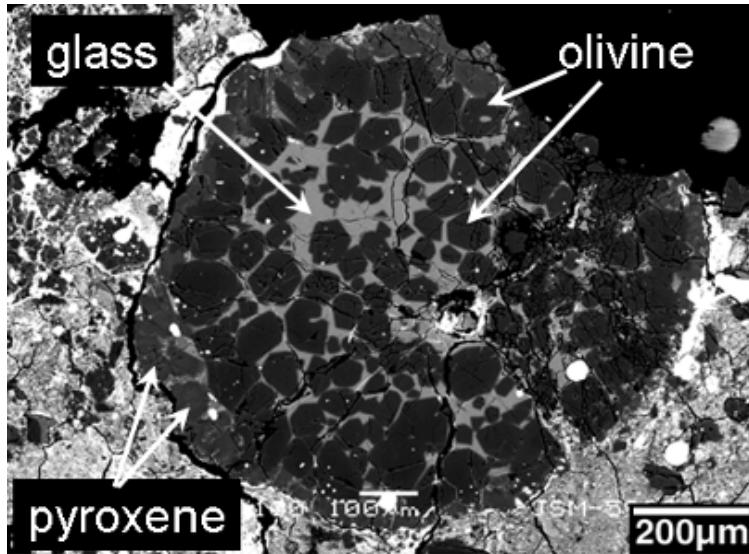
- porphyritic & nonporphyritic

- olivine-rich & pyroxene-rich

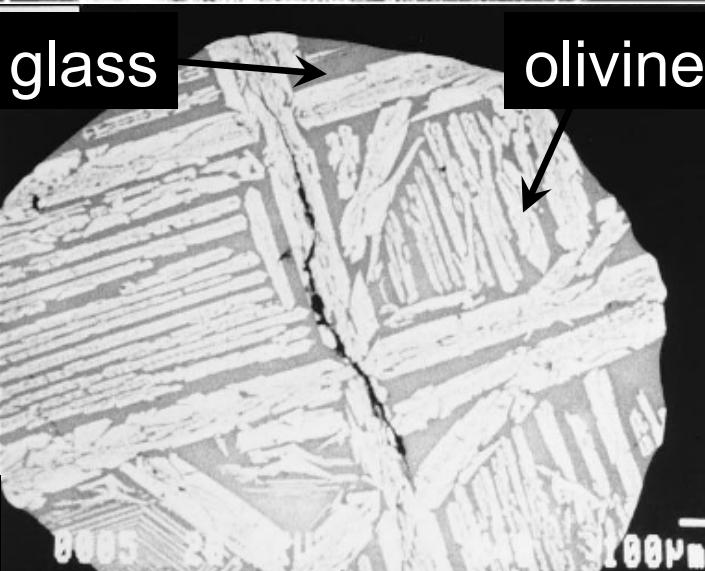
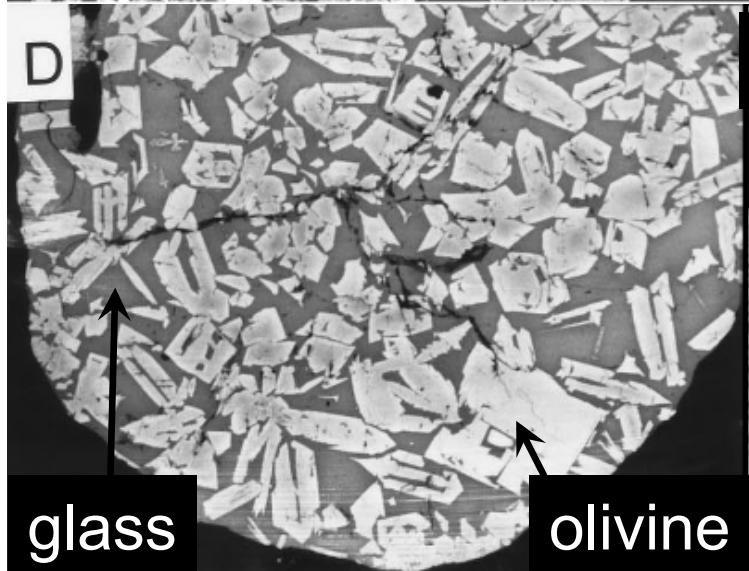
- FeO-poor (Type I)  
FeO-rich (Type II),  
Al-rich

# Dynamic crystallization (cooling rate) experiments

porphyritic



nonporphyritic

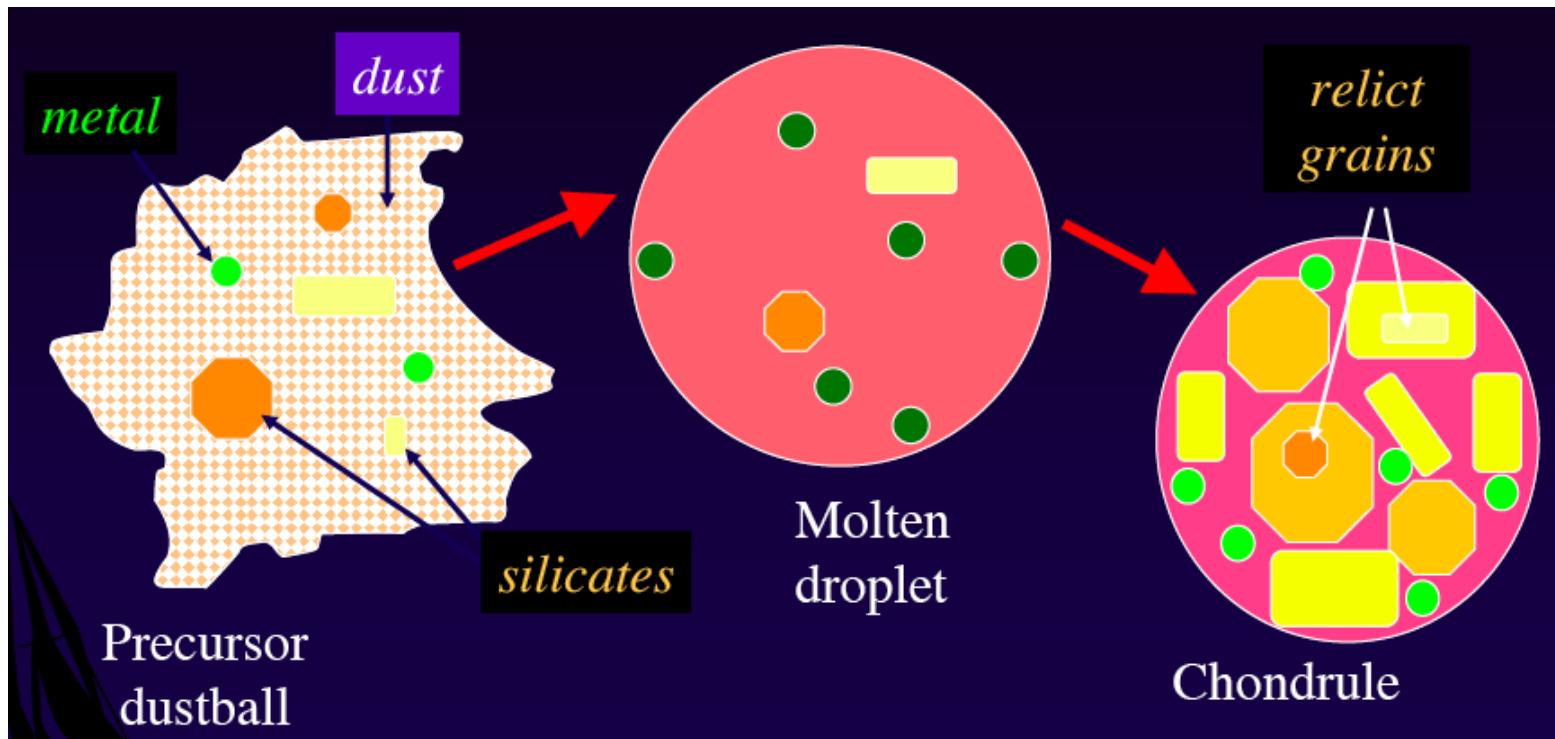


Connolly et al. 1998

# Chondrule formation process

## *Conditions of fast-melting of dust precursors*

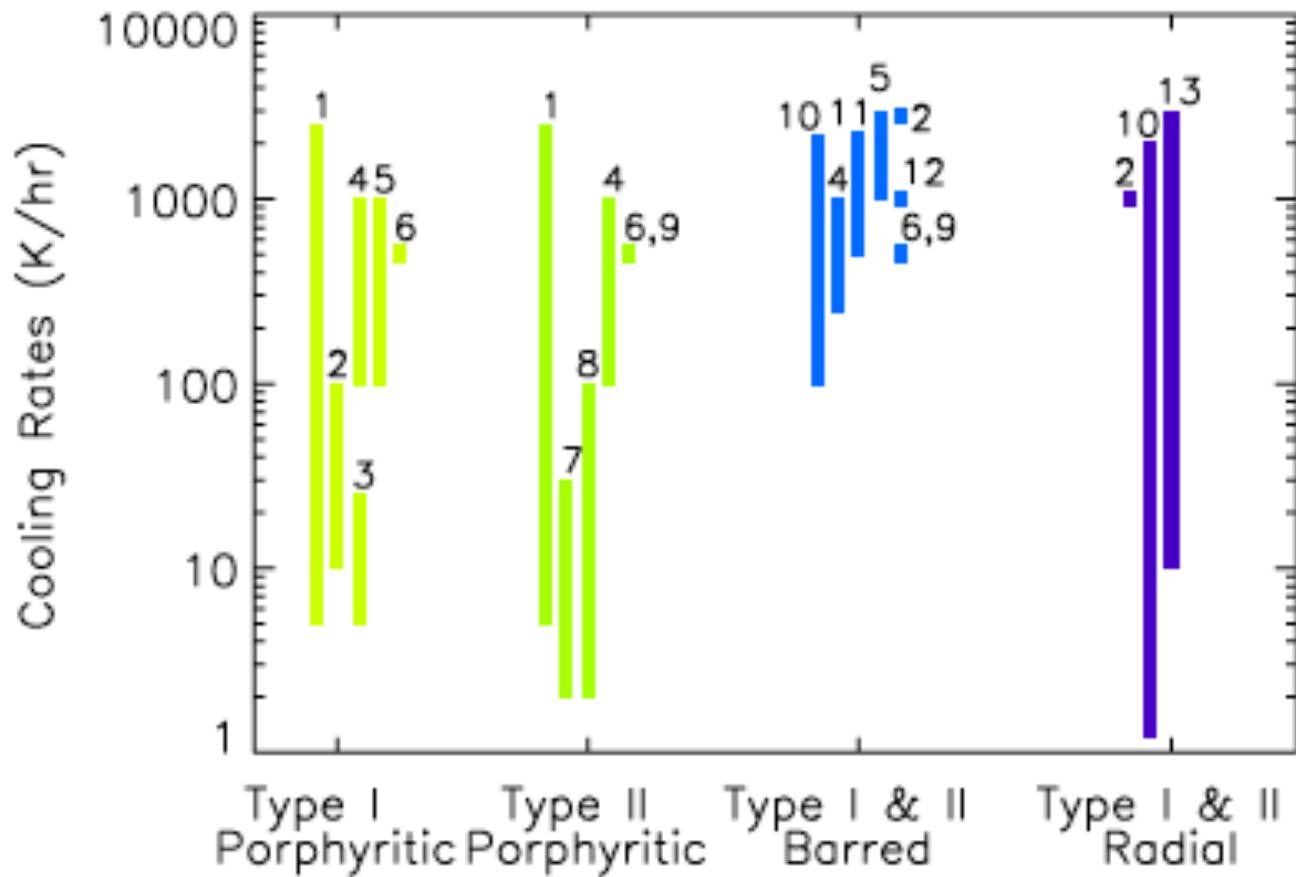
Pressure	$10^{-3} - 10^{-6}$ bar
Temperature	$1400 - 1750^\circ\text{C}$
Cooling rate	$10 - 1000^\circ\text{C.hr}^{-1}$
time	min to hours



Jones et al., 2005

*Chondrules form by brief heating events*

# Chondrule formation process



(Desch et al., 2011)

# Chondrule formation process

Table 2. Constraints on chondrule thermal histories.

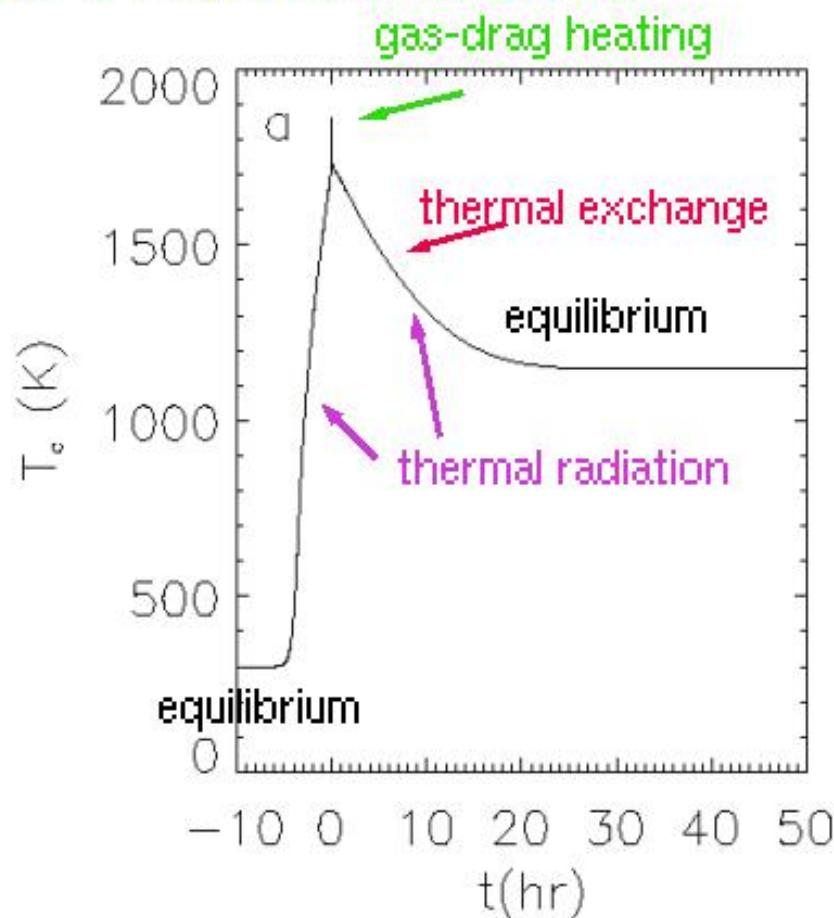
Constraint	X-wind	Lightning	Bow shocks	GI shocks
Ambient $T < 650$ K	X	✓	✓	✓
Heating duration $< 10$ min <sup>a</sup>	X	✓	✓	?
Peak $T \geq 2000$ K	X	?	✓	✓
Cooling rate from peak $\sim 10^3\text{--}10^4$ $\text{K h}^{-1}$ <sup>a</sup>	X	?	✓	✓
Crystallization cooling rate $\sim 10\text{--}10^3 \text{ K h}^{-1}$ (porphyritic)	✓	X	?	✓
Crystallization cooling rate $\sim 10^2\text{--}10^3 \text{ K h}^{-1}$ (barred)	X	X	?	✓
Cooling rate correlates with chondrule density	X	X	?	✓

## How Shock Waves Melt

Shock waves heat up chondrules in three ways:

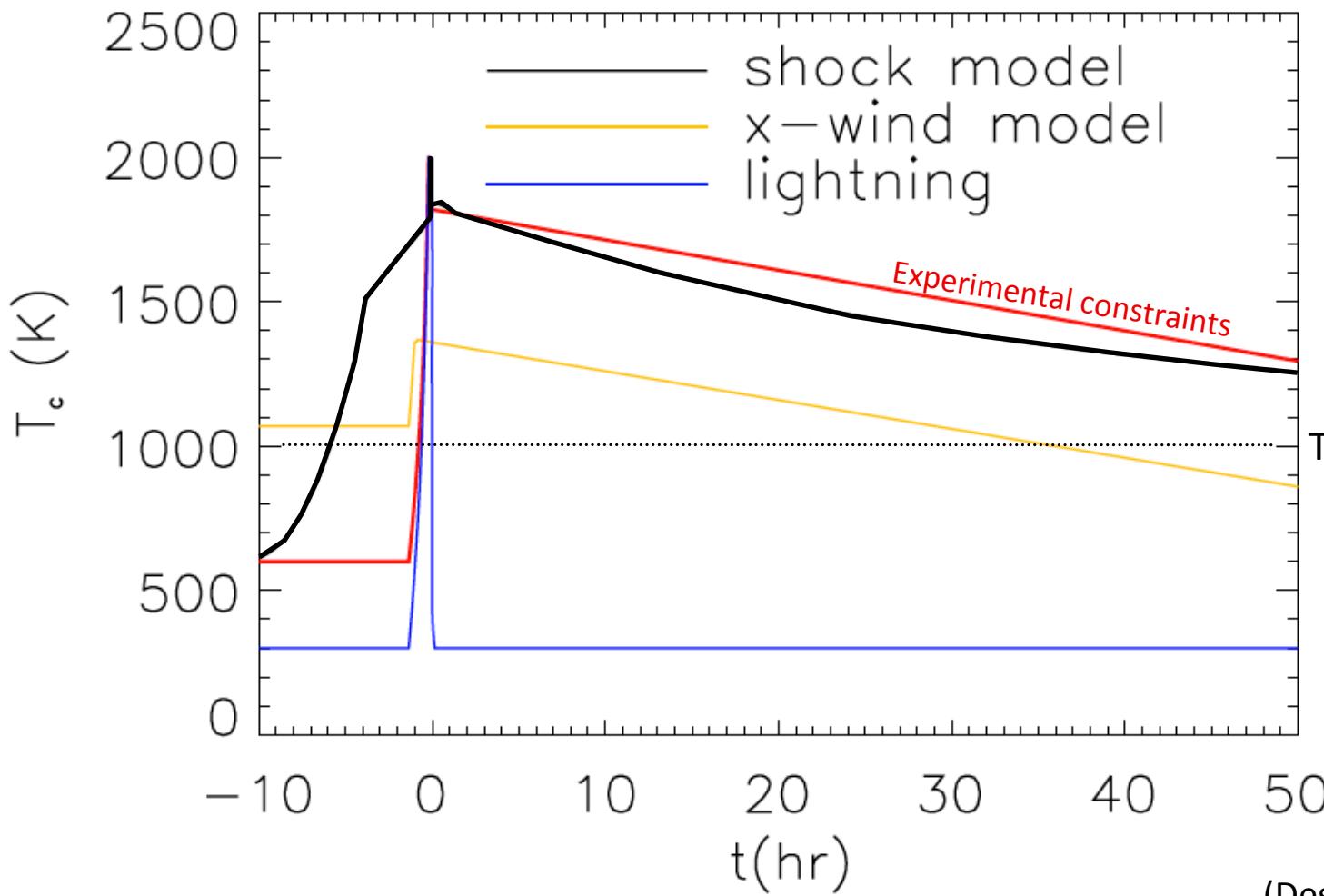
- Gas-drag friction
- Thermal exchange with hot gas
- Thermal radiation from dust, chondrules

(Hood & Horanyi 1993; Ruzmaikina & Ip 1994; Desch & Connolly 2002)



# Chondrule formation process

## Porphyritic chondrule thermal histories



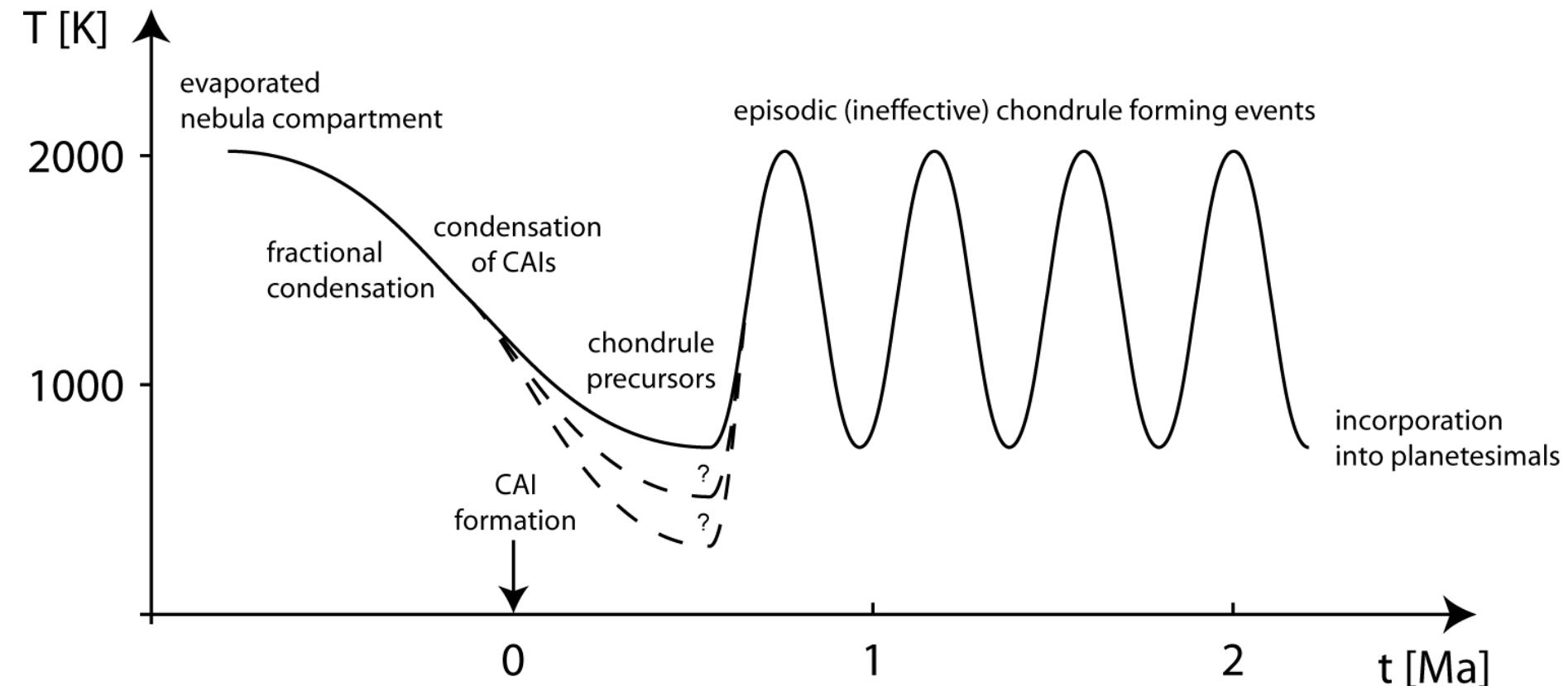
- Crystallization cooling rate  $10-10^3 \text{ K.h}^{-1}$
- Time at high temperature  $> 50 - 100 \text{ h}$



Chondrule formation:  
Quicker and faster?

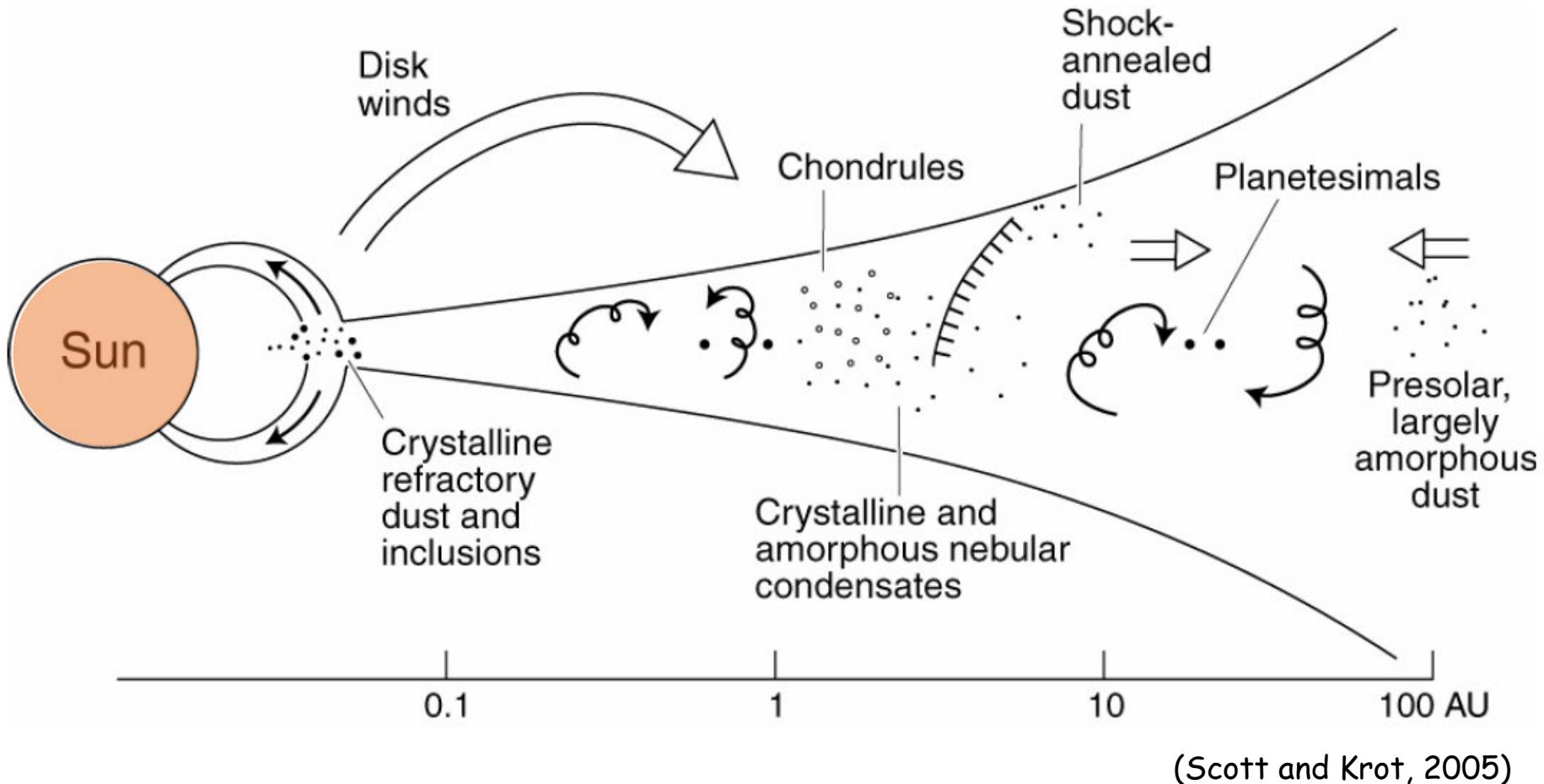
(Desch et al., 2011)

# Chondrule formation process



Schematic model of the formation of solid matter in the early solar system

# Chondrule formation process

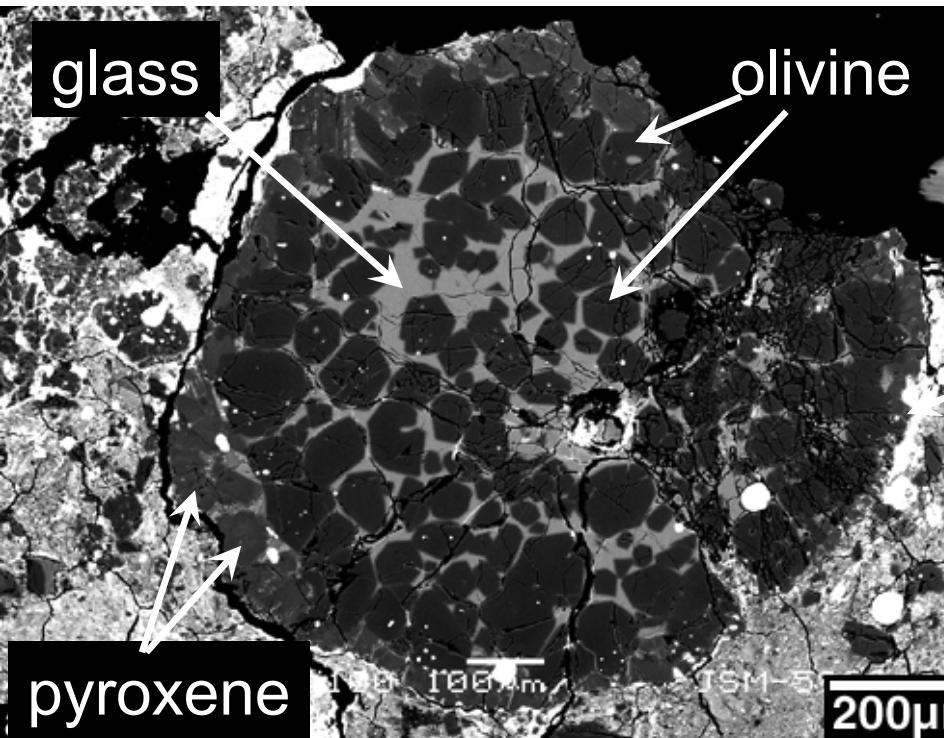


(Scott and Krot, 2005)

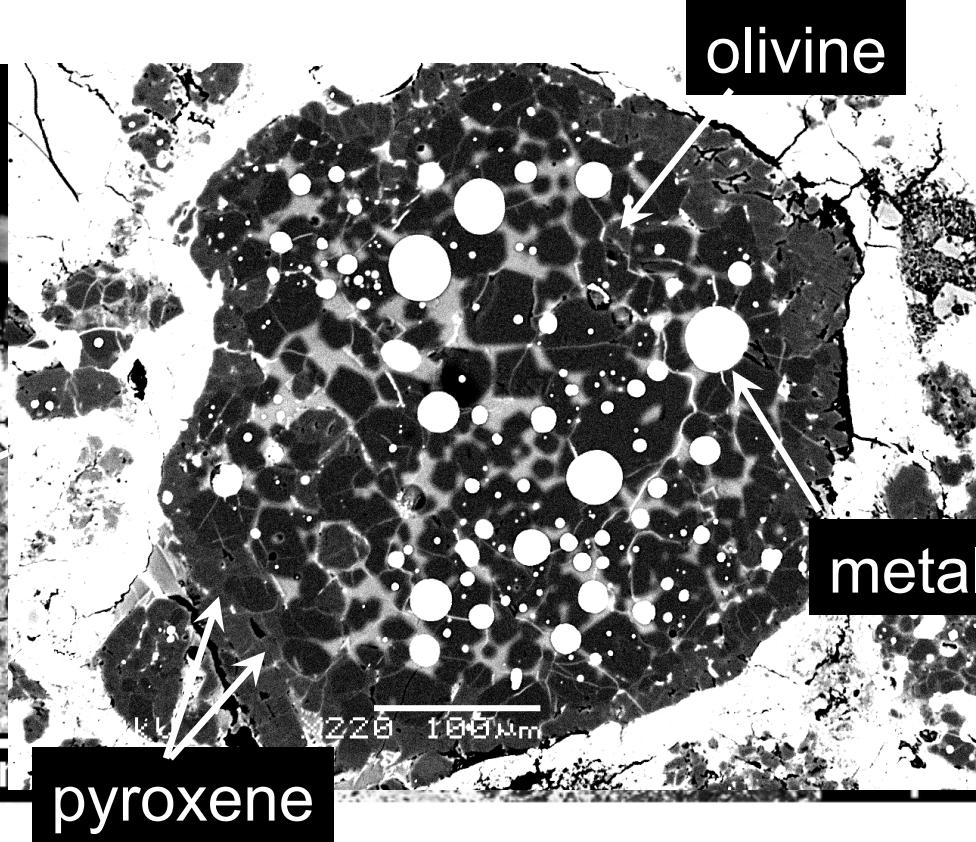
Constraints on the protoplanetary disk evolution

# Diversity of chondrule textures & chemistry

## Type I porphyritic chondrules



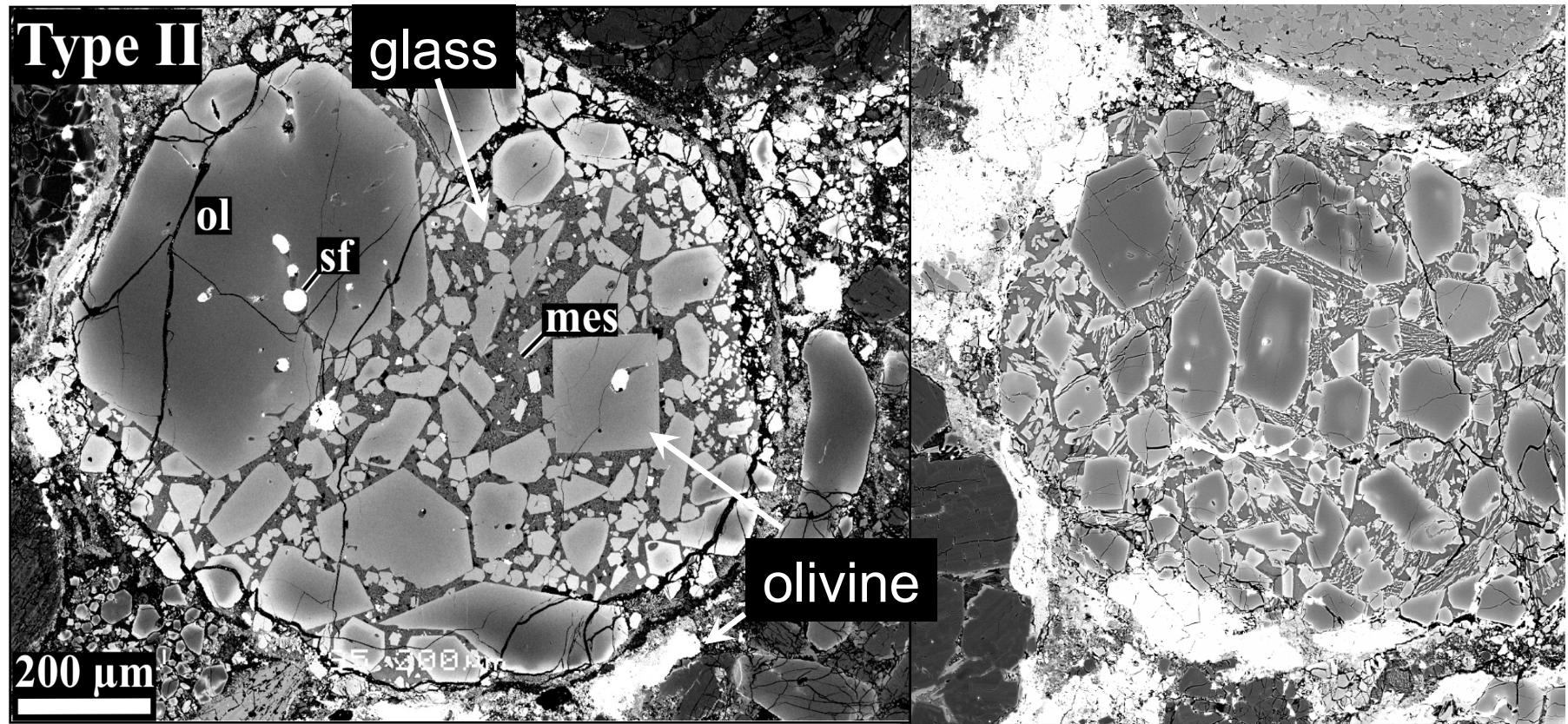
$\text{Fo}_{99.8-95}$ ;  $\text{Fs}_{>95}$



$\text{Fo}_{99.8-95}$ ;  $\text{FeNi}_{5-10}$

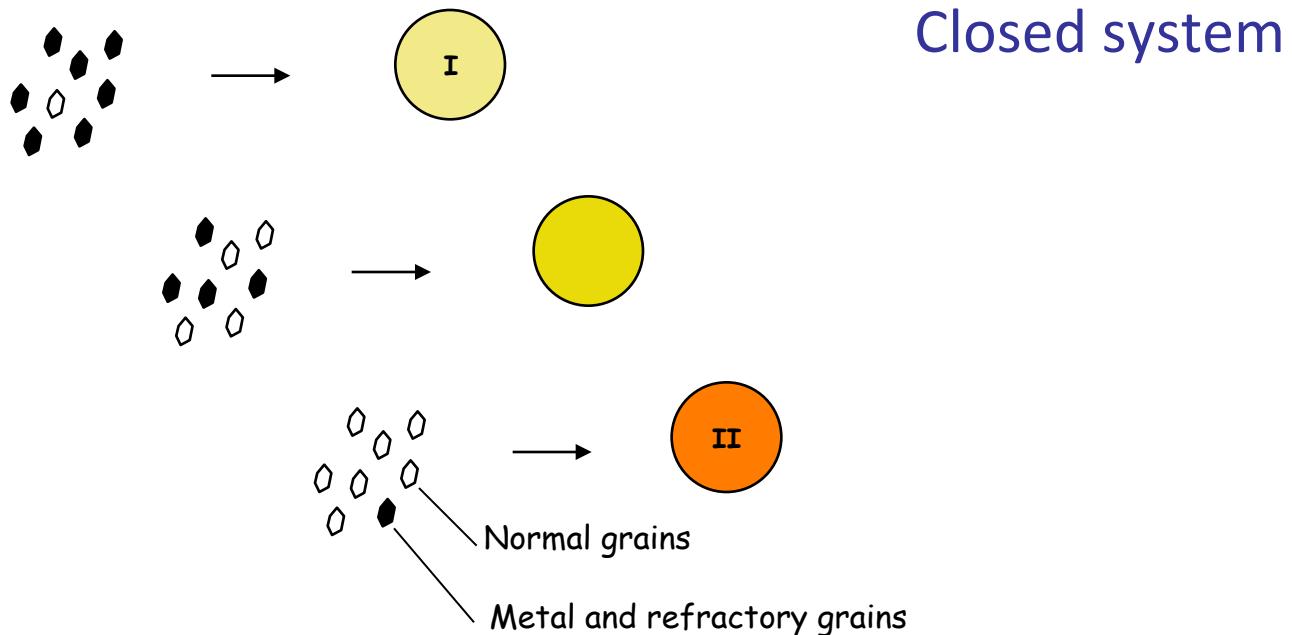
# Diversity of chondrule textures & chemistry

## Type II Porphyritic olivine chondrules



$\text{Fo}_{90-55}$

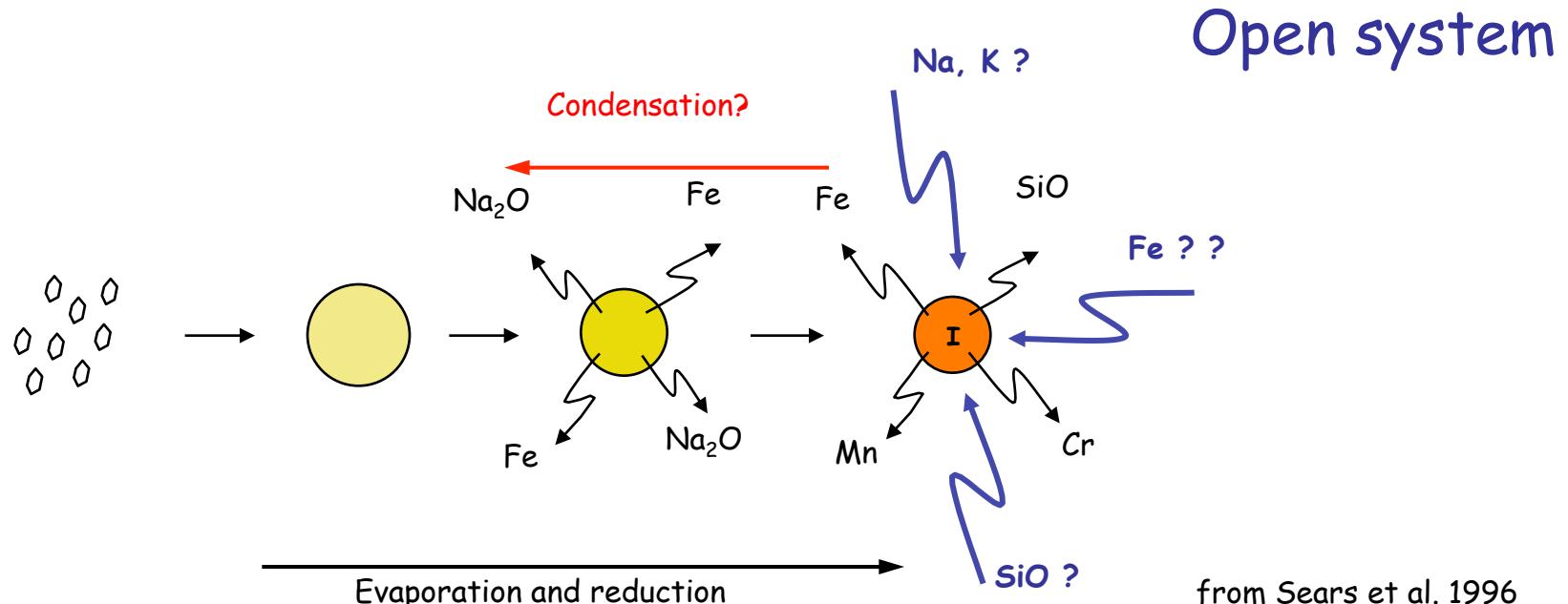
# Chondrule formation process



(Gooding et al., 1983; Grossman, 1988; Hewins, 1991;  
Jones, 1994, Alexander et al. 2008 ...)

Information on precursors

# Chondrule formation process

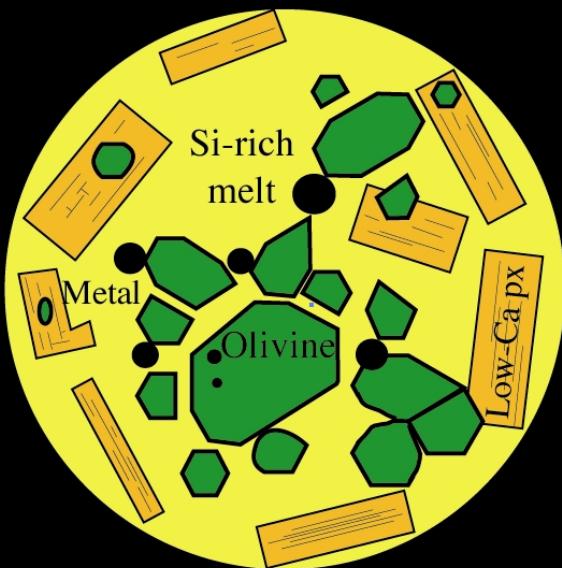


(Lewis et al., 1993, Georges et al., 2000, Matsunami et al., 1993, Alexander, 1996, Tissandier et al., 2002, Krot et al., 2005, Libourel et al. 2007 ...)

Information on the protoplanetary disk conditions

# Chondrule formation process

Type I chondrules are complex objects composed of:



- fragments of differentiated planetesimals
- Mg-rich olivine  $\pm$  Fe,Ni-metal  $\pm$  Ca-Al-rich glass
- and
- an igneous component “equilibrated” with the gaseous environment
- Si-Na rich glass  $\pm$  low-Ca pyroxene
- $\pm$  high-Ca pyroxene  $\pm$  silica phase.

Impacts on planetesimals with a vapor plume

## Plan

Mg-rich olivine

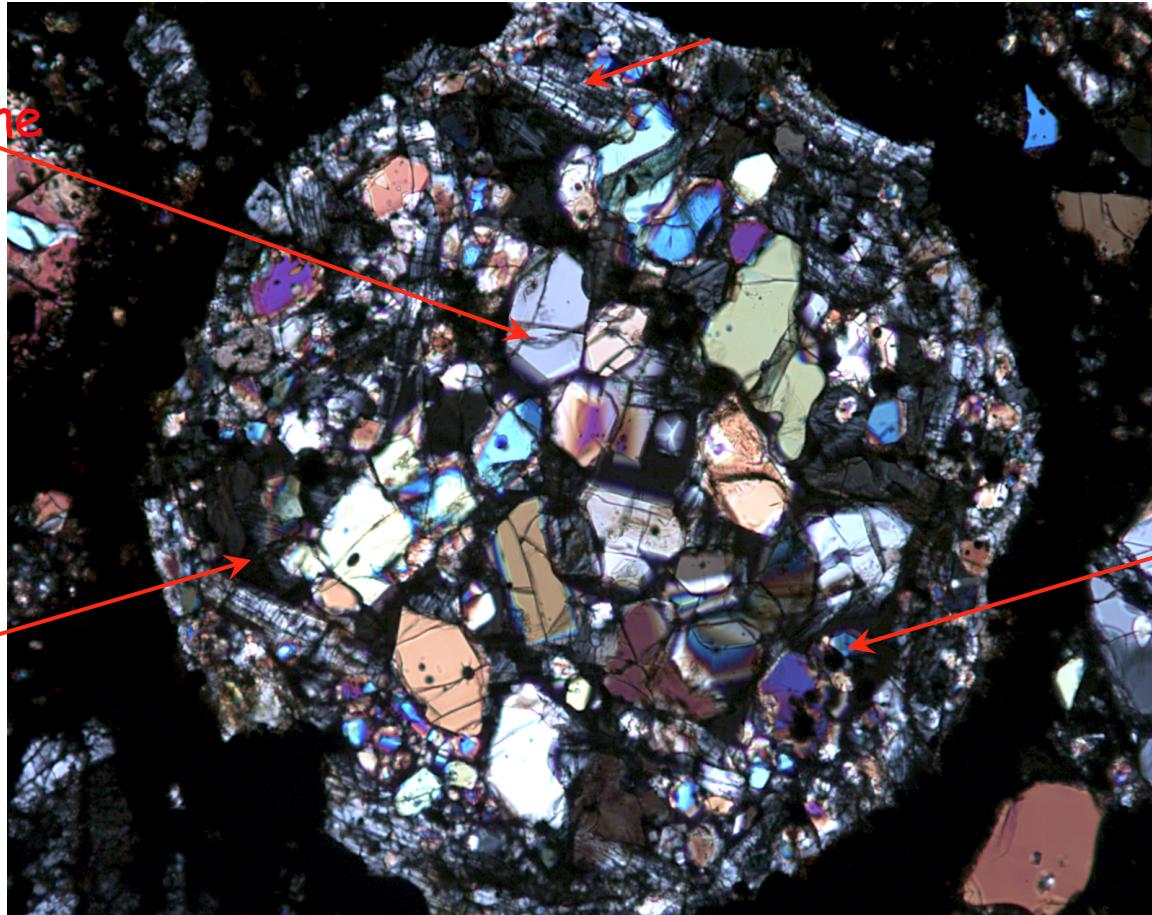
$(\text{Mg}, \text{Fe})_2\text{SiO}_4$

Glass

$(\text{Si}, \text{Al},$   
 $\text{Ca}, \text{Mg},$   
 $\text{Fe},$   
 $\pm \text{Na})$

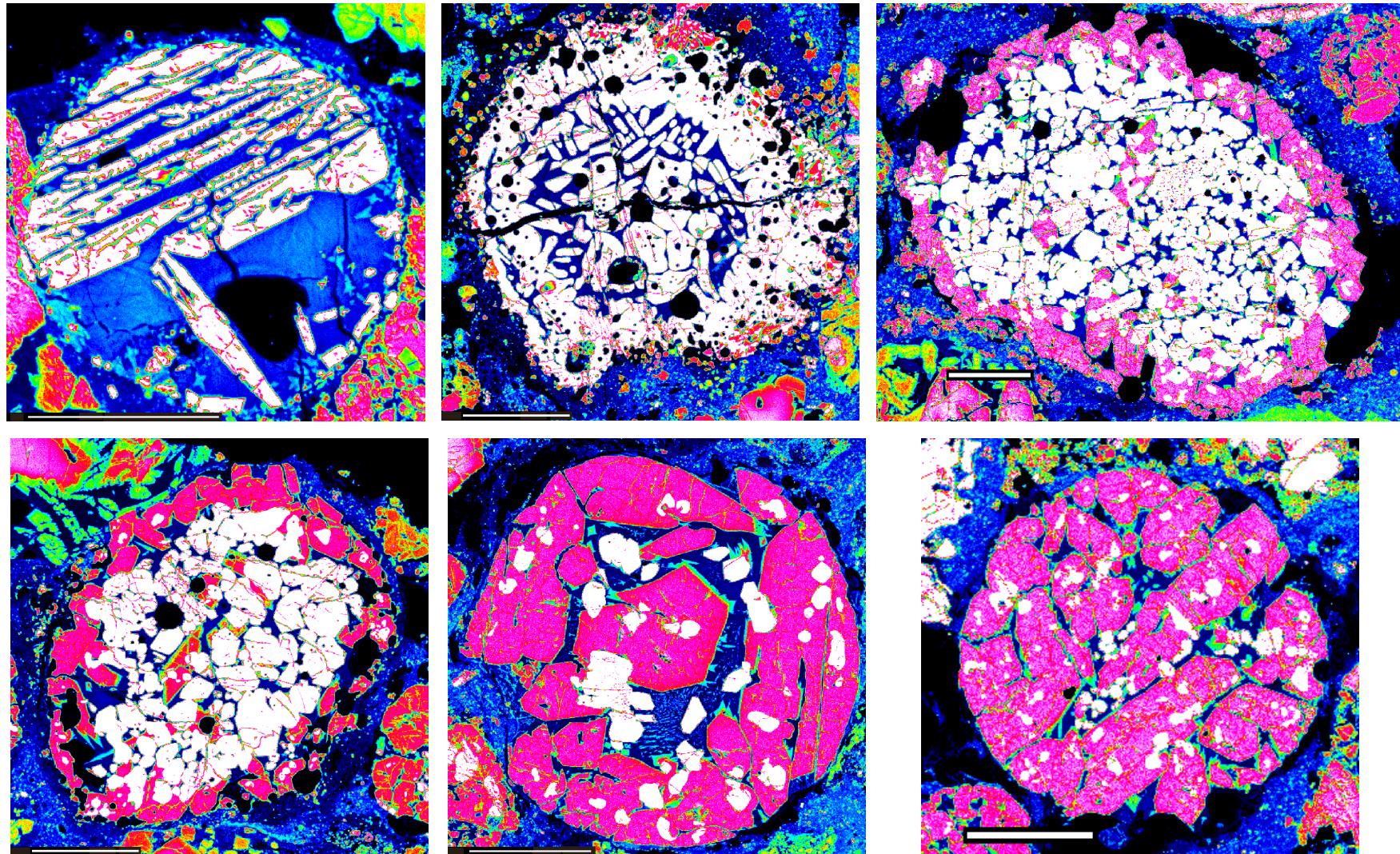
Pyroxene  $(\text{Mg}, \text{Fe})_2\text{Si}_2\text{O}_6$

Fe-Ni Metal



- Evidence for interaction with gas phase
- Mg-rich olivines from differentiated planetesimals?
- Constraints on the formation of chondrules

# Type I FeO-poor chondrules in Semarkona (PO, POP, PP)



200 mm

Forsterite

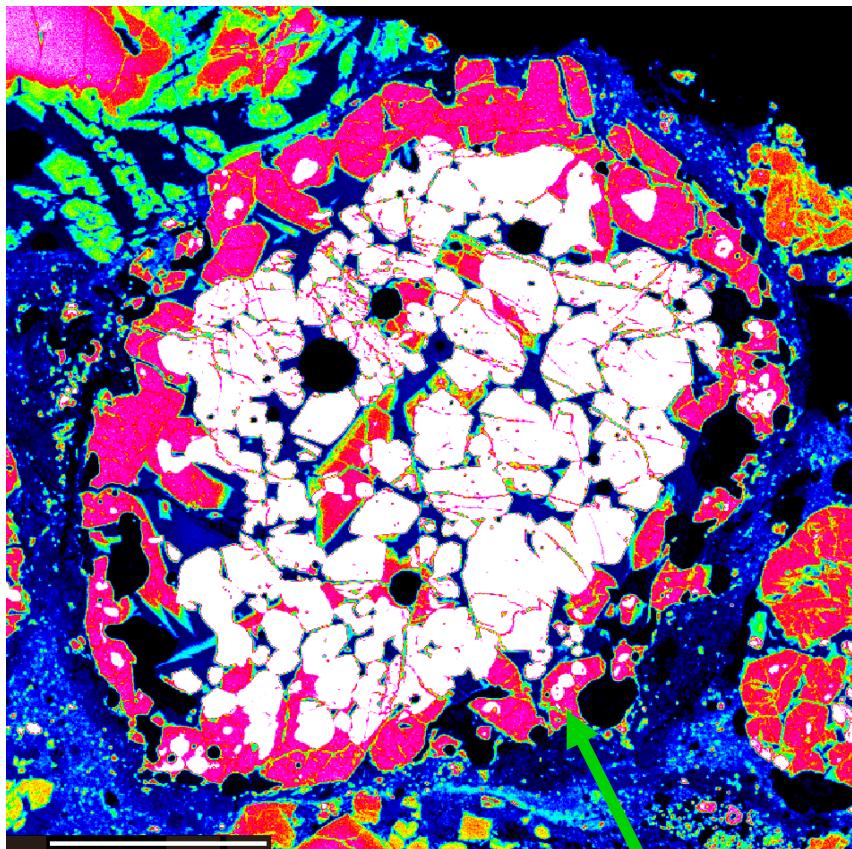
Enstatite  
 $Mg\text{-}K\alpha$  x-ray maps

Glass

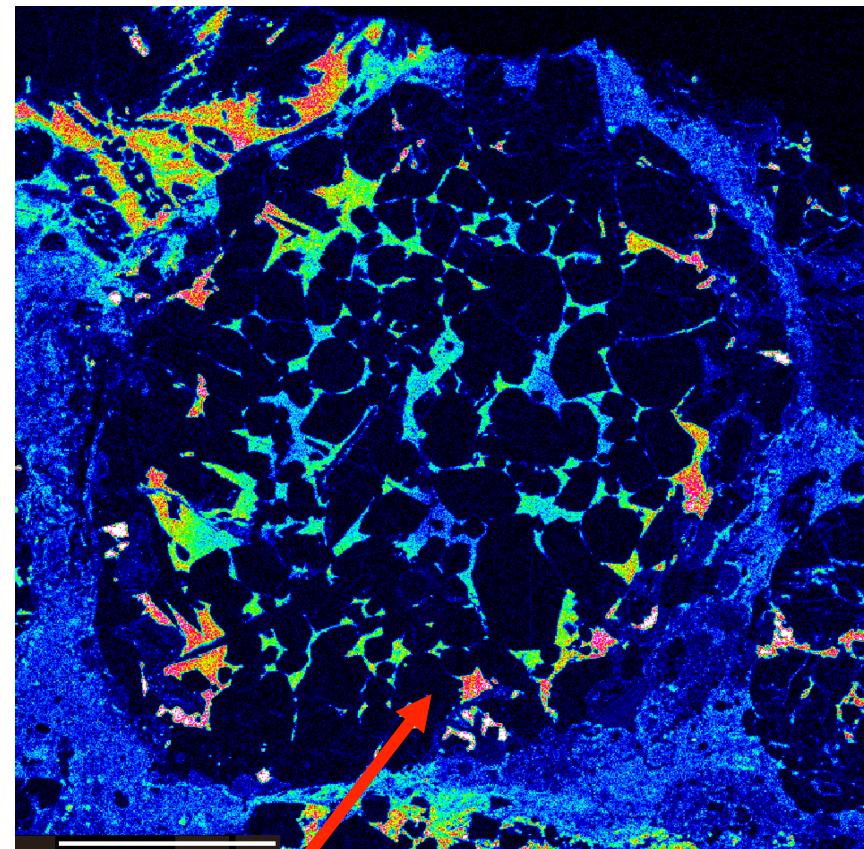
Metal  
Grossman et al. 2000

## Texture

Low Na  High Na



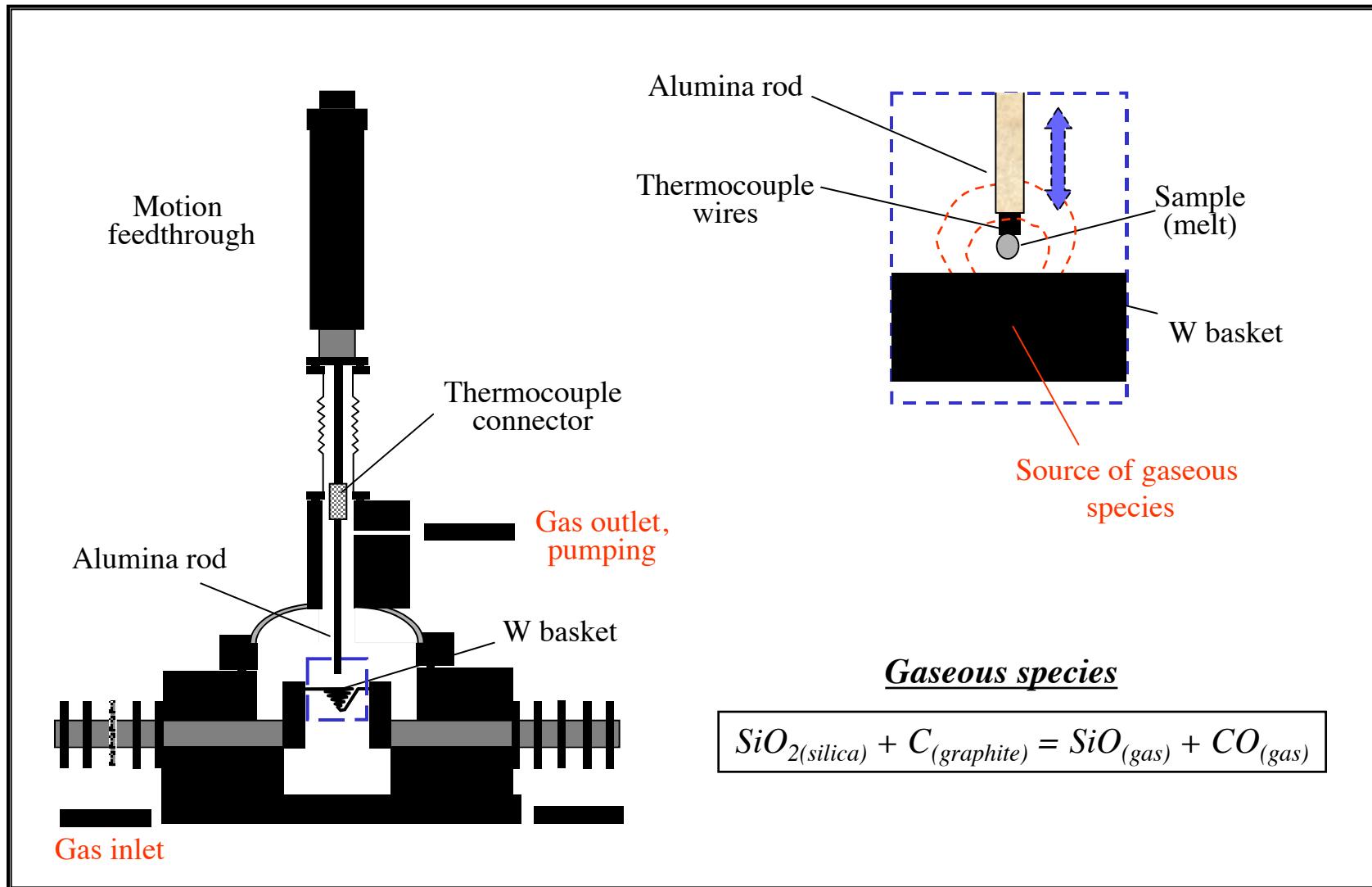
Pyroxene-rich (high-Si) zone  $\approx$  Alkali-rich zone



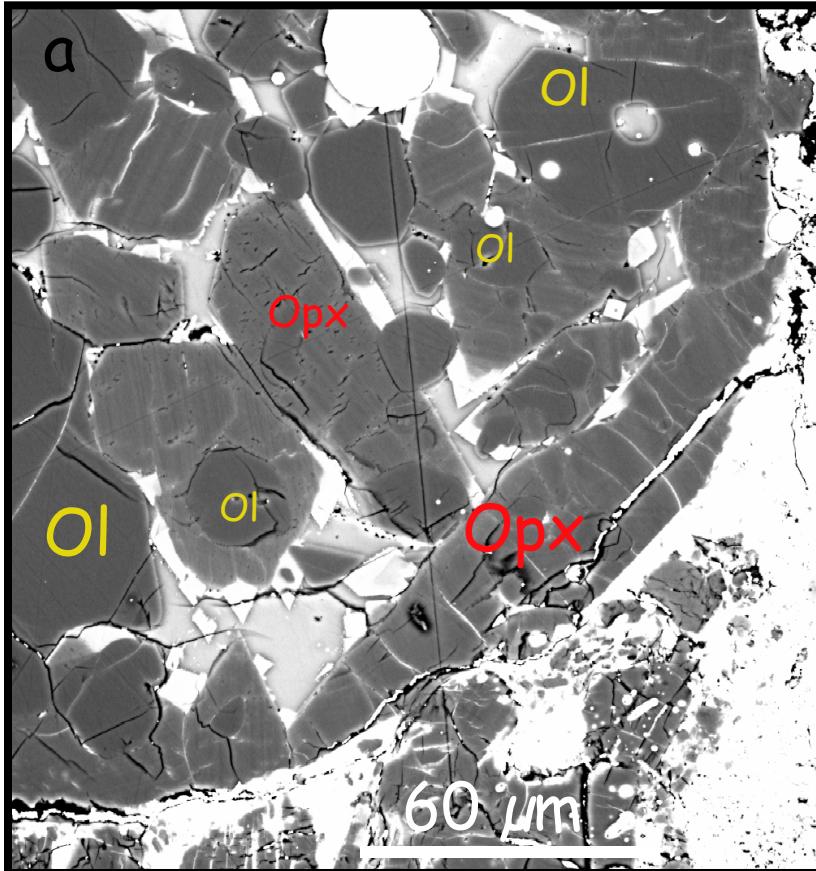
(from Grossman et al. 2000)

Increasing  $a_{\text{SiO}_2}$  from core to rim in the mesostase.

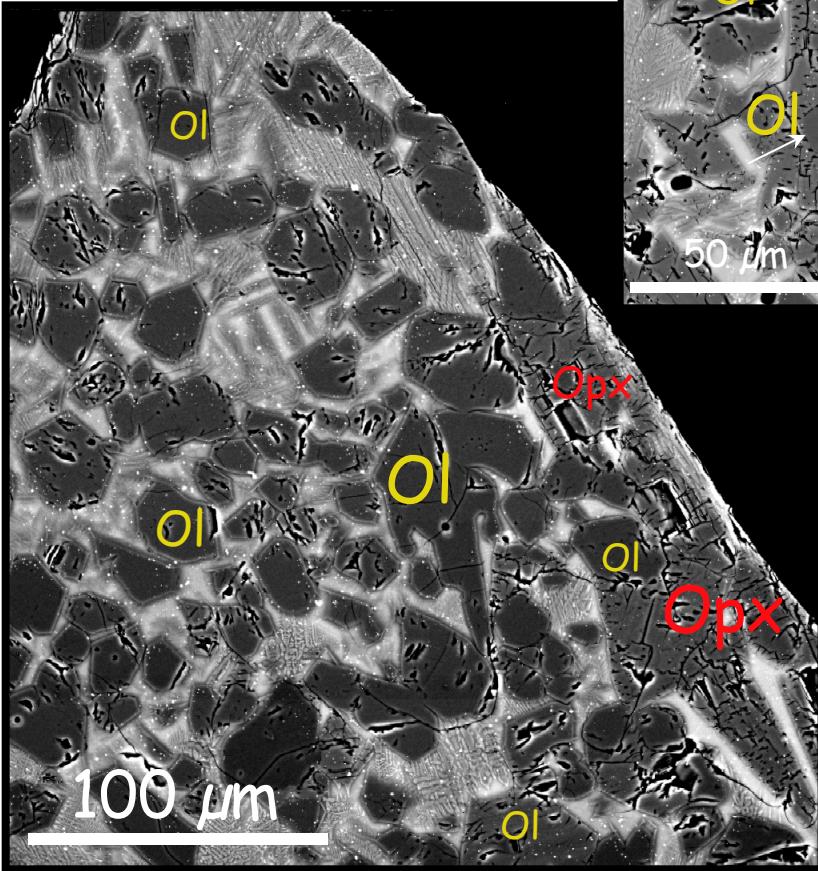
# Gas - melt interaction experiments : Nebulotron



## $\text{SiO}_{\text{gas}}$ - melt interaction



Semarkona POP Chondrule



SiMS3-9, 300 s à 1451 °C,  $\text{PSiO}_{(\text{g})}$

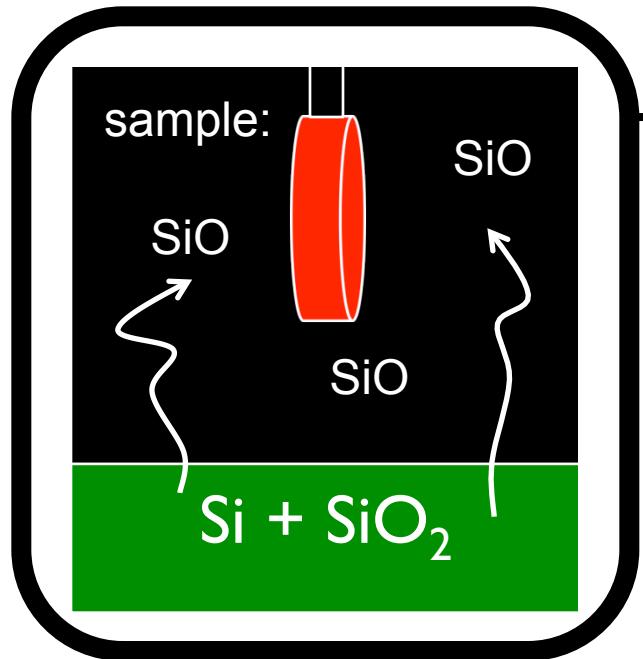
Mineralogical zonation similar to chondrules



Direct  $\text{SiO}_{(\text{gas})}$  condensation into chondrule melts

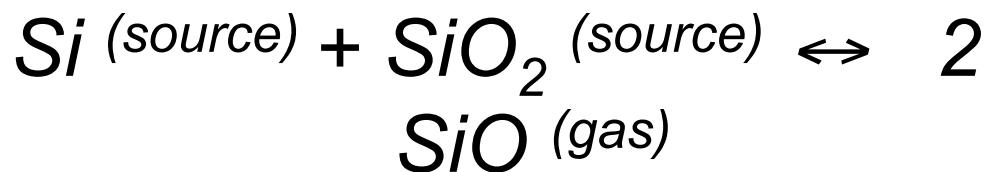
## $\text{SiO}$ gas - solid interaction

# $\text{SiO}$ evaporation-condensation experiments



source + sample in closed crucible

**Source** (evaporation):



**Sample** (condensation):

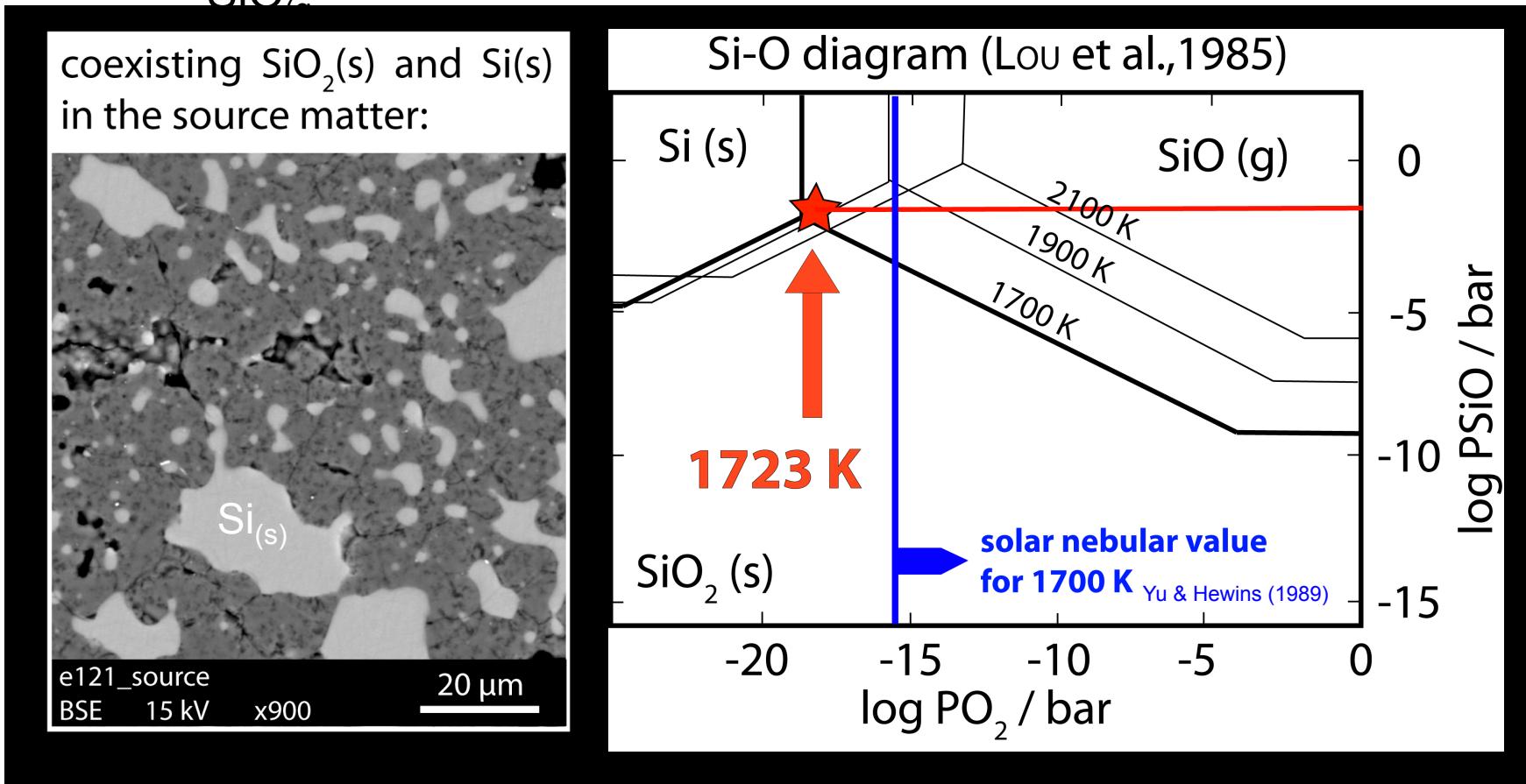


$$= (P_{\text{SiO}}) \cdot (P_{\text{O}_2})^{1/2} / (K_{\text{eq}(T,P)} \cdot \gamma_{\text{SiO}_2 \text{ (sample)}})$$

# $\text{SiO}$ gas - solid interaction

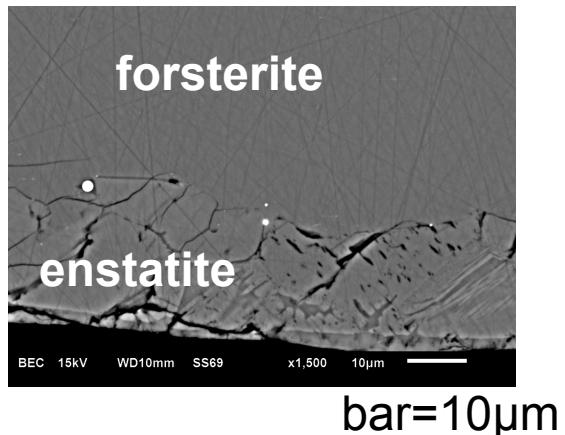
## Production of $\text{SiO(g)}$

- $T_{\text{exp}} = 1723 \text{ K} = 1450^\circ\text{C}$ :
- using "amorphous"  $\text{SiO}$  powder:  $\text{Si}_{(\text{s})} + \text{SiO}_{2\text{(s)}} \rightleftharpoons 2 \text{ SiO}_{\text{(g)}}$



# Results: C pure forsterite monocrySTALLIN

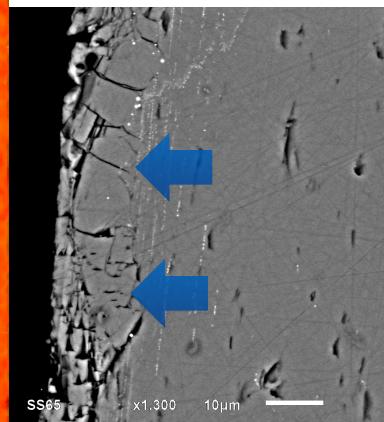
30 minutes



bar=10µm



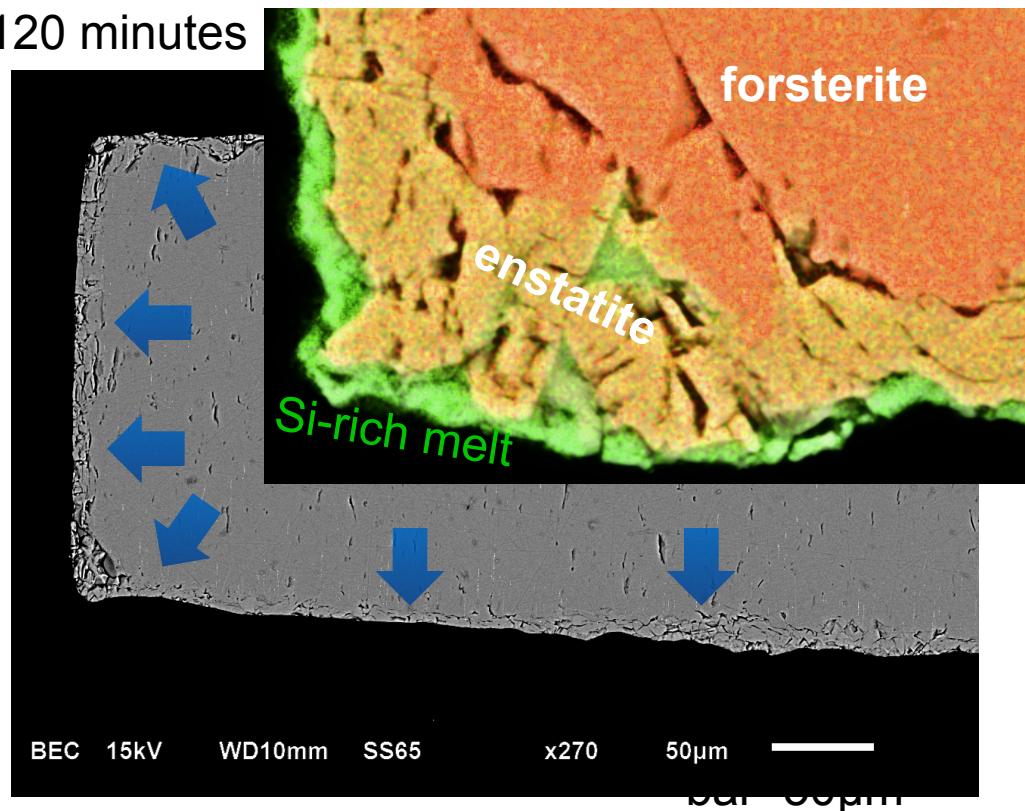
60 minutes



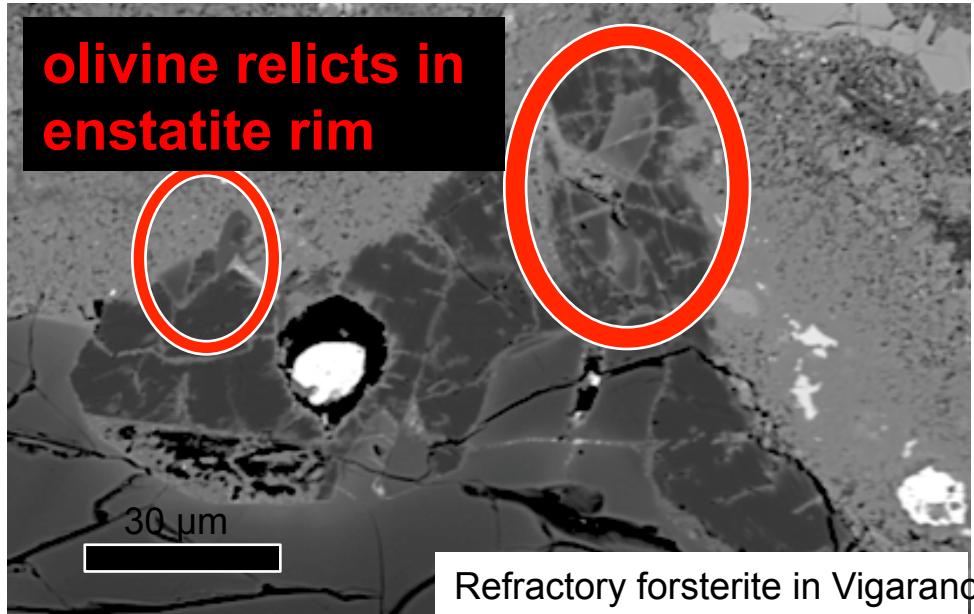
bar=10µm

- in all ~~monocrySTALLIN~~ experiments formation of an **enstatite rim**
- En thickness 10-30 µm
- all samples have **Si-rich melt** with 70-98 wt.% SiO<sub>2</sub>

120 minutes

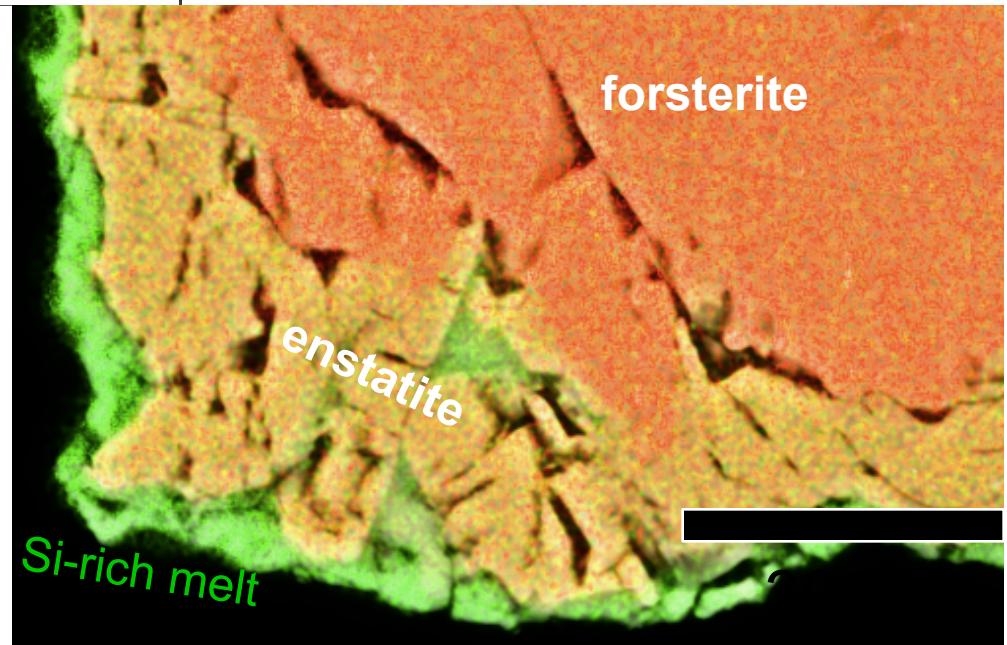


# Application to chondrules and refractory forsterite

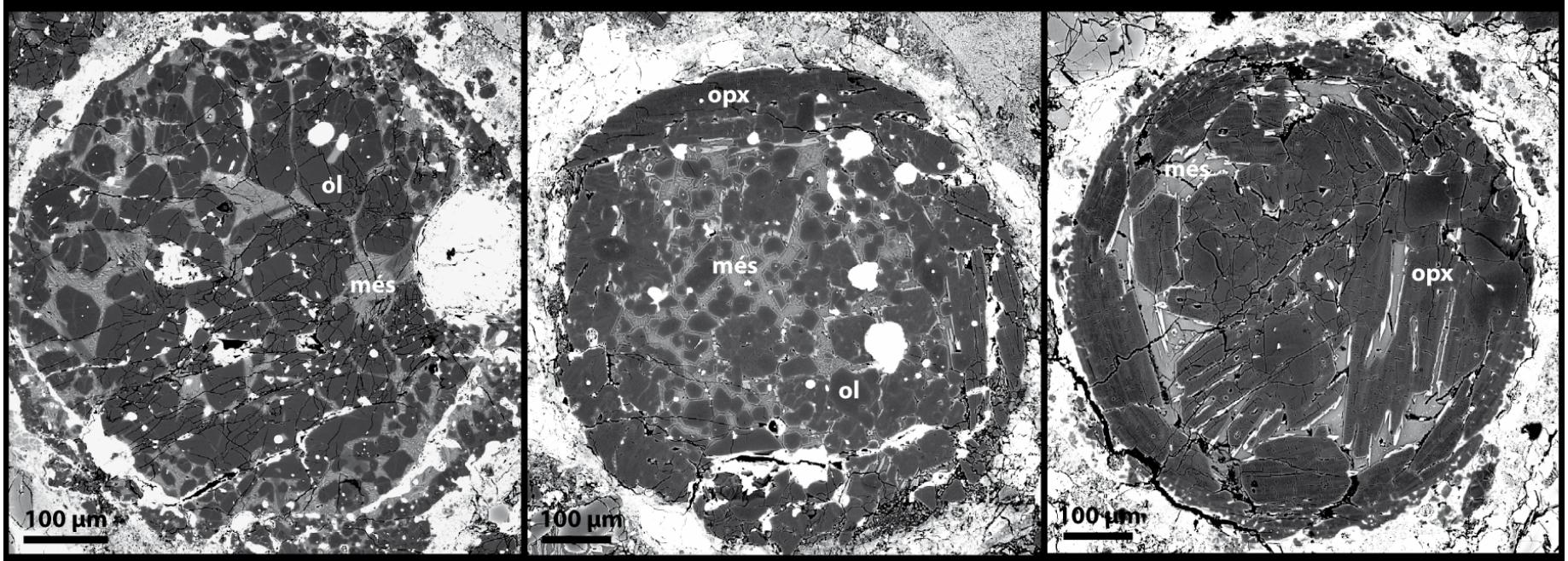


Enstatite replaces olivine!  
(enstatite is not condensed)

120 minutes



# Chondrule formation process



Sem-Ch2  
type I PO

(SiO<sub>2</sub> = 54,44%; Na<sub>2</sub>O = 1,31%; K<sub>2</sub>O = 0,07%)

Sem-Ch8  
type I POP

(SiO<sub>2</sub> = 61,47%; Na<sub>2</sub>O = 5,16%; K<sub>2</sub>O = 0,59%)

Sem-Ch10  
type I PP

(SiO<sub>2</sub> = 65,58%; Na<sub>2</sub>O = 6,19%; K<sub>2</sub>O = 0,59%)

-

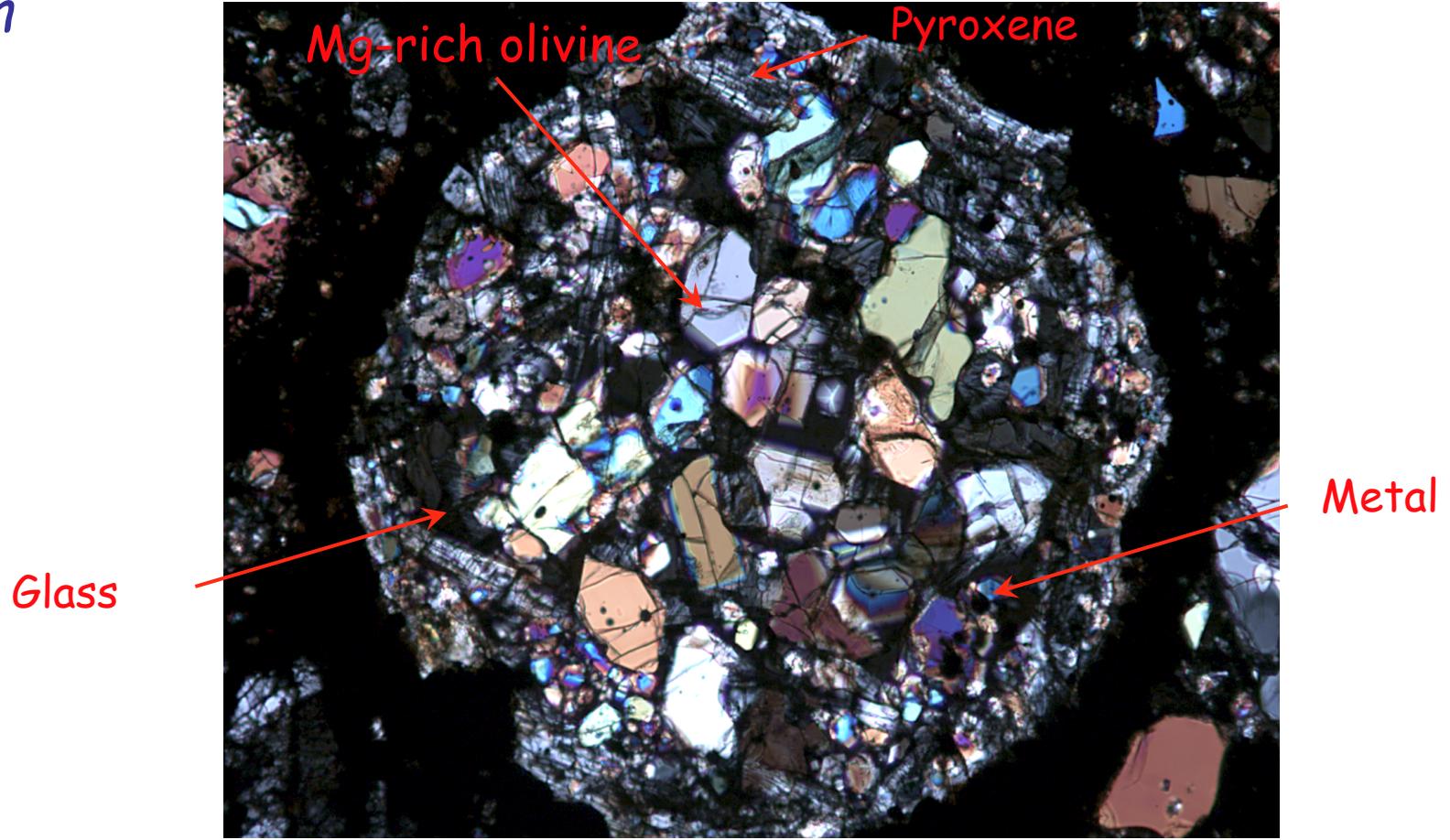


+

Gas-melt interactions

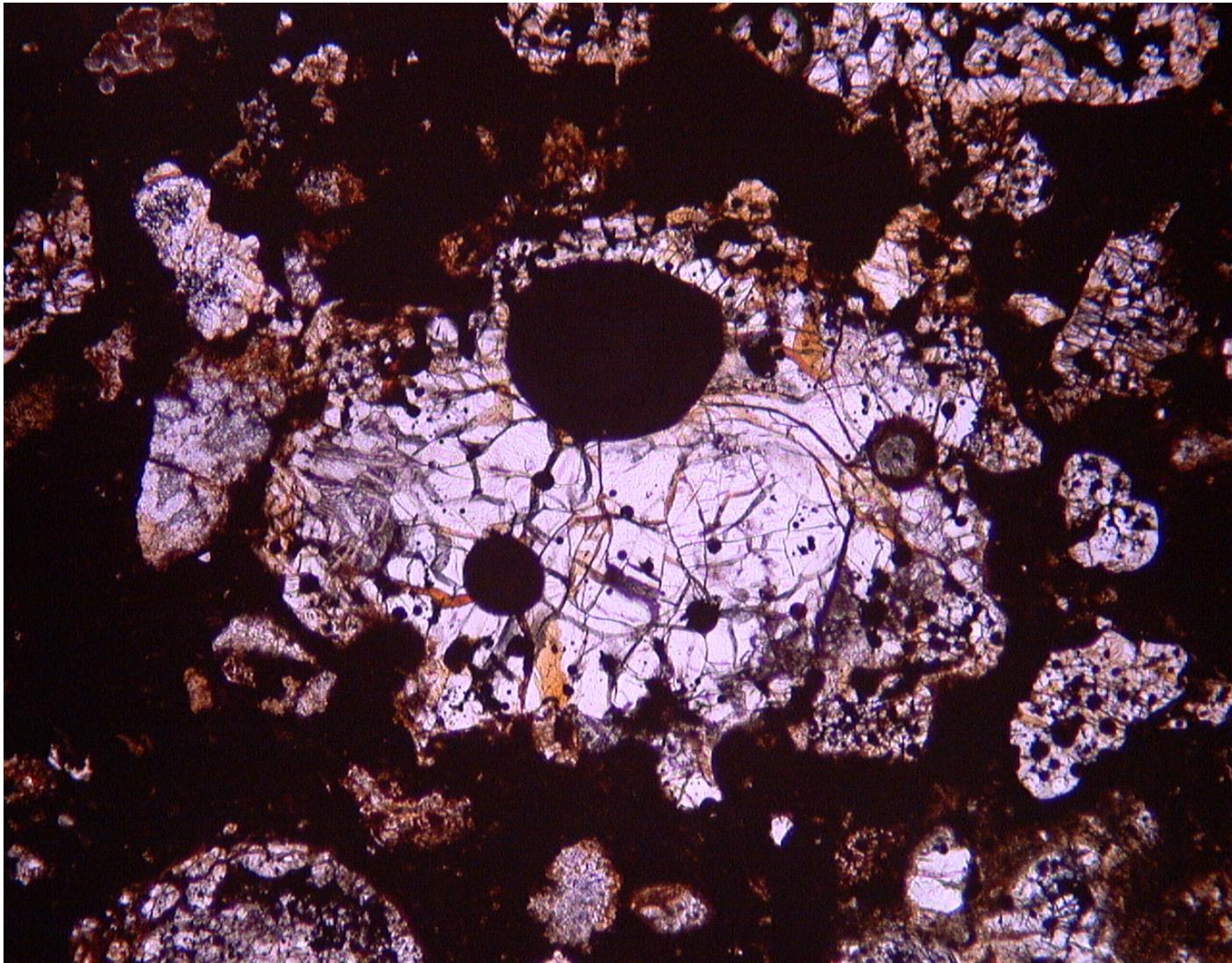
(e.g. Tissandier et al., 2002; Krot et al., 2004; Libourel et al., 2003, 2006; Chaussidon et al. 2008)

# Plan



- Evidence for interaction with gas phase
- Mg-rich olivines from differentiated planetesimals?
- Constraints on the formation of chondrules

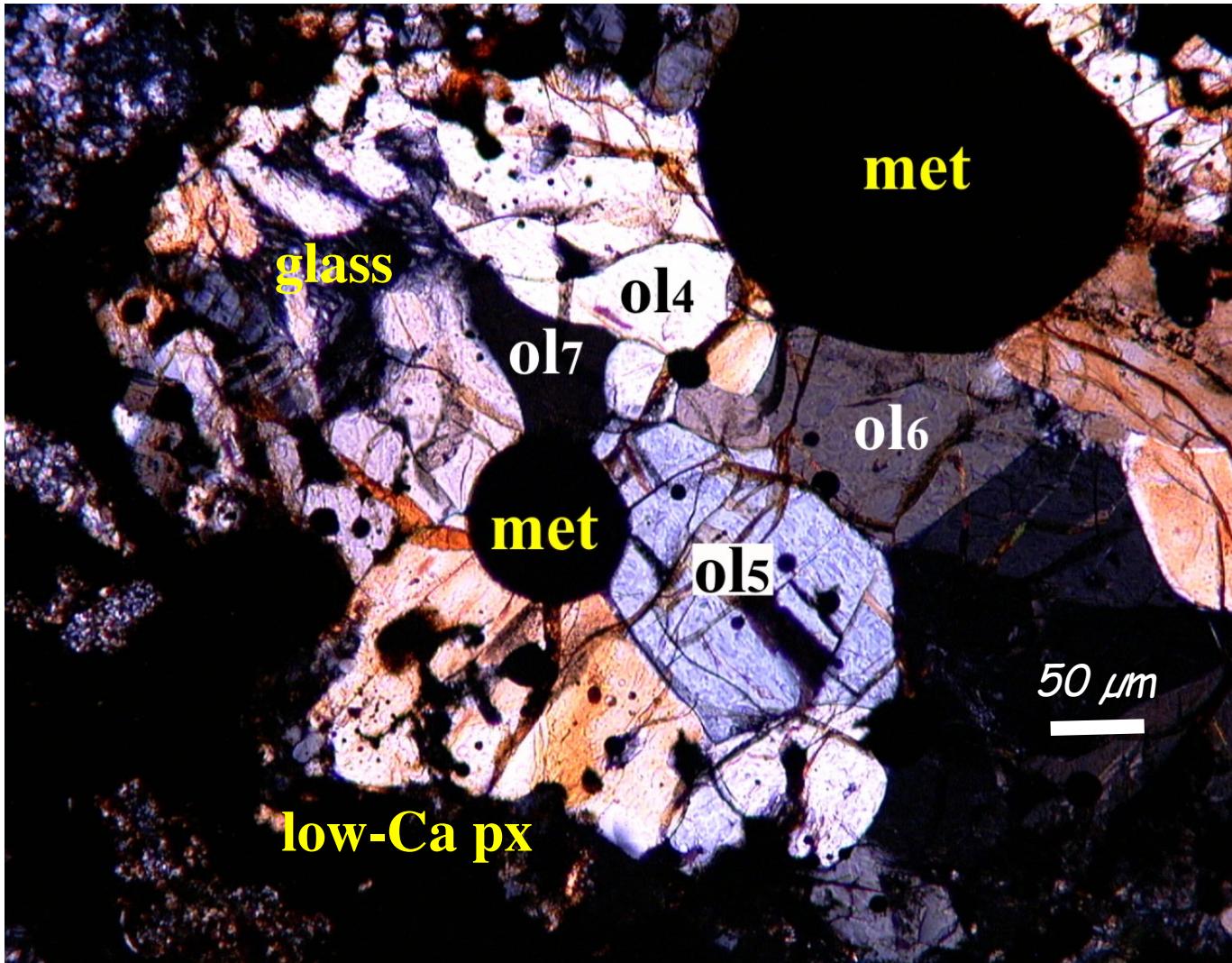
# *Chondrule #2 Vigarano (PO)*



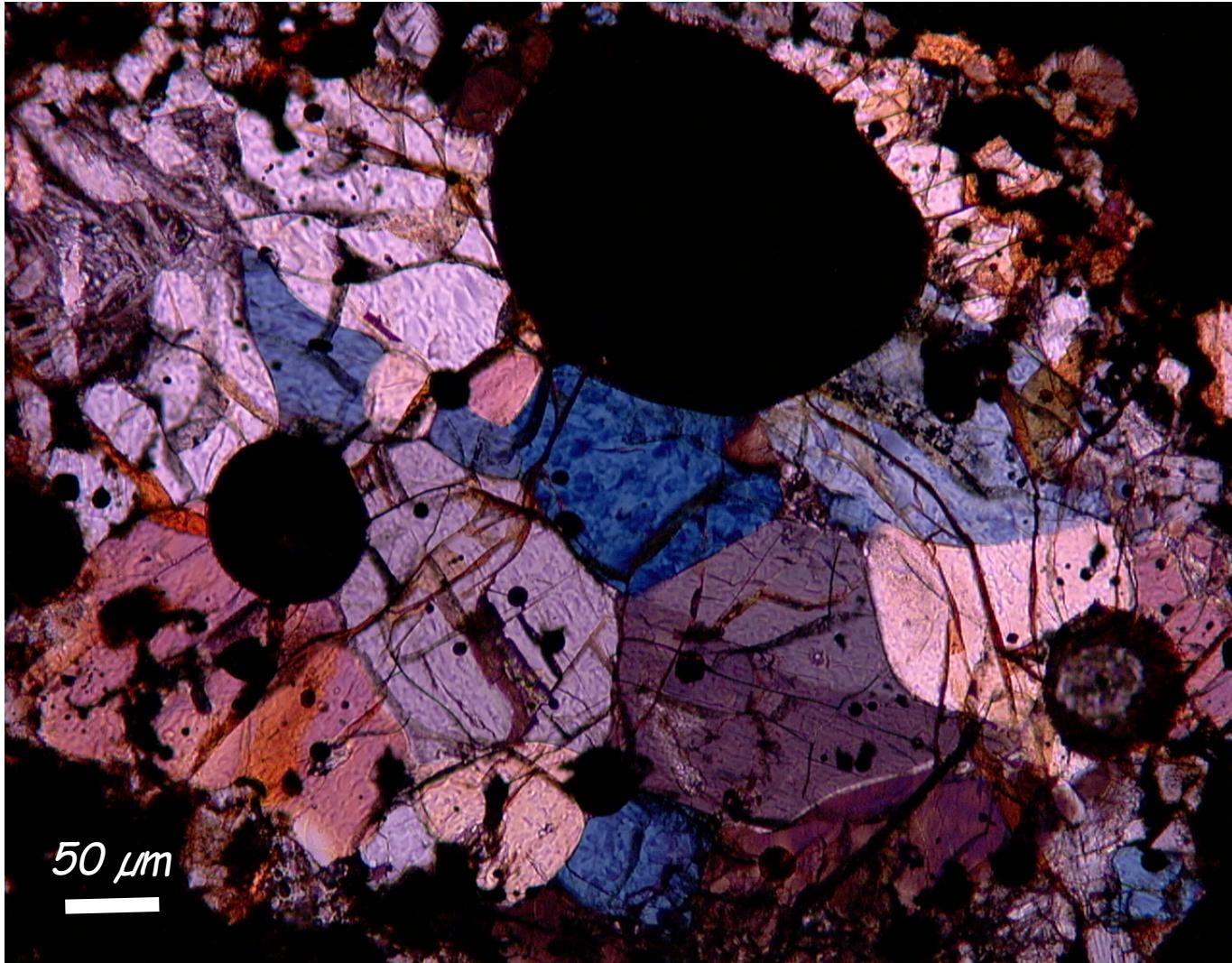
*Transmitted light*

Libourel & Krot, 2007

## *Chondrule #2 Vigarano*



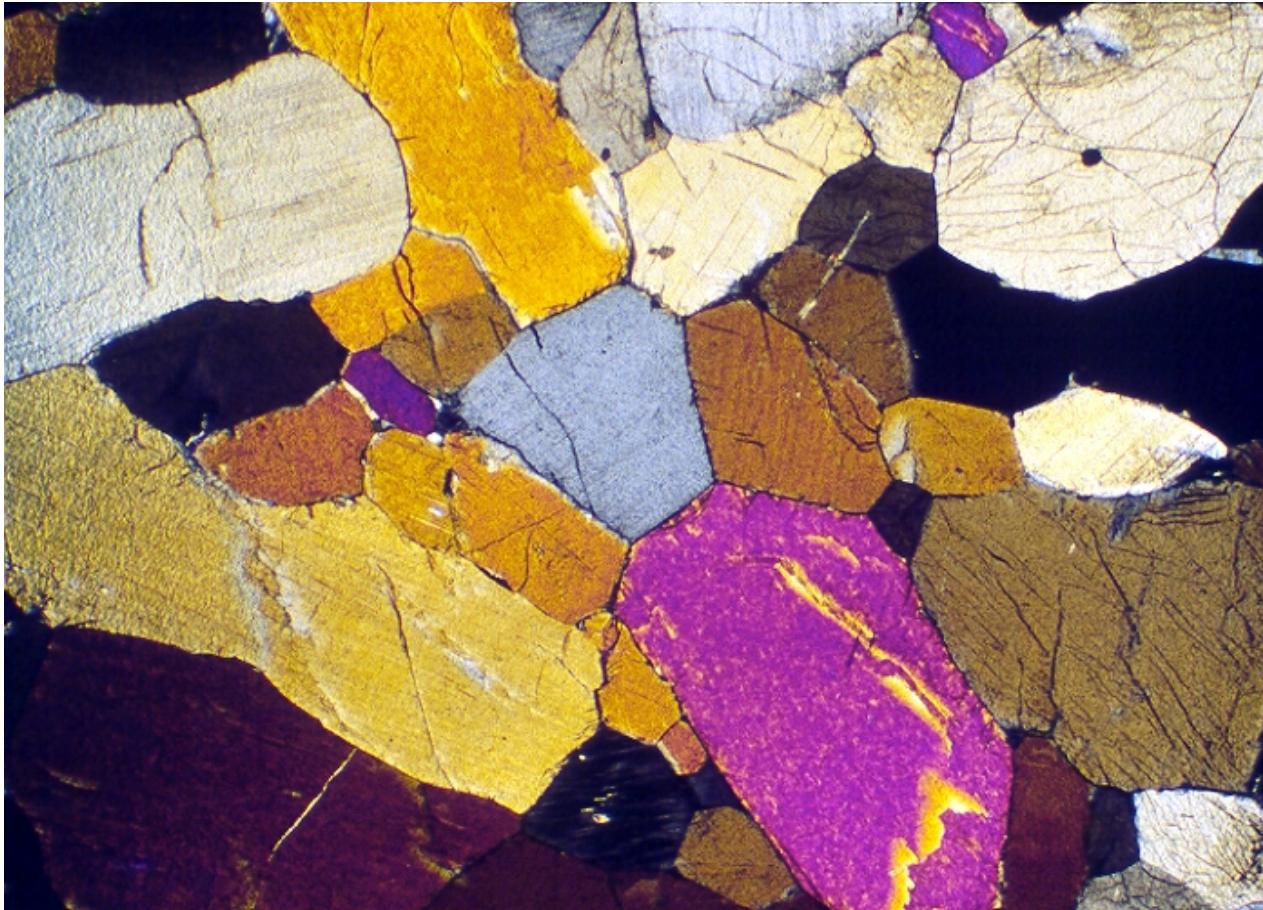
# Chondrule #2 Vigarano (PO)



$\langle \text{ol}-\text{ol}-\text{ol} \rangle$  triple junctions

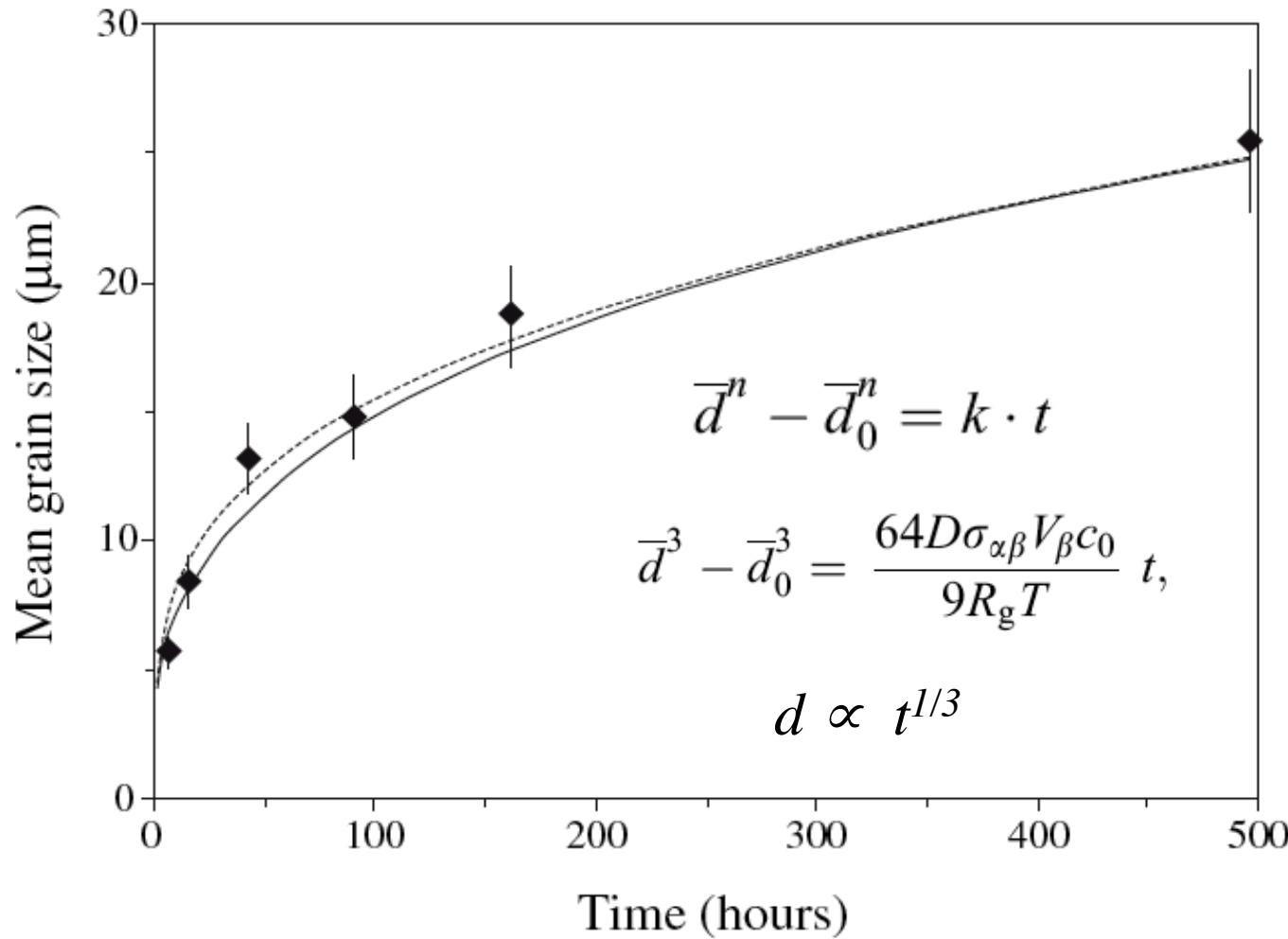
*Triple junctions indicate equilibrium textures*

Earth mantle peridotite



*Such textures (sintering and annealing) can not be produced by crystallization from chondrule melts but could have been achieved on differentiated parent bodies.*

# Crystal growth: oswald ripening



Cabanne et al. 2005; Faul & Scott, 2006

## *Ostwald ripening*

$$\bar{d}^3 = 36.1 \ t + 13.4$$

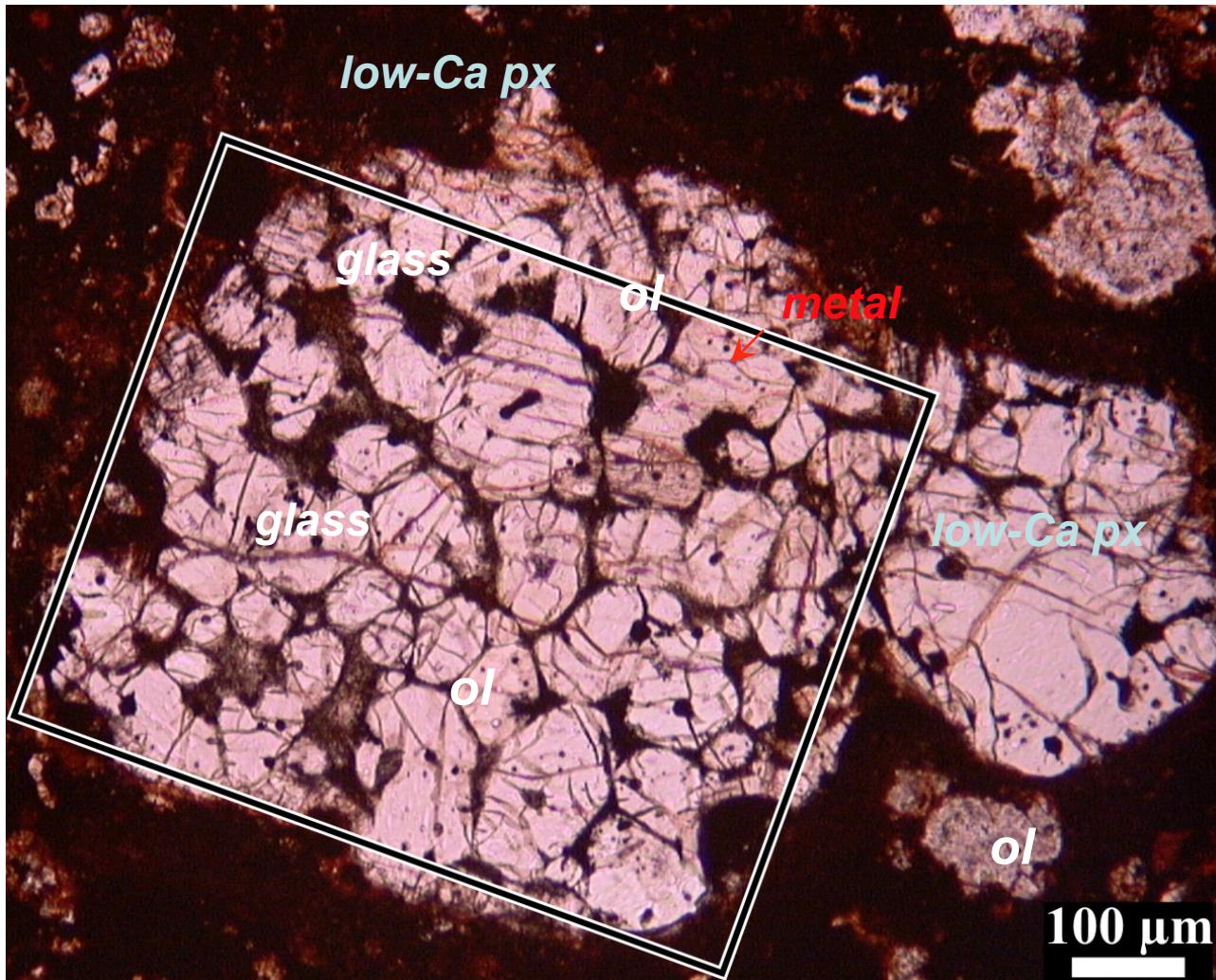
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Duration (Years)	Mean grain size ( $\mu\text{m}$ )
<hr/>	
	Olivine <sup>a</sup>
1	$68 \pm 10$
10	$147 \pm 21$
1,000	$680 \pm 100$
$10^5$	$3160 \pm 460$

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Cabanne et al. 2005; Faul & Scott, 2006

## *Chondrule #3 Vigarano (POP)*



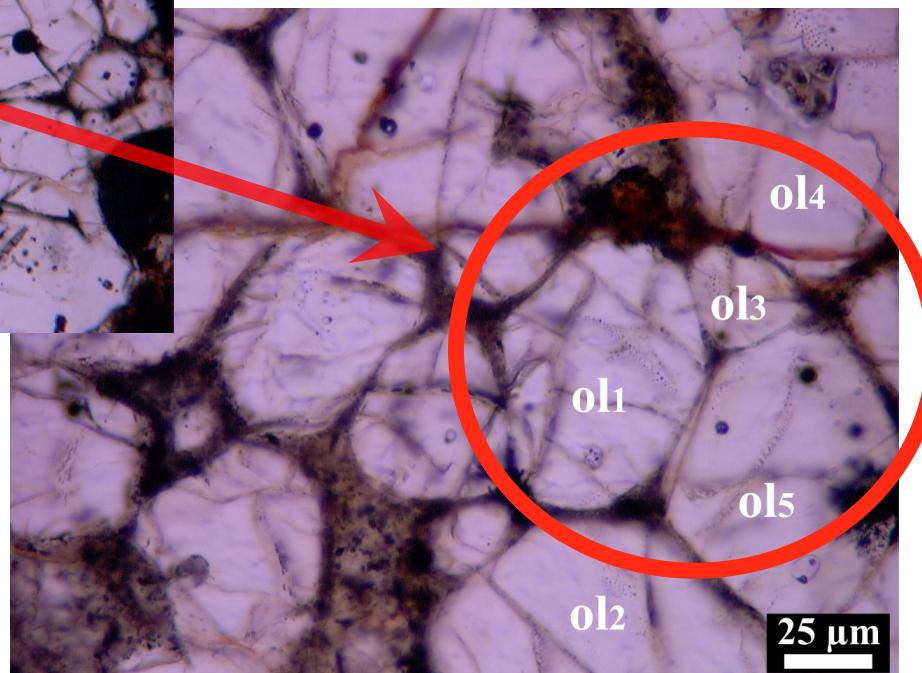
*Transmitted light*

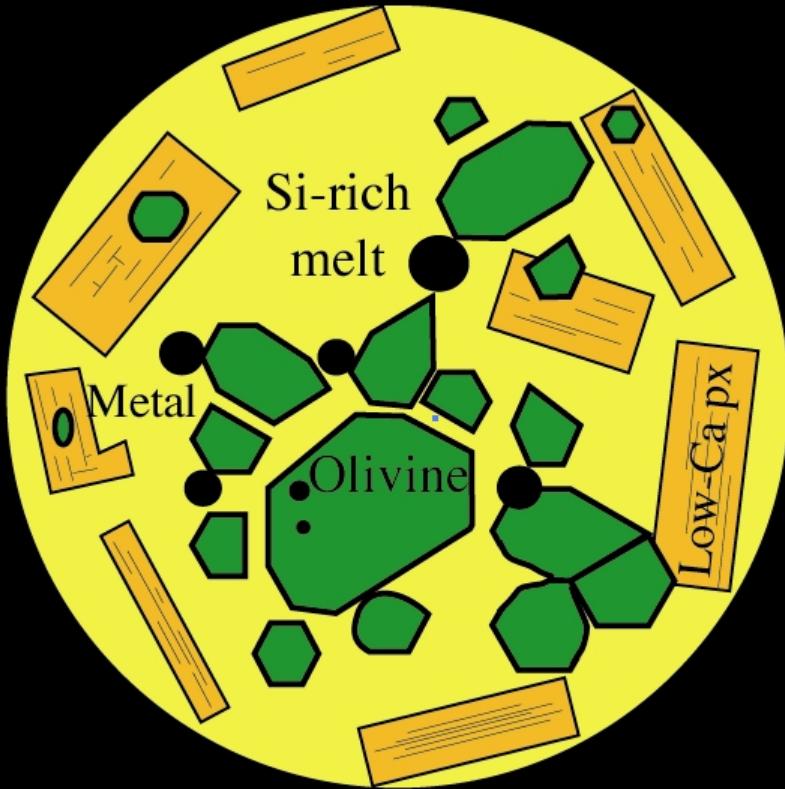
## *Chondrule #3 Vigarano (POP)*



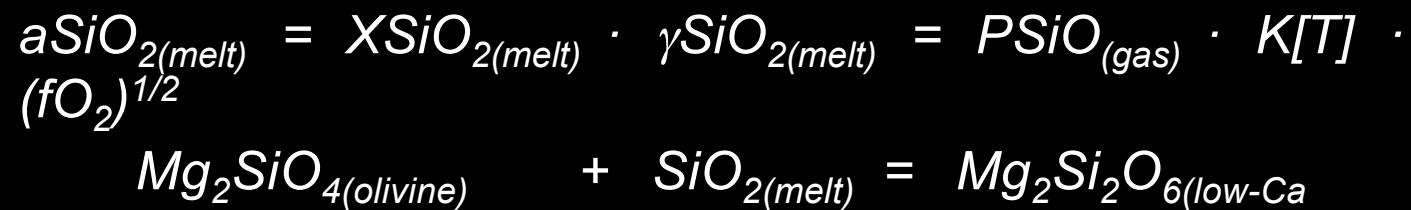
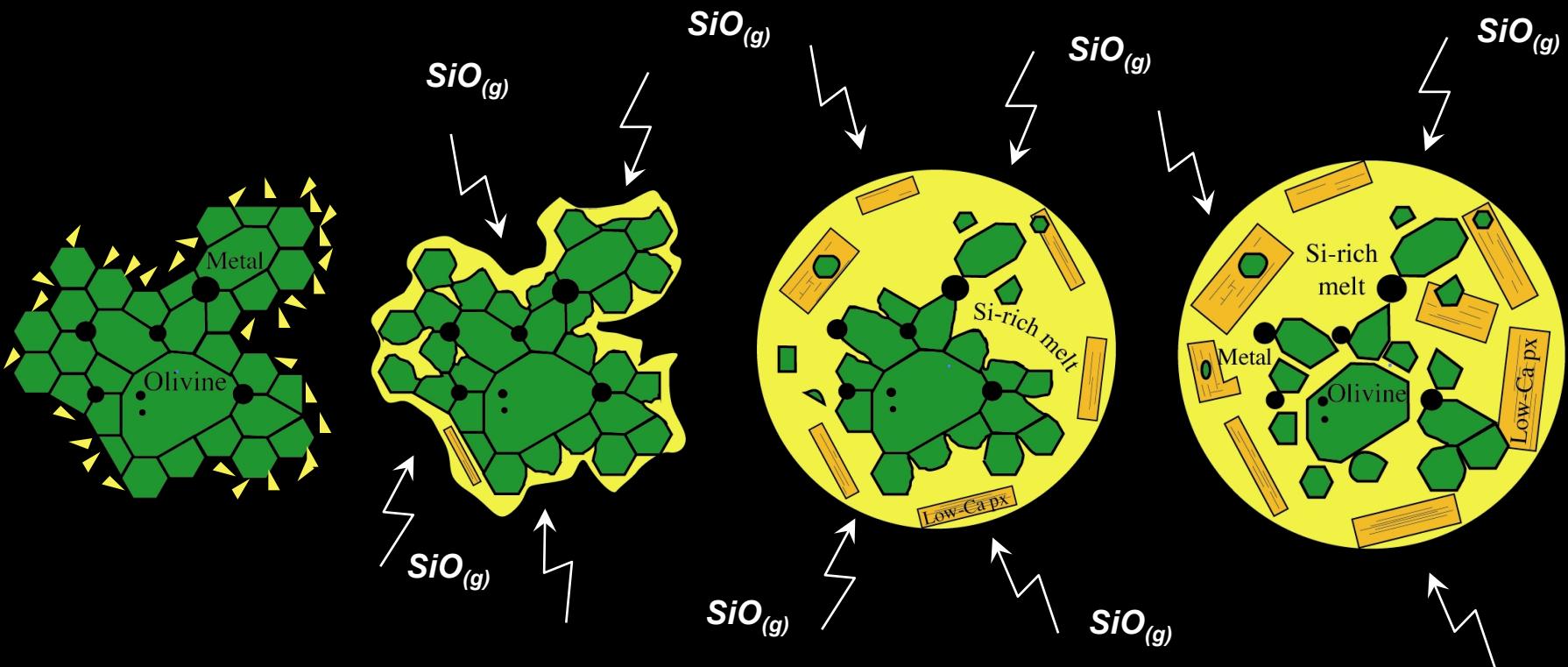
Olivine grains separated by glass  
have rounded outlines and  
embayments, indicating dissolution.

*Olivines with triple junctions.*

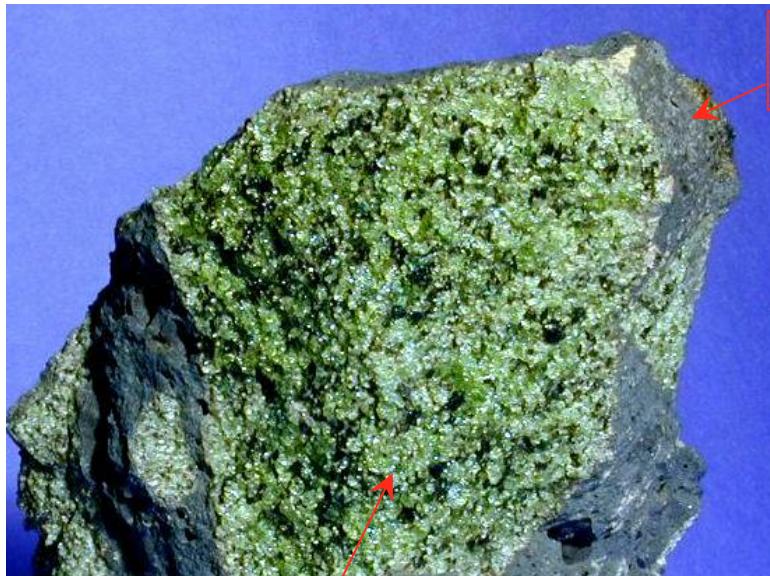




## Magnesian chondrule formation



## Terrestrial analogy



basalt = liquid

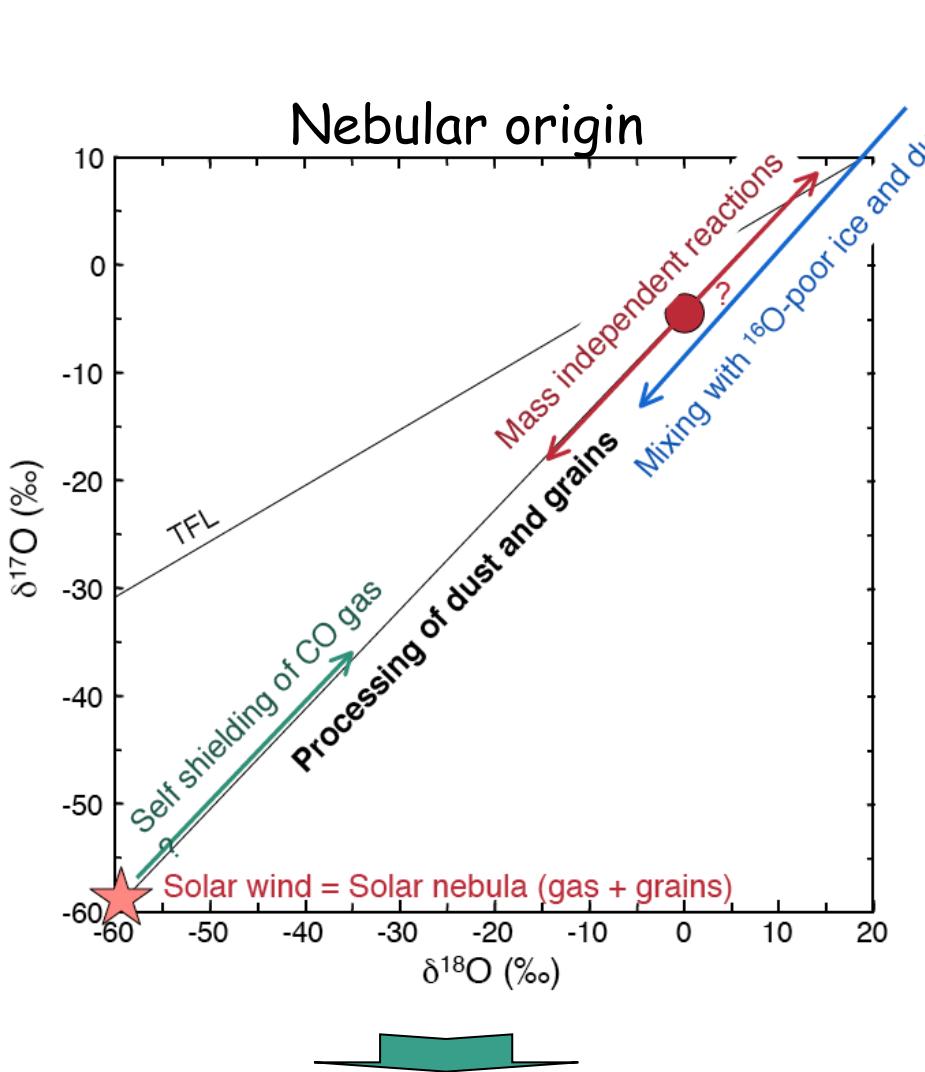
xenolith = mantle

Mg-rich olivines in chondrules:  
- xenocrysts (isolated grains)  
- xenoliths (fragment)

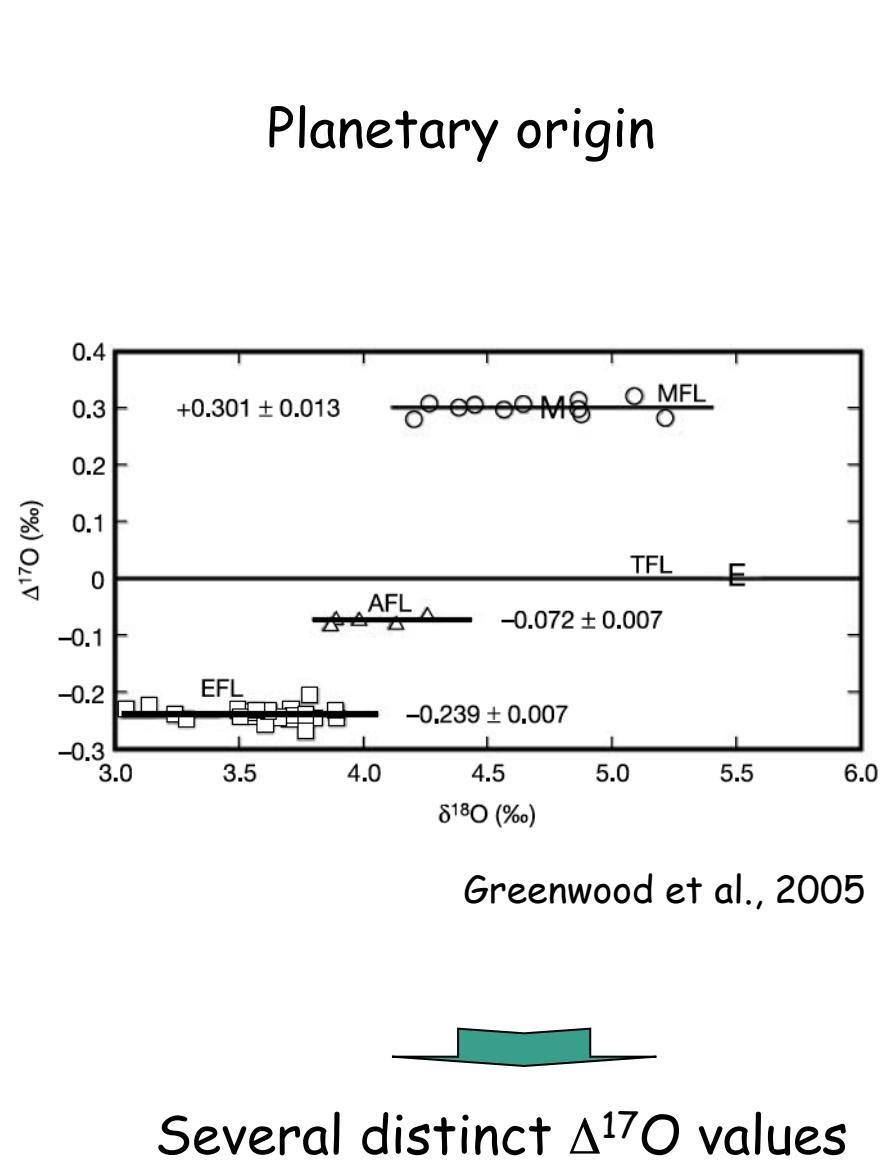


San Carlos, AZ/ USA

## Two very different predictions for the distribution of $\Delta^{17}\text{O}$ values of Mg-rich olivines depending on their origin

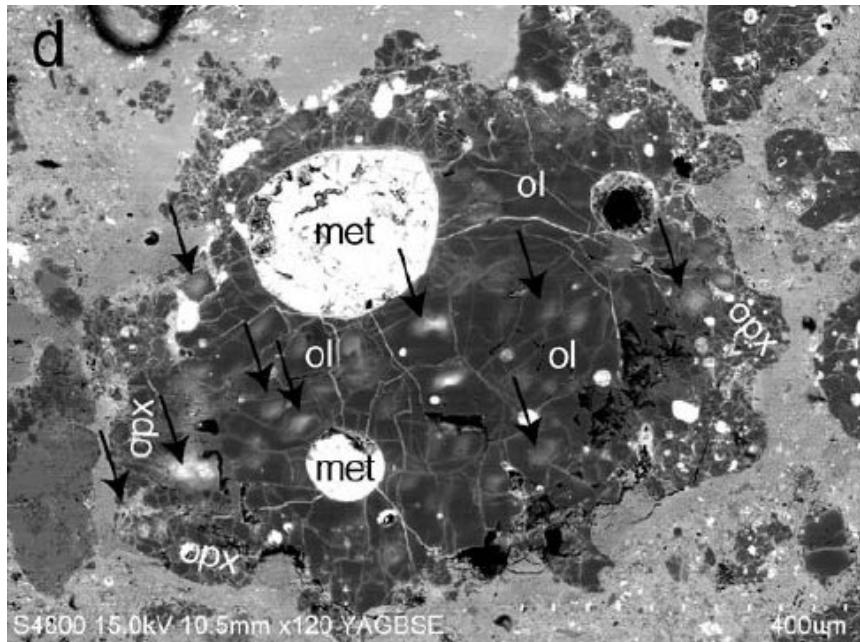


$\approx$  Continuum of  $\Delta^{17}\text{O}$  values

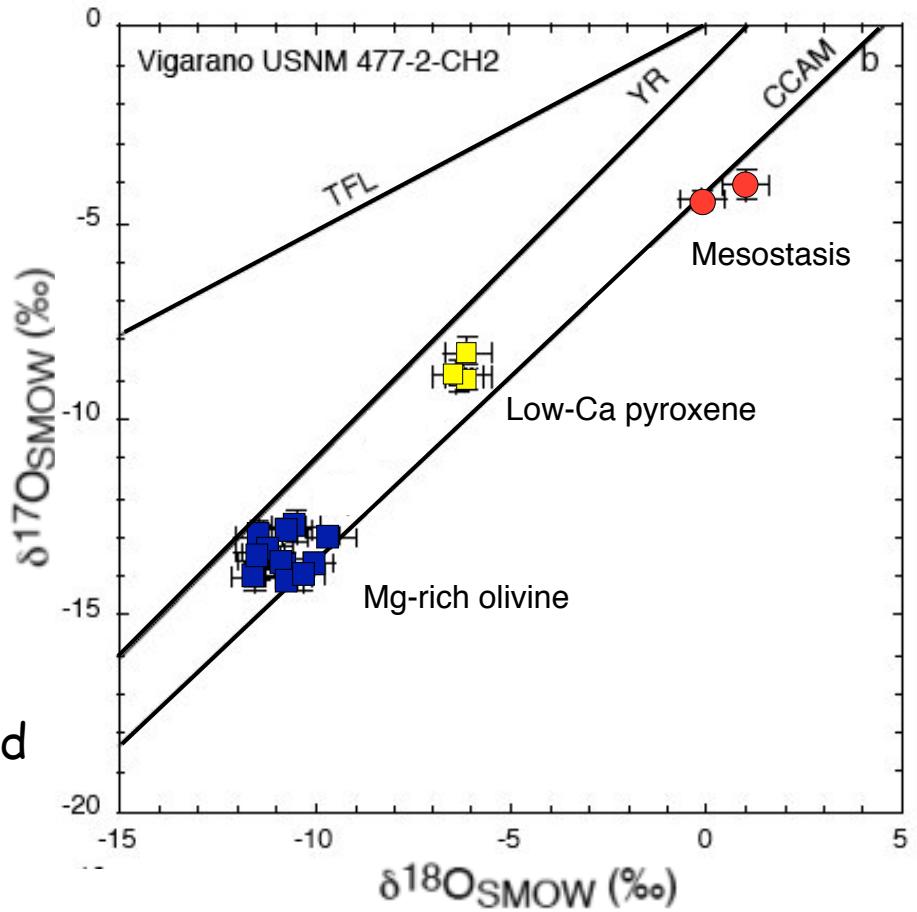


Several distinct  $\Delta^{17}\text{O}$  values

## Mg-rich olivines aggregates: Oxygen isotopic compositions



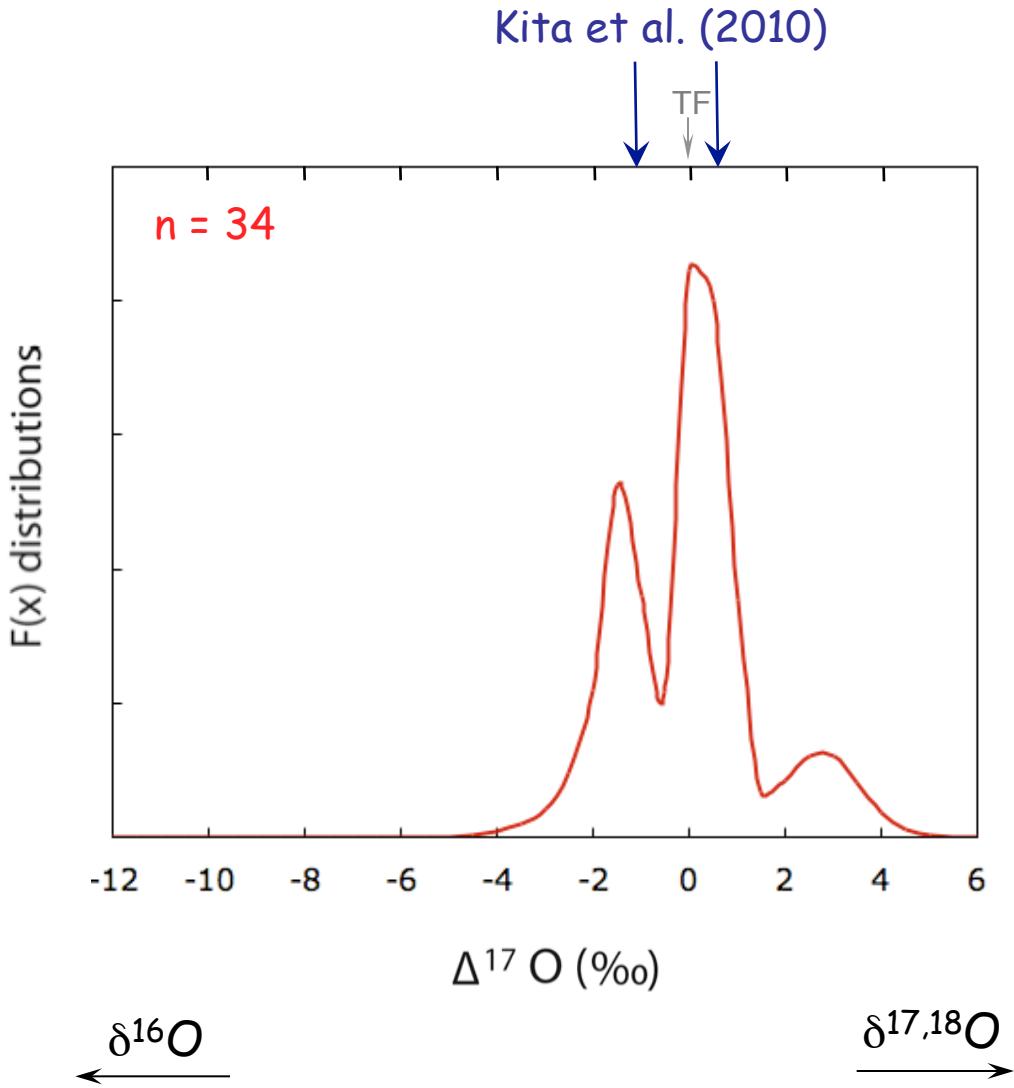
Mg-rich olivines within coarse-grained aggregates are in isotopic disequilibrium with pyroxene and mesostasis.



Chaussidon et al., 2008

Mg-rich olivines preserved their pristine oxygen isotopic composition even if they underwent partial dissolution (consistent with oxygen diffusion).

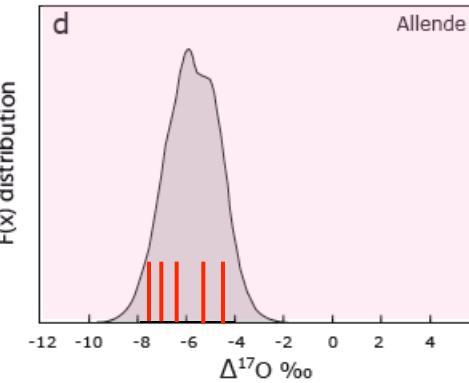
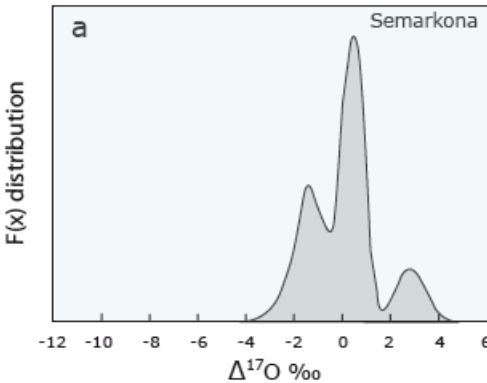
# Mg-rich olivines in type I chondrules of Semarkona LL3.0



- No continuum of  $\Delta^{17}\text{O}$  values
- 3 discrete  $\Delta^{17}\text{O}$  ( $\pm 0.5\text{\textperthousand}$ ) modes
- 2 modes are consistent with Kita et al. 2010.

# Mg-rich olivines in type I chondrules

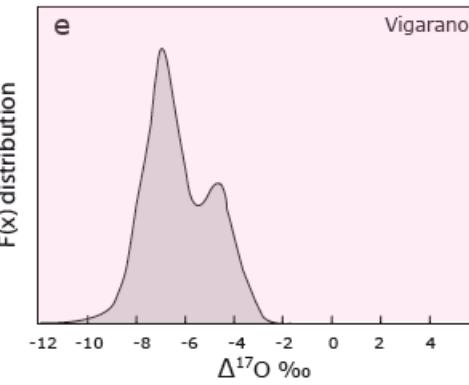
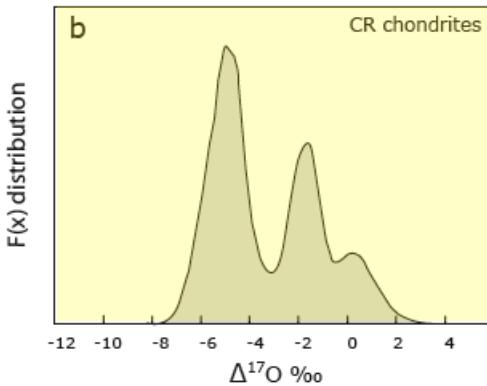
OC



CV

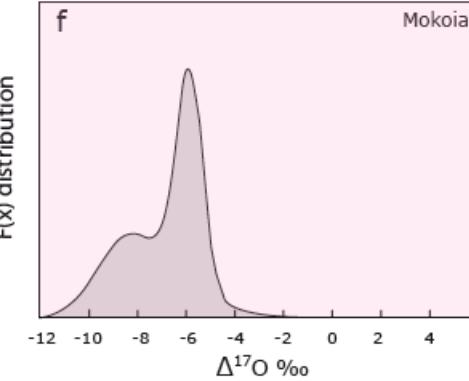
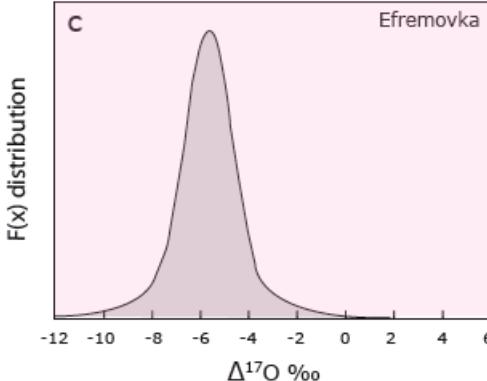
Chaussidon et al. MetSoc 2010

CR



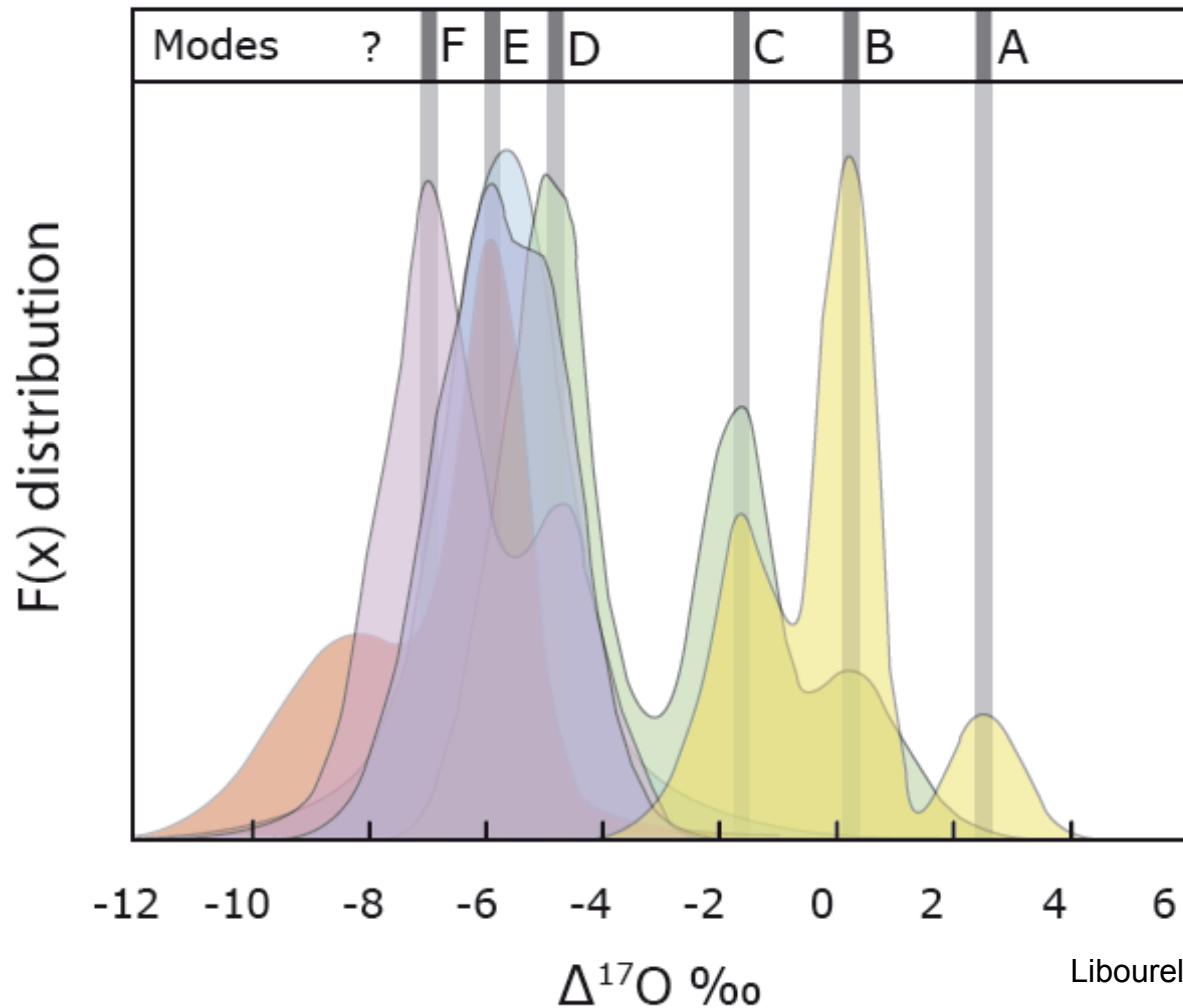
CV

CV



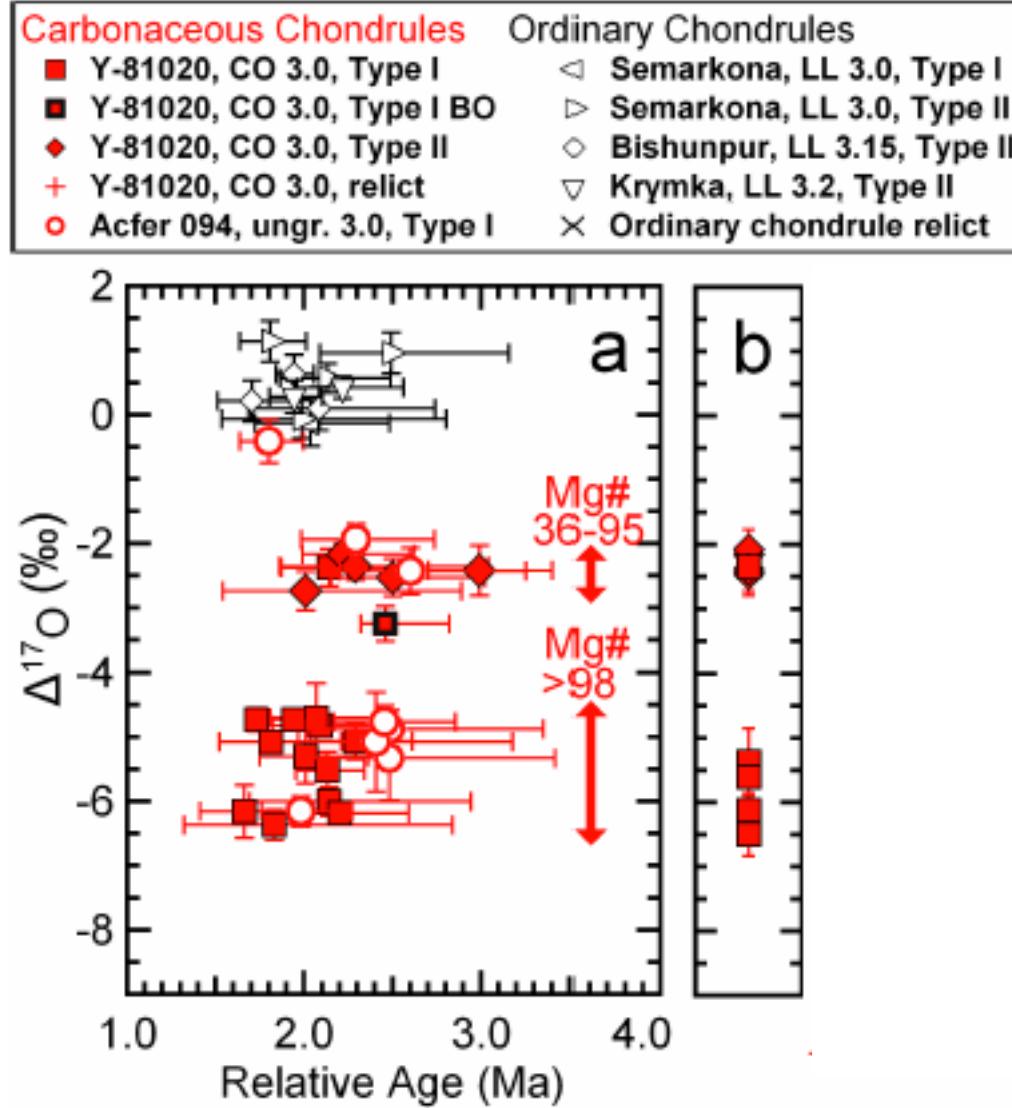
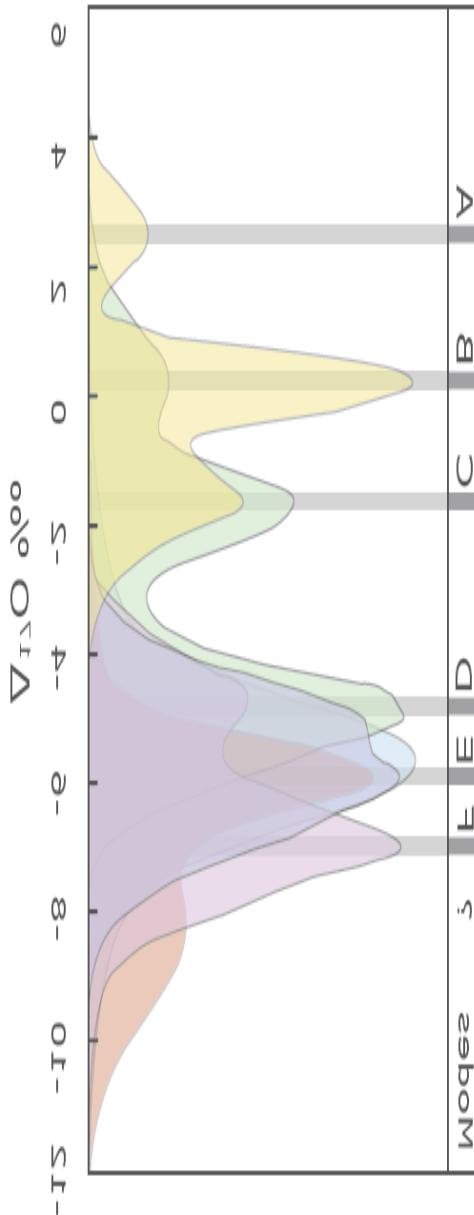
CV

# Mg-rich olivines in type I chondrules



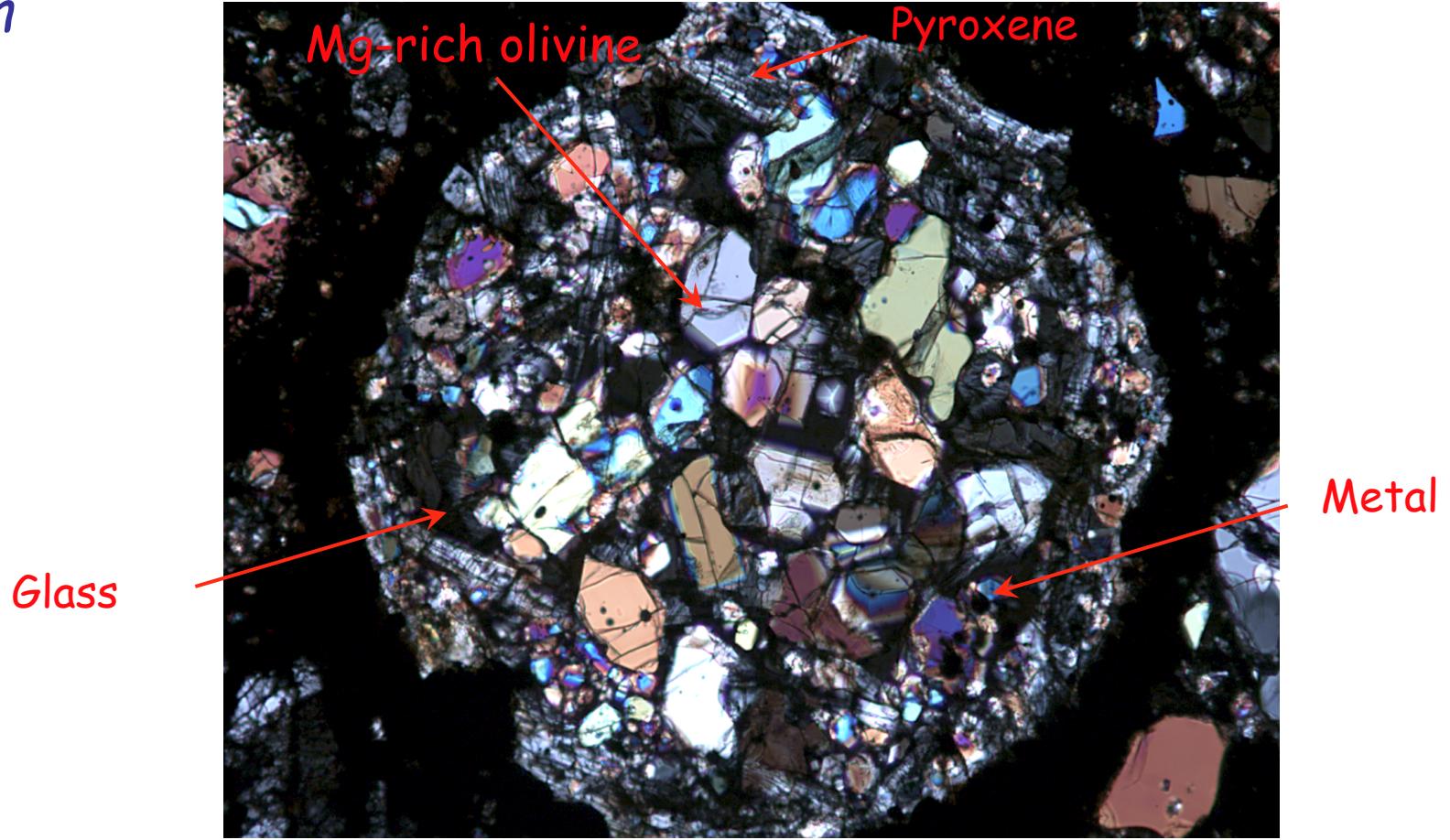
Mg-rich olivines originating from the disruption of the mantles of differentiated planetesimals

# Mg-rich olivines in type I chondrules



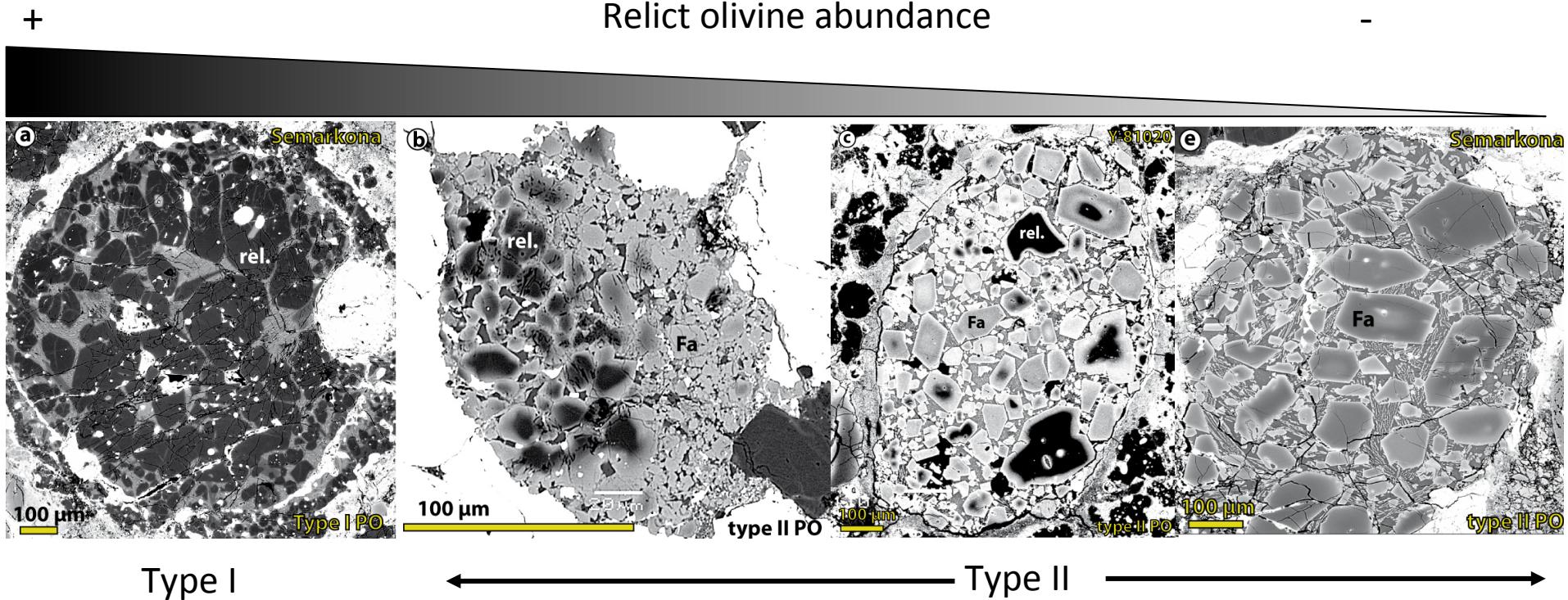
**Fig. 3:** a)  $\Delta^{17}\text{O}$  versus the  $^{26}\text{Al}$  age relative to CAI. Relative ages are from [2, 4, 5]. Chondrules from Y-81020 form 2

## Plan



- Evidence for interaction with gas phase
- Mg-rich olivines from differentiated planetesimals?
- Constraints on the formation of chondrules

- Type I and type II chondrules seem contemporaneous from  $^{26}\text{Al}$  chronology
- Type I and type II chondrules are both chondritic in bulk composition
- Type I-relict phases (forsterite, metal) are often occurring in type II chondrules

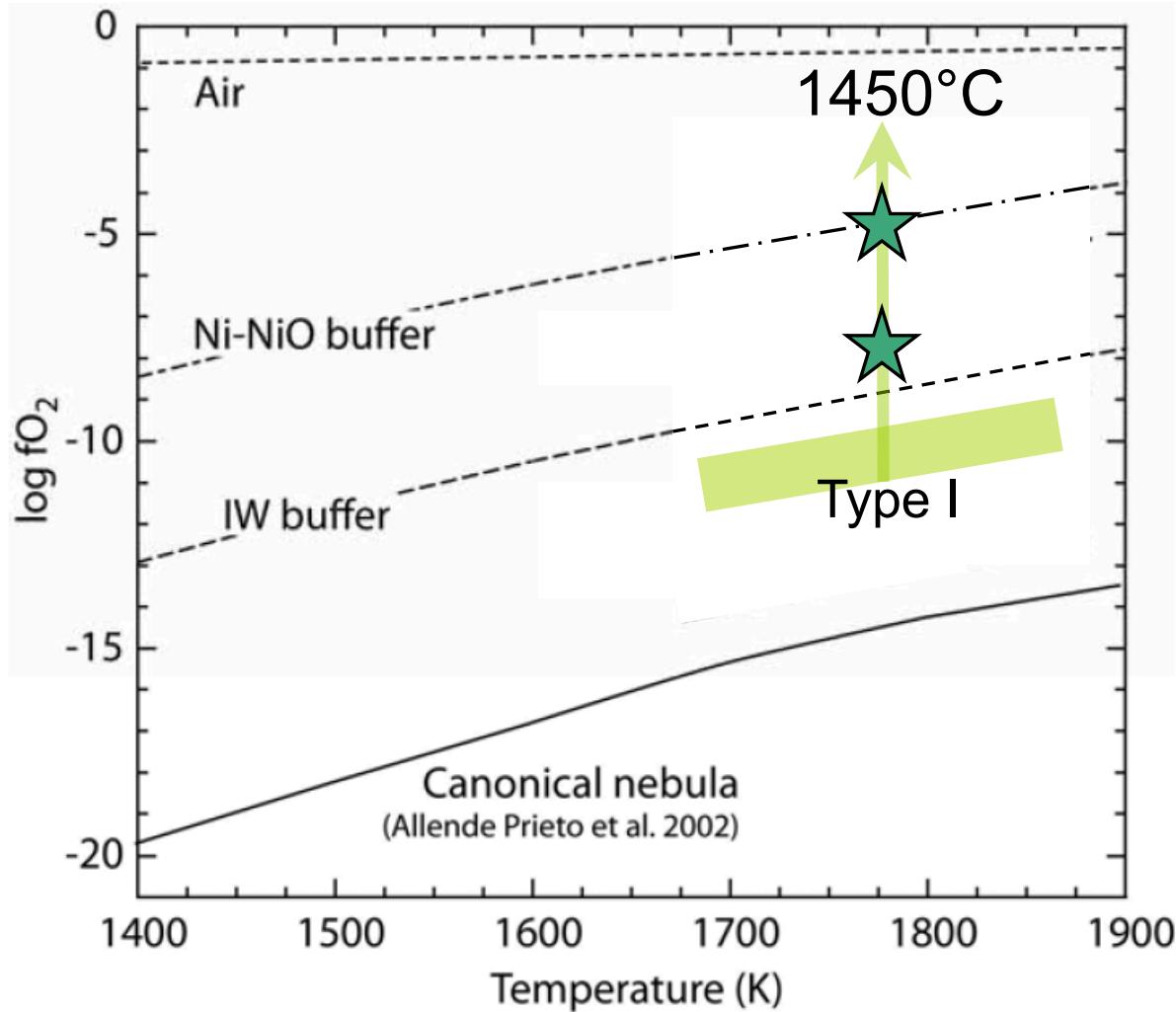


Can PO type I be transformed into type II by oxidation ?  
 (an alternative to classical dichotomy)

YES

(Villeneuve 2010)

## Isothermal oxidation experiments



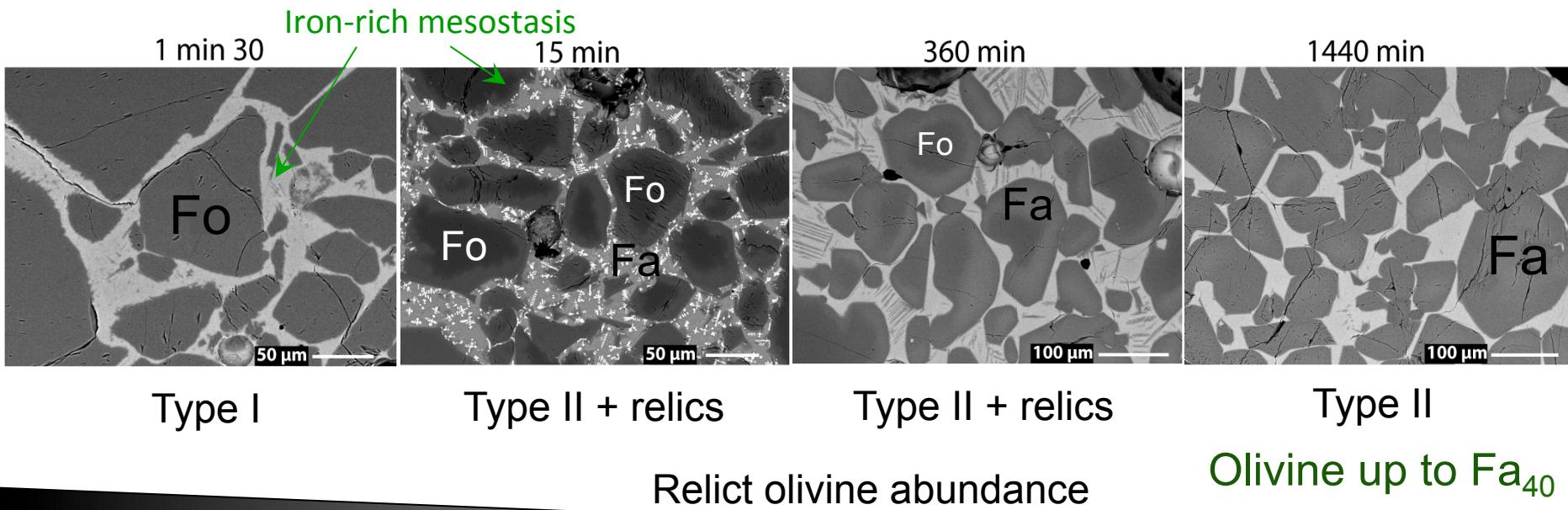
Type I proxy

Starting Composition: Forsterite + Ca, Al-rich glass + **0, 5, 10, 15, 20 wt% Fe metal**

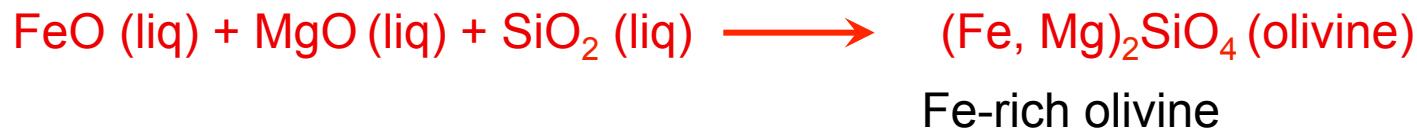
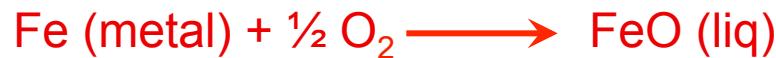
# Isothermal oxidation experiments

IW+1 (1450°C)

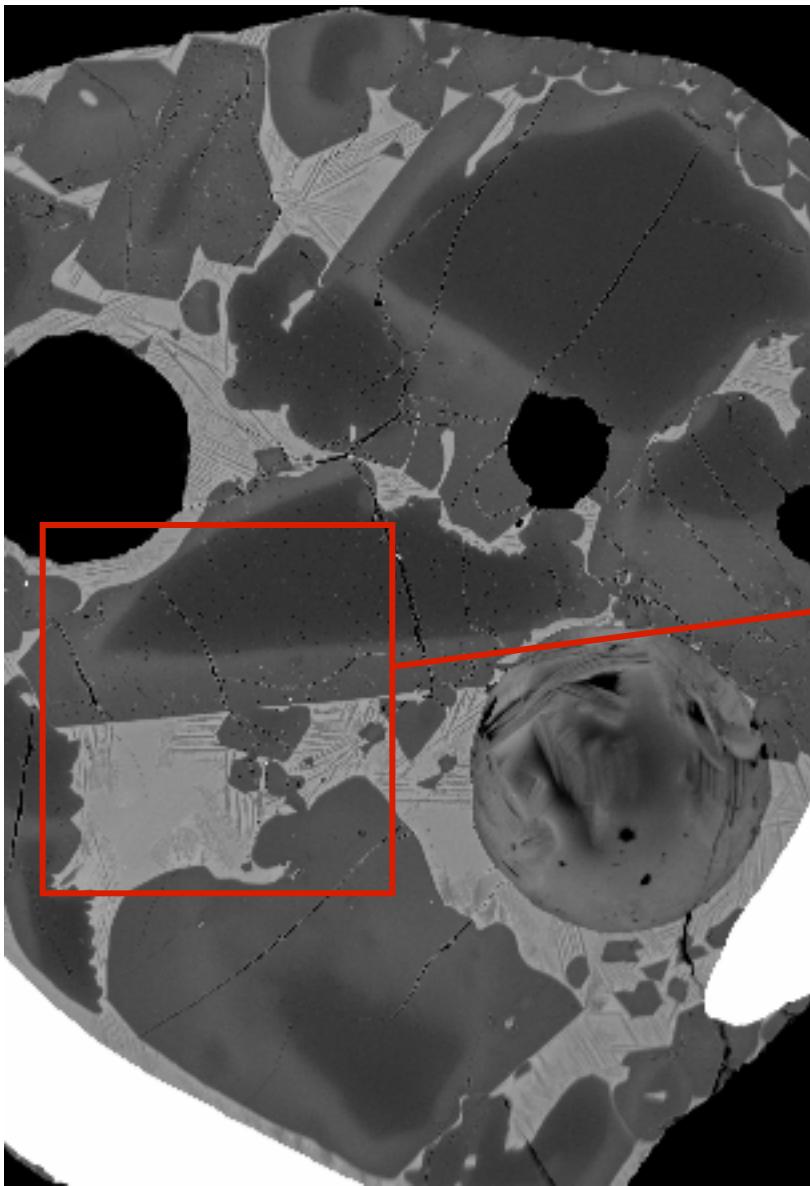
Start. Comp. 55 wt% Forsterite + 25 wt% Ca, Al-rich glass + **20 wt% Fe metal**



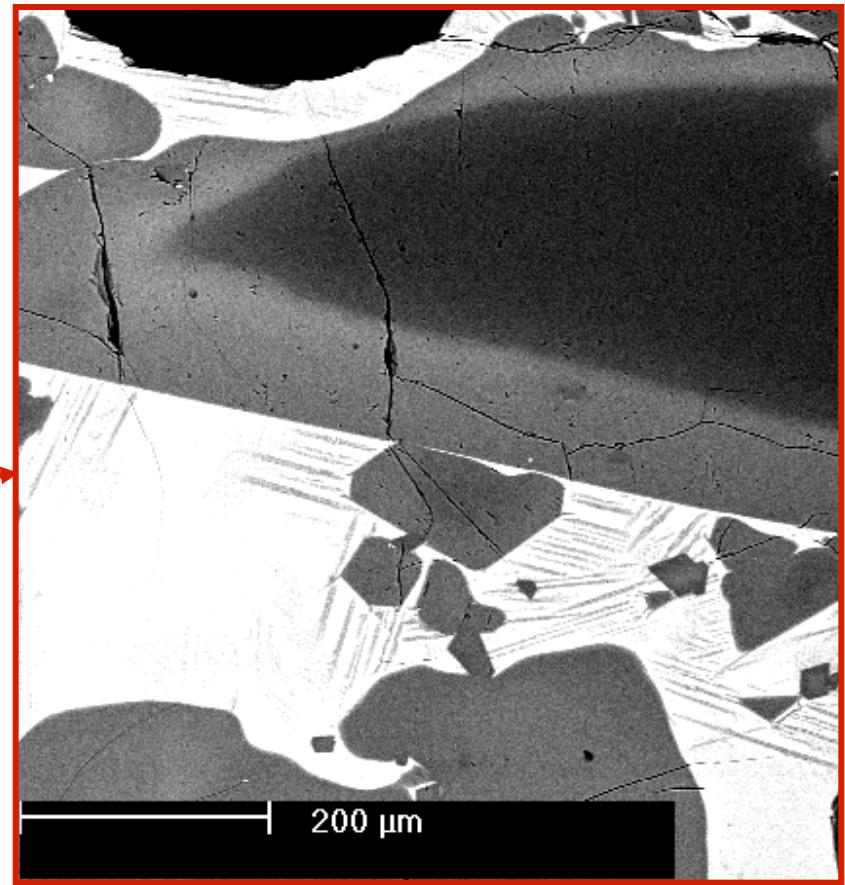
$$v = d\xi/dt = d\text{FeO}/dt = d(\text{Fe}, \text{Mg})_2\text{SiO}_4/dt$$



# Chemical evolution of olivines

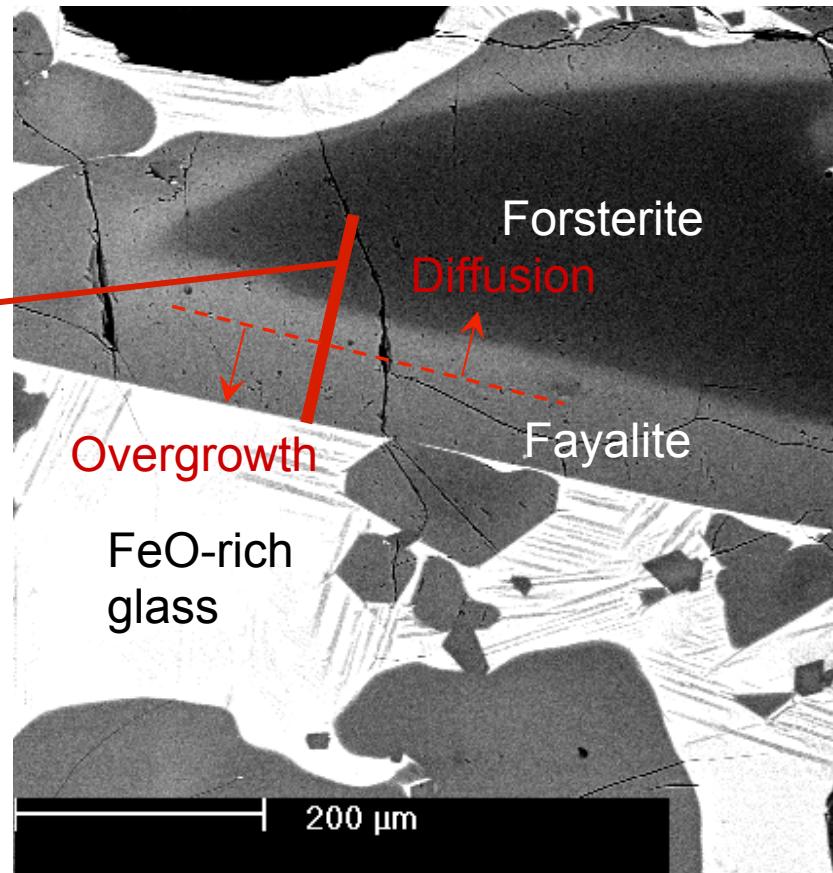
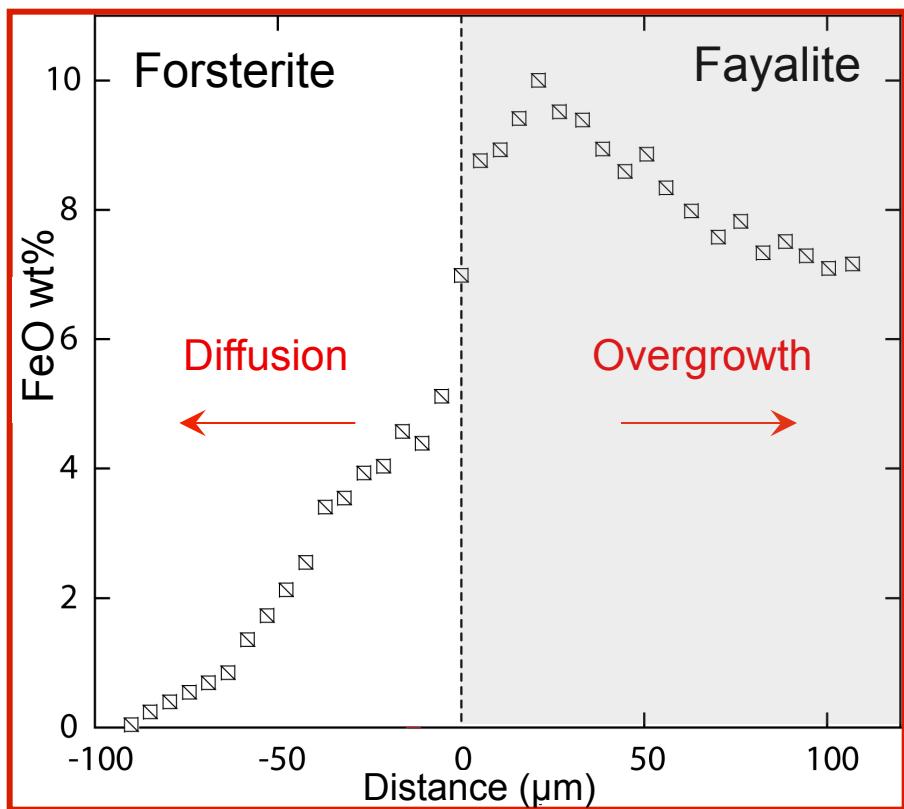


1450°C, IW +1, 24 hours



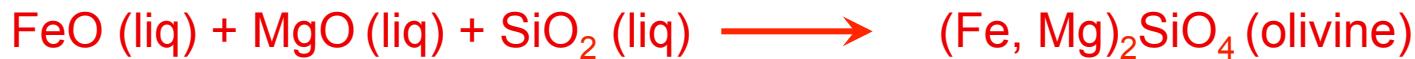
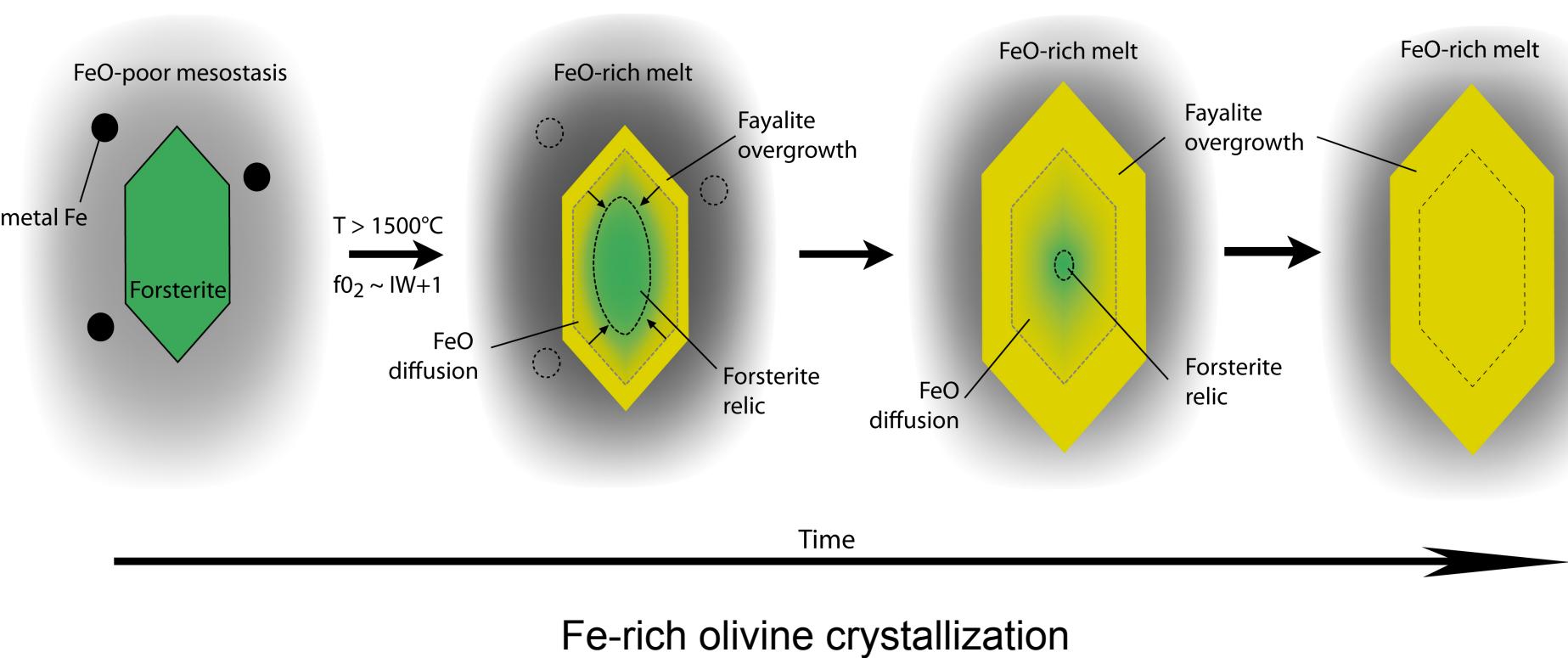
# Chemical evolution of olivines

1450°C, IW +1, 24 hours

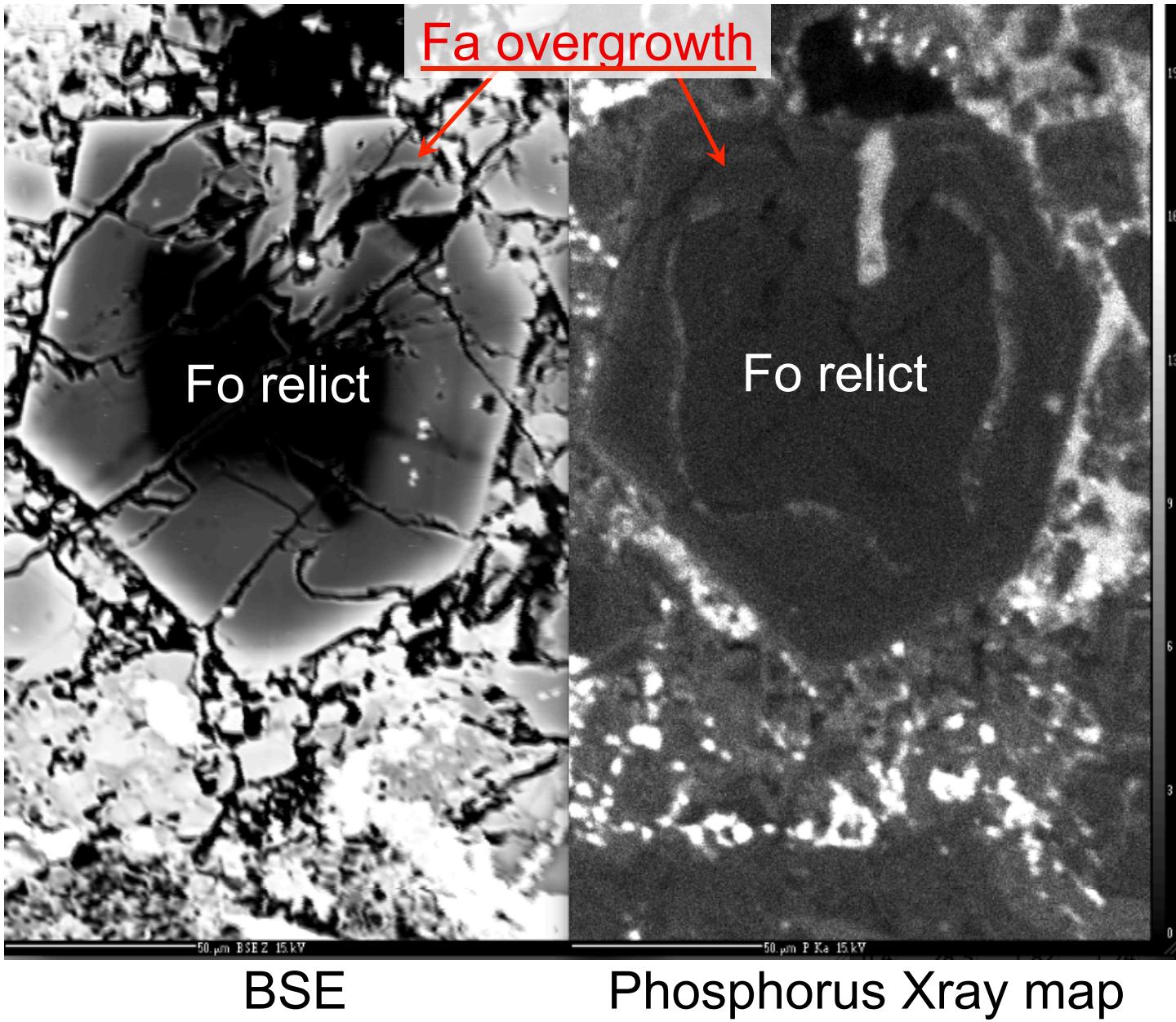


Driving force for overgrowth and diffusion =  $\Delta C$  (and not  $\Delta T$ )

# Chemical evolution of olivines

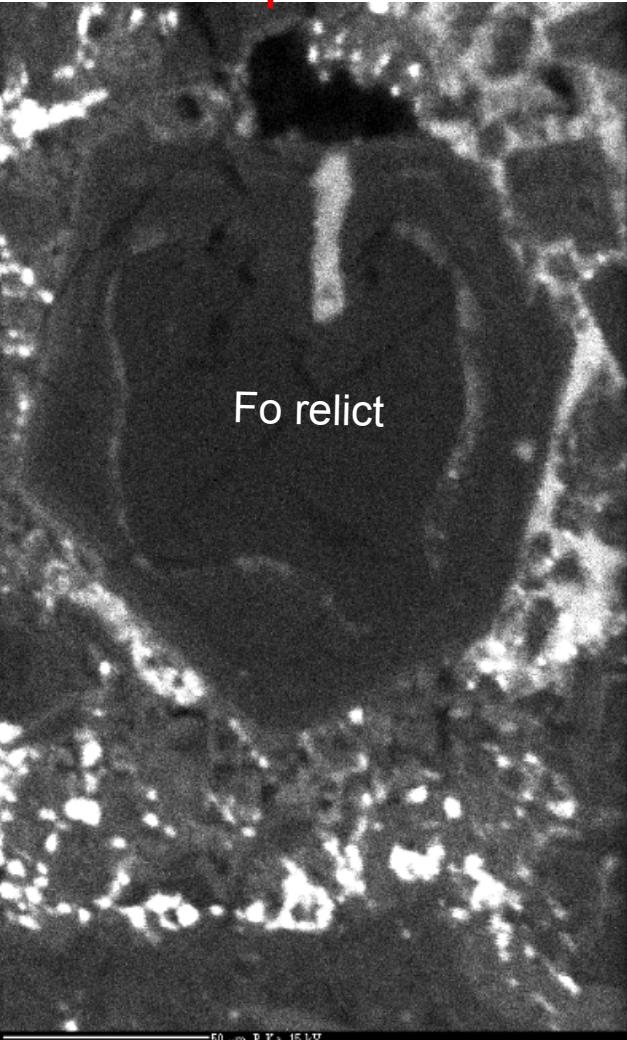


# Semarkona Type II PO chondrule

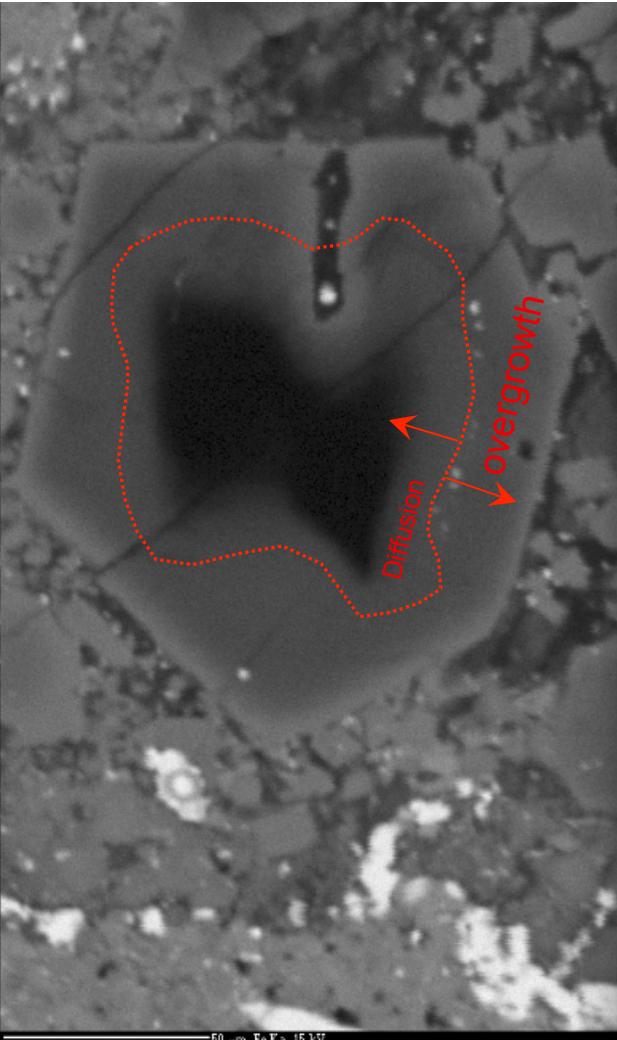


# Semarkona Type II PO chondrule

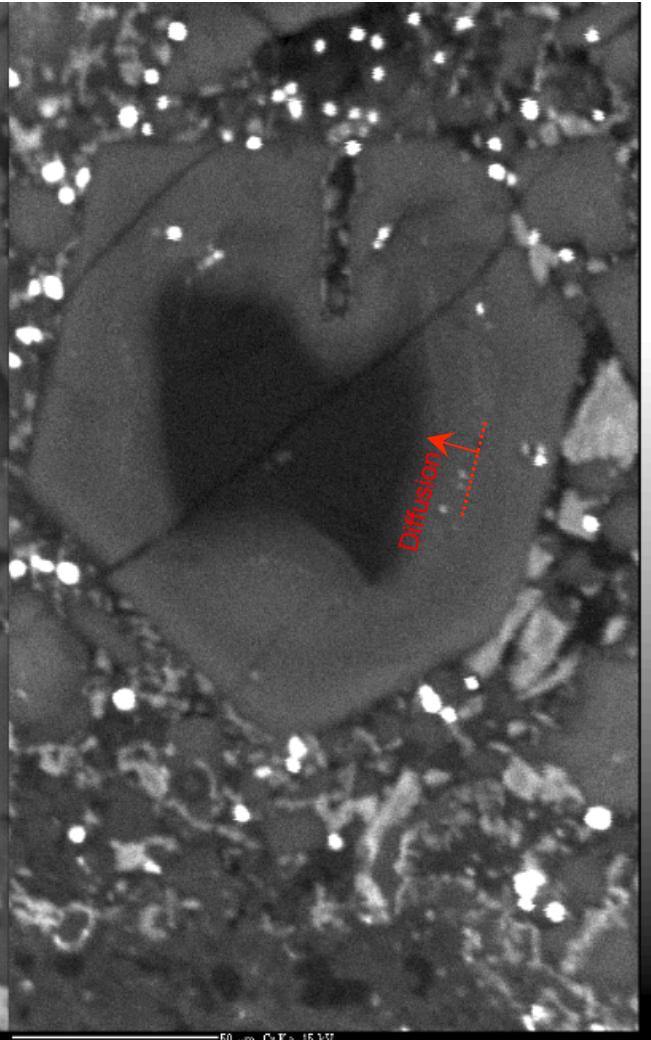
Phosphorus



Iron

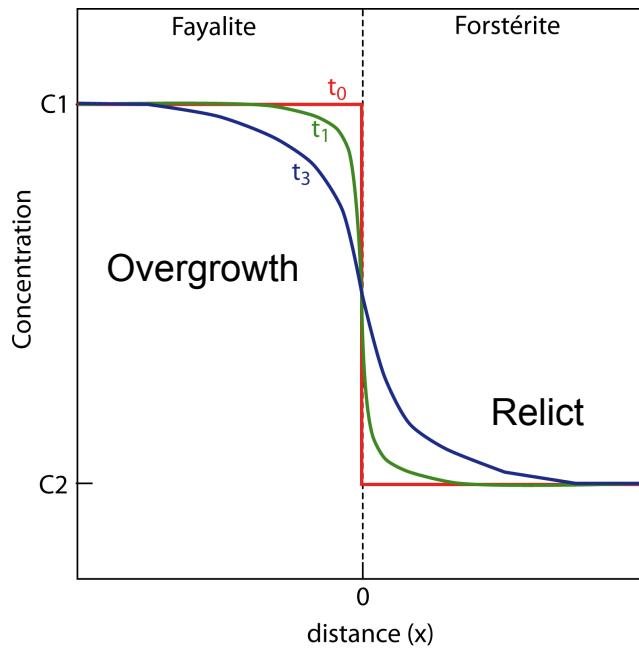


Chromium



- Enrichment of Fe, Ni, Co, Cr, P siderophile elements
- Oxidation and dissolution of Fe, Ni metal blebs in mesostasis

# Application to the thermal history of chondrules



- $\Delta T$  is the driving force for Fe-rich olivine crystallization (and relict olivine resorption).
- As a consequence, diffusion profiles provide information on chondrule thermal history.

$$D(T(t)) = D_0 \times \exp\left(\frac{-E}{RT(t)}\right)$$

## Cooling laws (S = cooling rate)

- Linear :

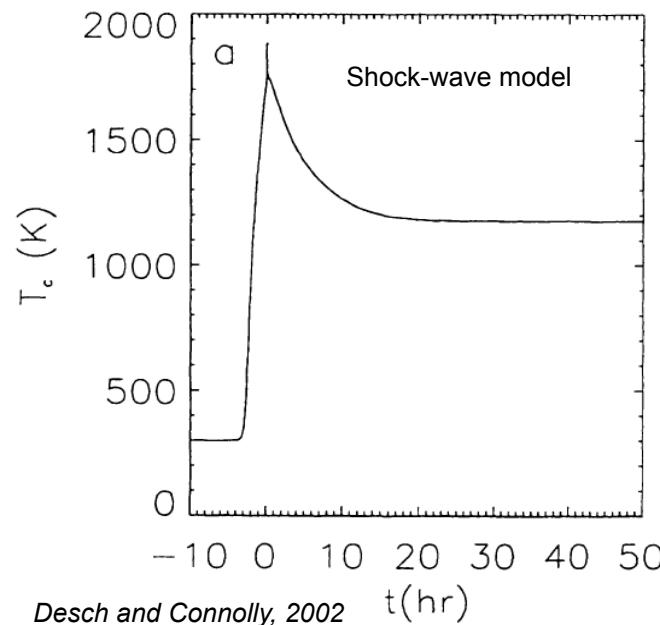
$$T(t) = T_0 - St \text{ (Lasaga, 1983)}$$

- Asymptotic :

$$1/T(t) = 1/T_0 + \eta t \text{ with } S = \eta T^2 \text{ (Ganguly et al., 1994)}$$

- Exponential :

$$T(t) = T_0 \times e^{-\alpha t} \text{ with } S = \alpha T$$

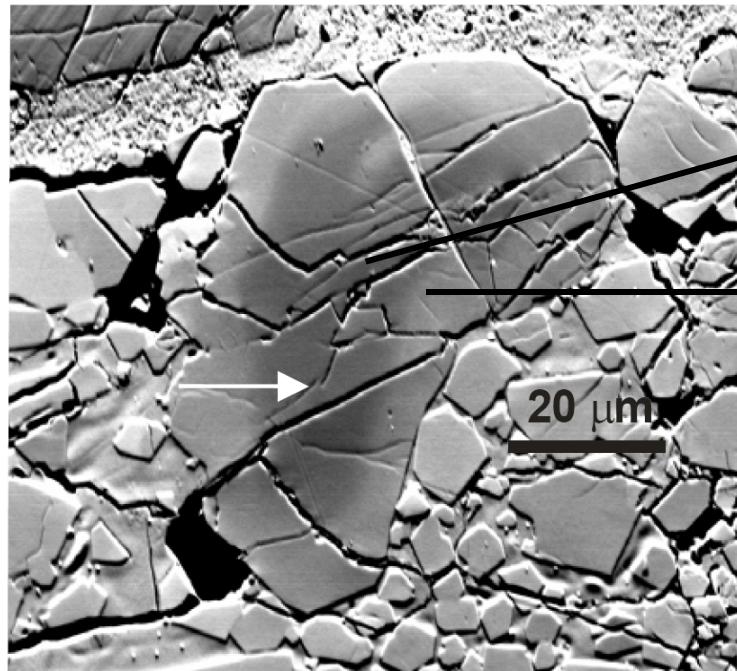


Driving force for diffusion =  $\Delta C$  (and not  $\Delta T$ )

**Caution on the use of diffusion profile to obtain cooling rate of chondrules !!**

# Application to the thermal history of chondrules

Semarkona 13-66A



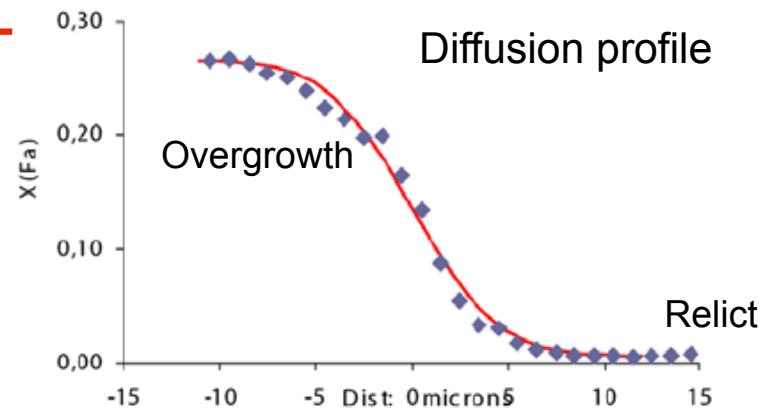
Hewins et al., 2010

•  $\Delta T$

Relict

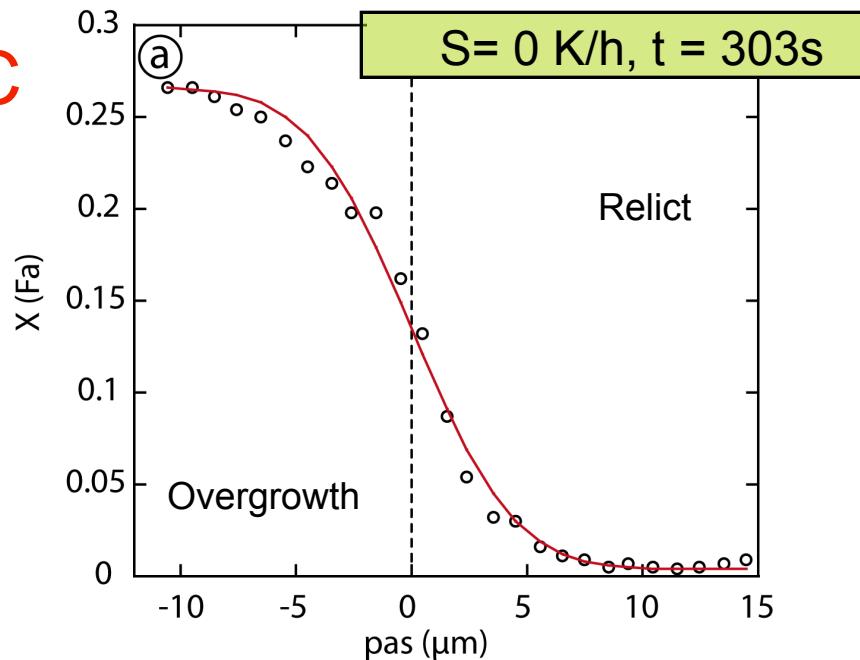
Overgrowth

•  $\Delta C$



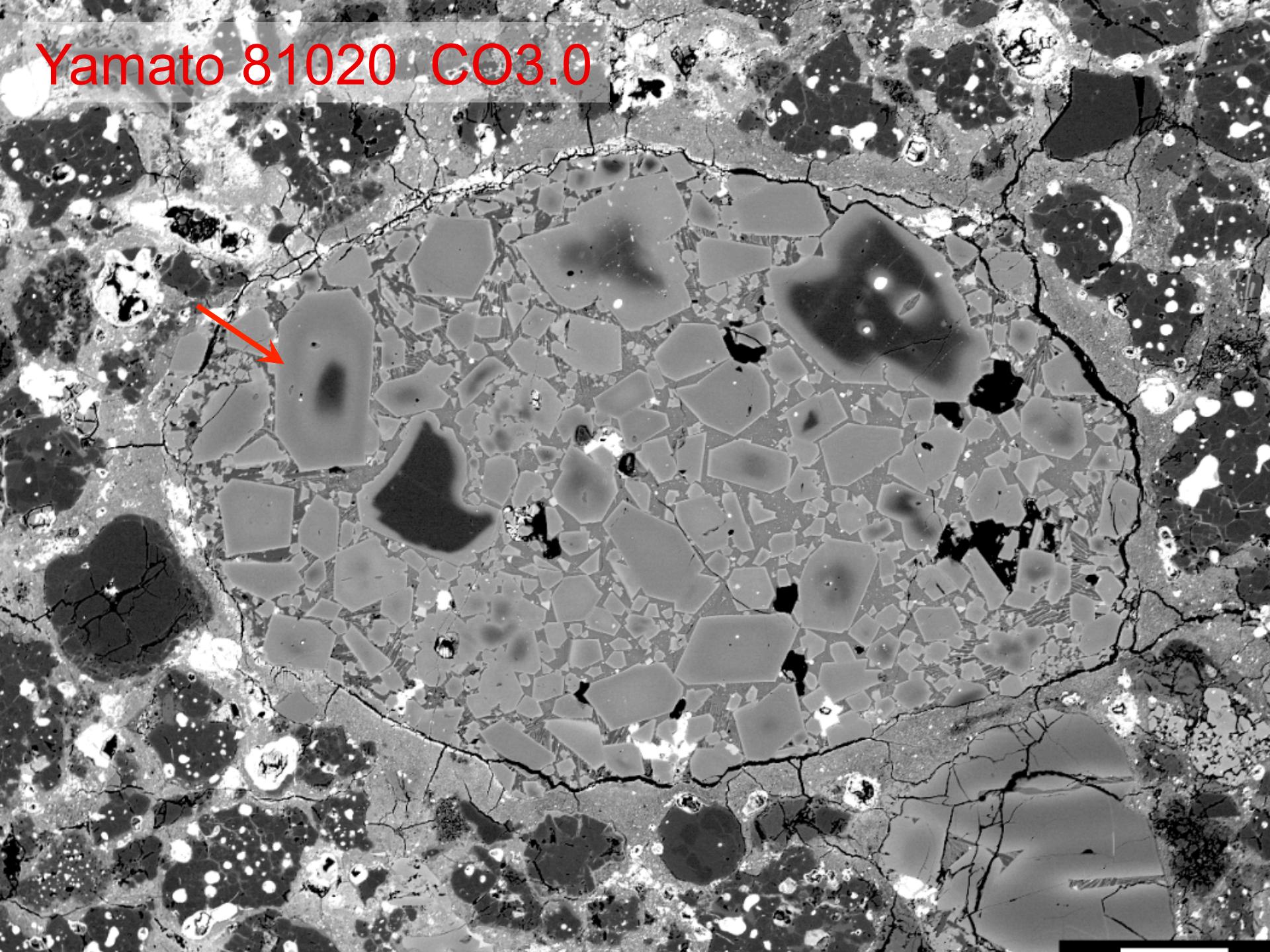
1634°C

$S = 400 \text{ K/h}, t \approx 1080$

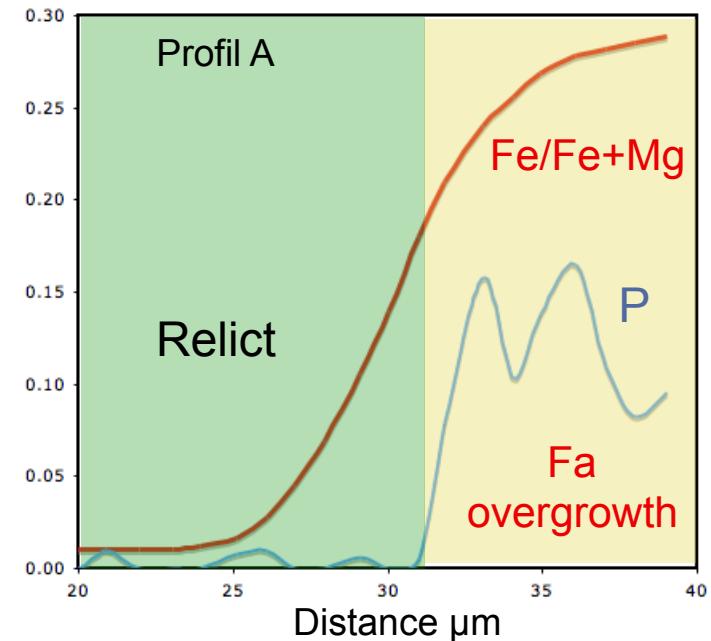
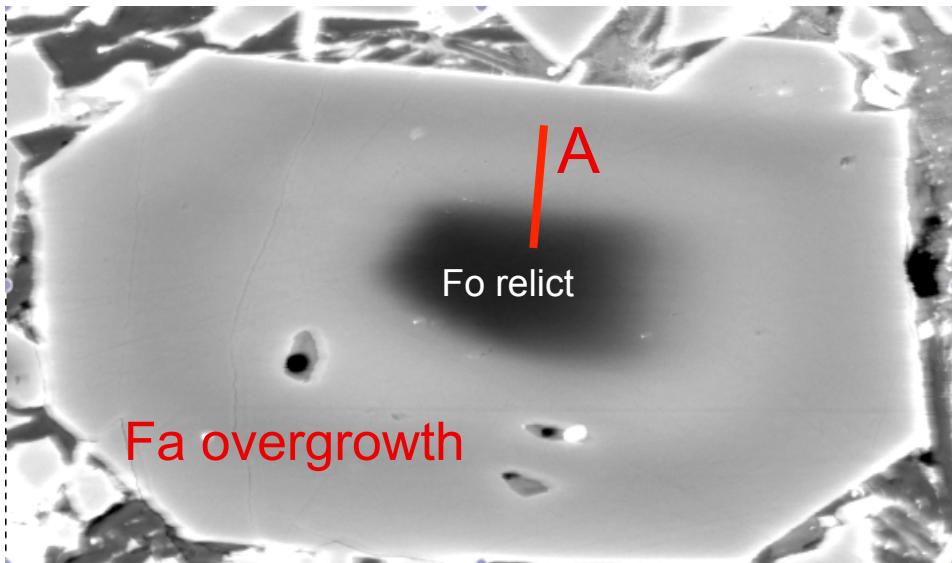


( $D_0, E$ ) Dohmen and Chakraborty (2007)

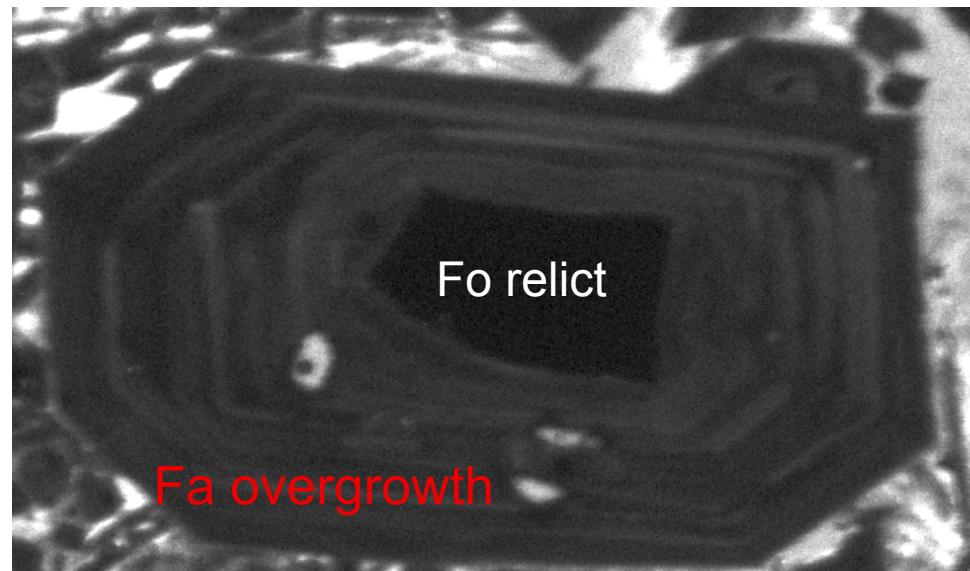
Yamato 81020 CO3.0



# BSE map

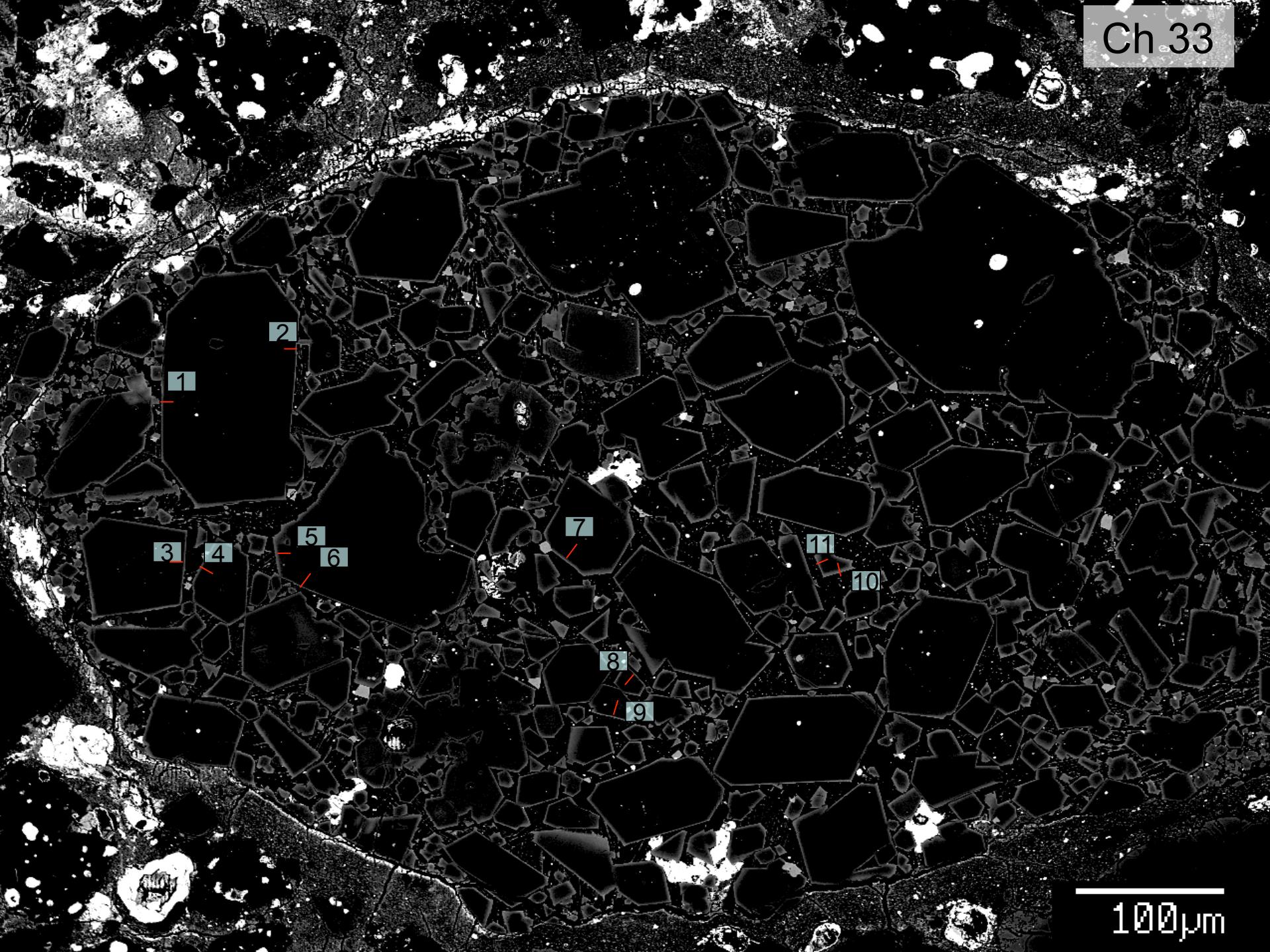


Yamato 81020 CO3.0

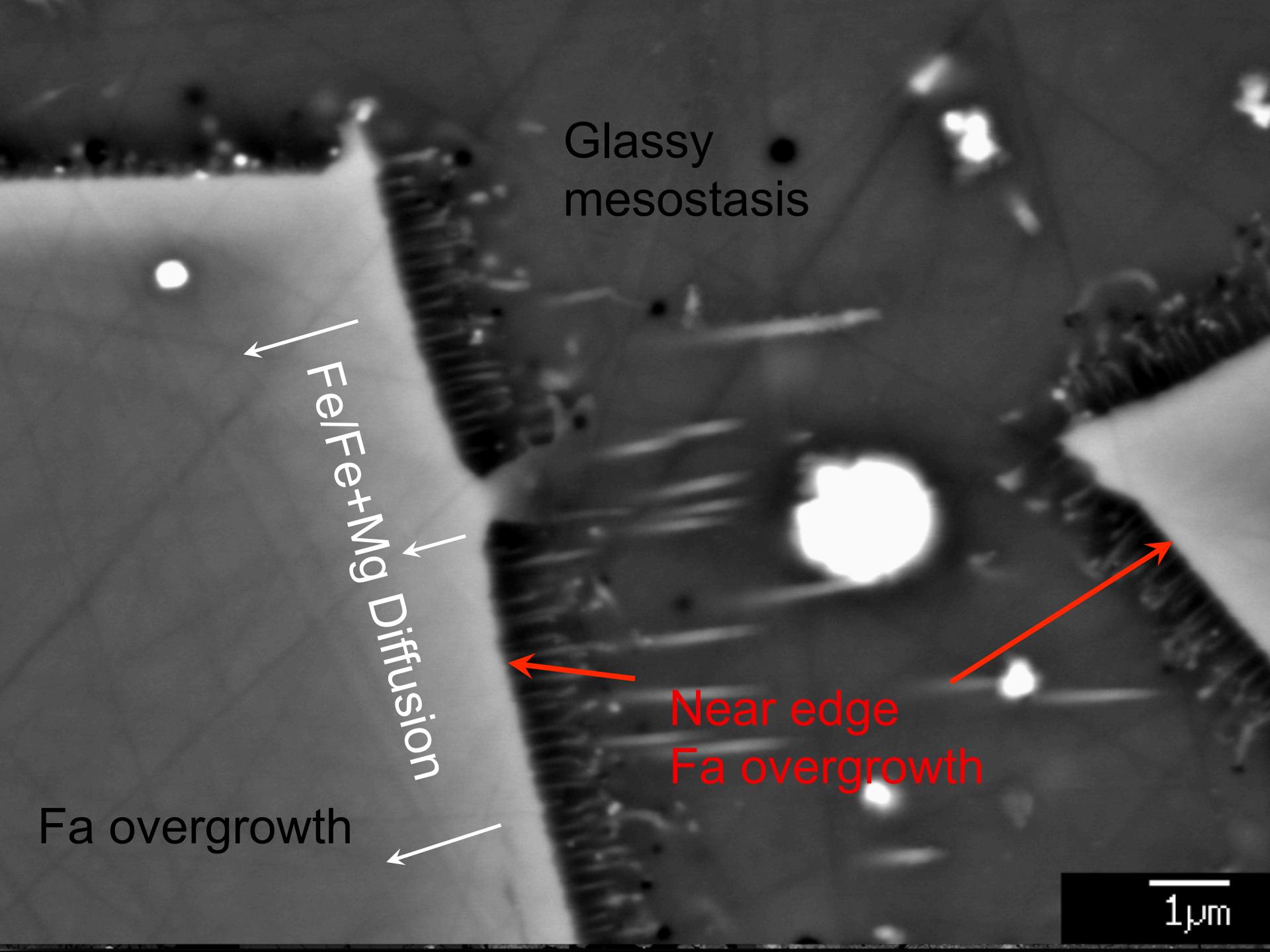


# Phosphorus Xray map

Ch 33



$100\mu\text{m}$

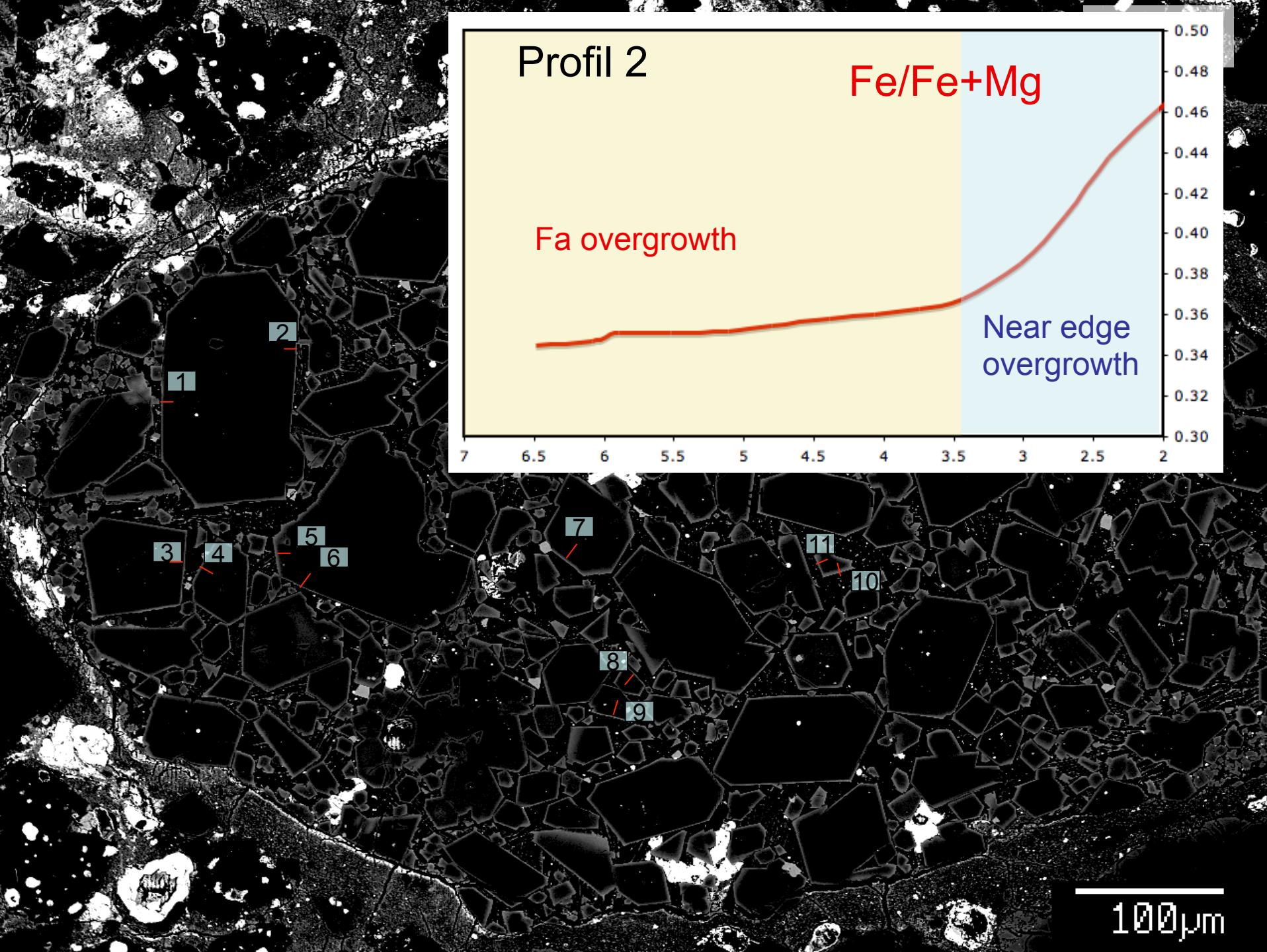


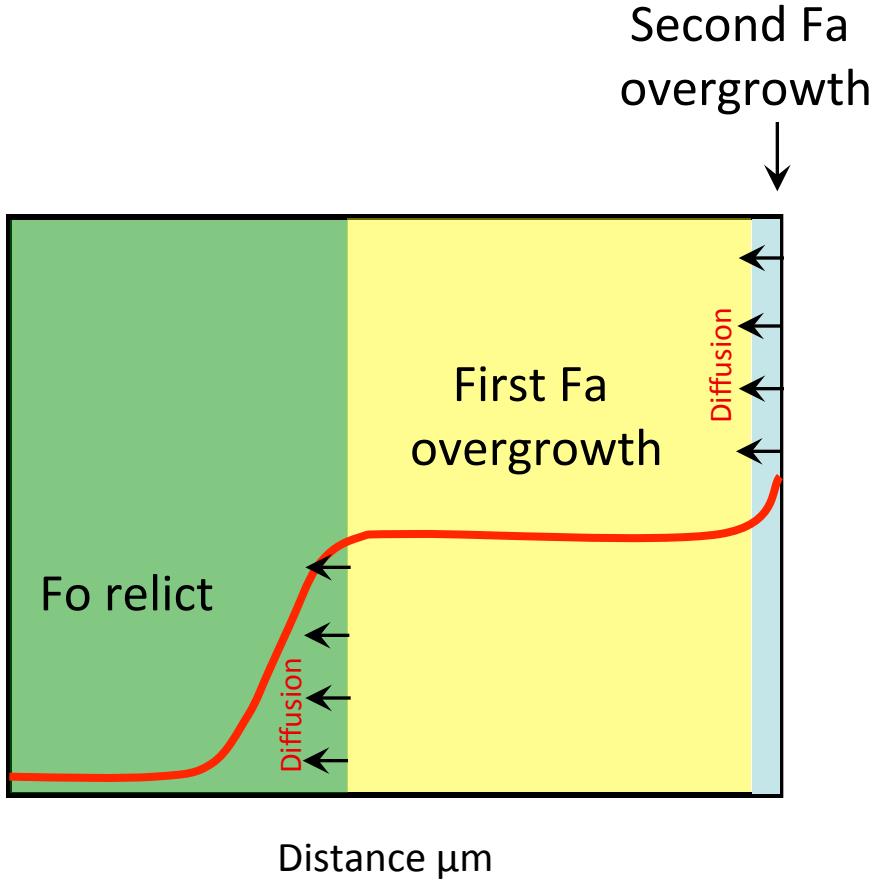
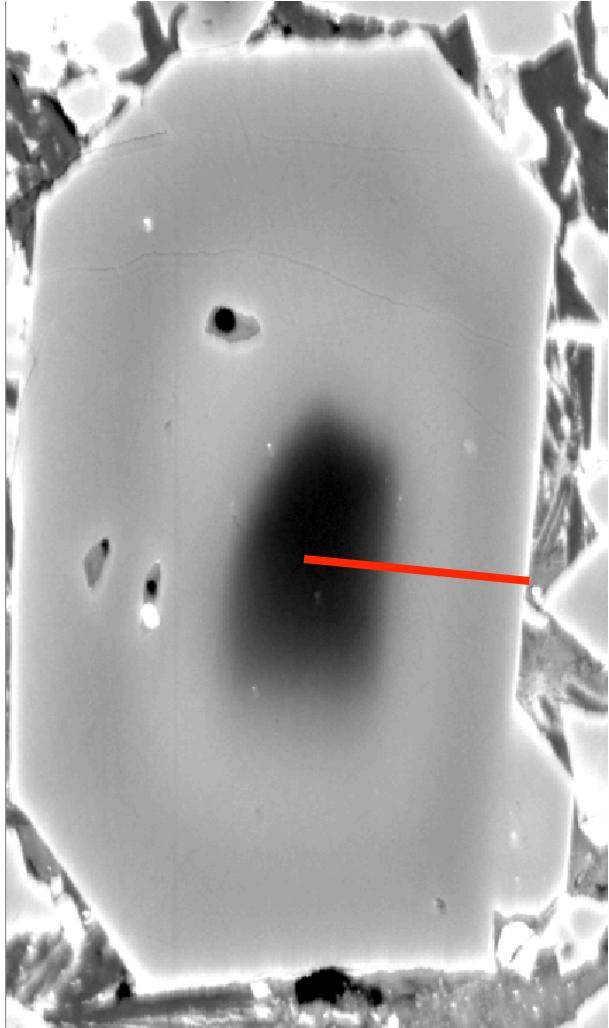
Glassy  
mesostasis

Fa overgrowth

Near edge  
Fa overgrowth

1 $\mu$ m



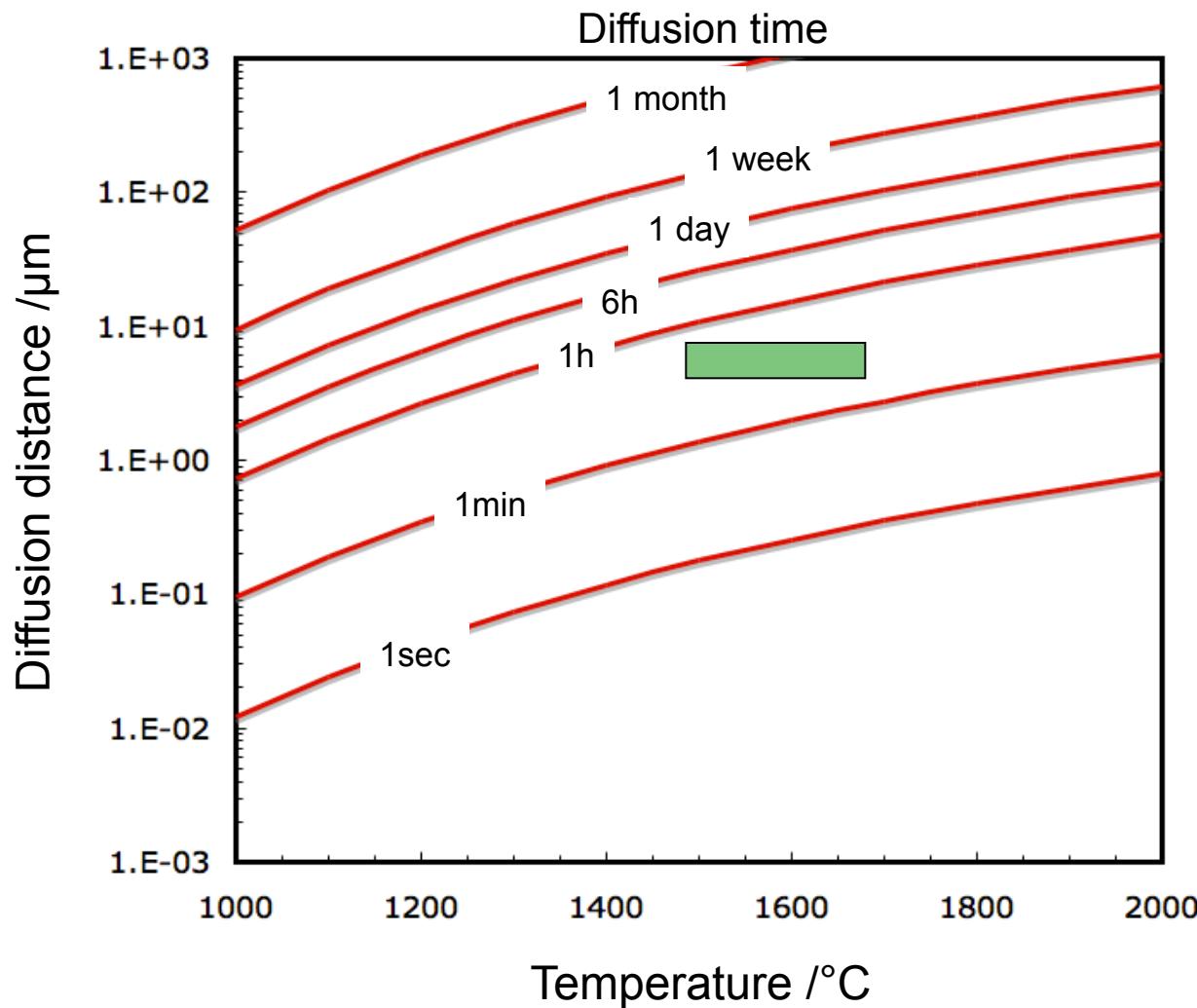


- First fayalitic overgrowth
  - Sub isothermal oxidation
- Second fayalitic overgrowth
  - Rapid cooling (glass)

# First Fa overgrowth

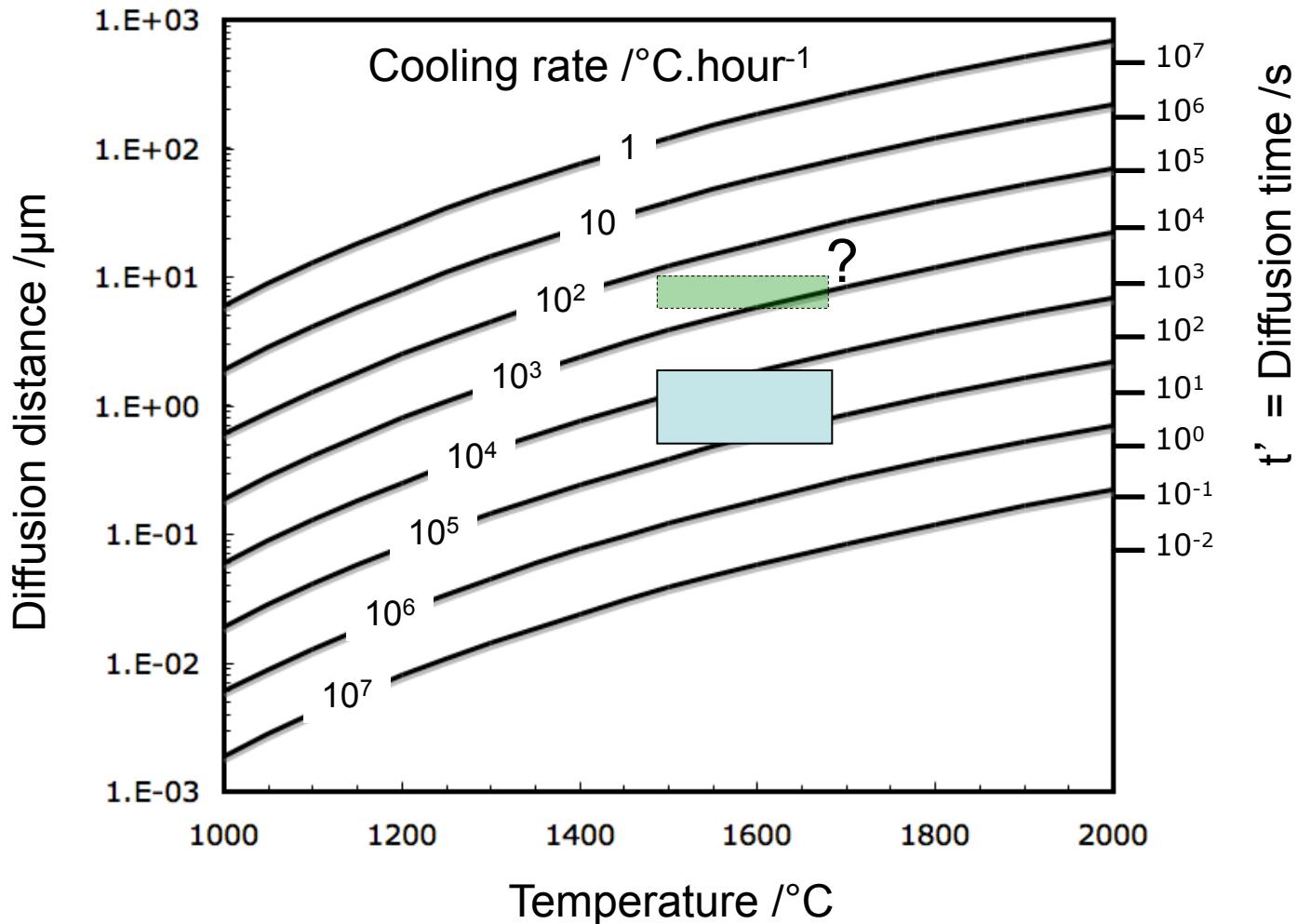
$$\Delta x = 2 \cdot \sqrt{T \cdot t}$$

$$D(T) = D_0 \times \exp\left(\frac{-E}{R \cdot T}\right)$$

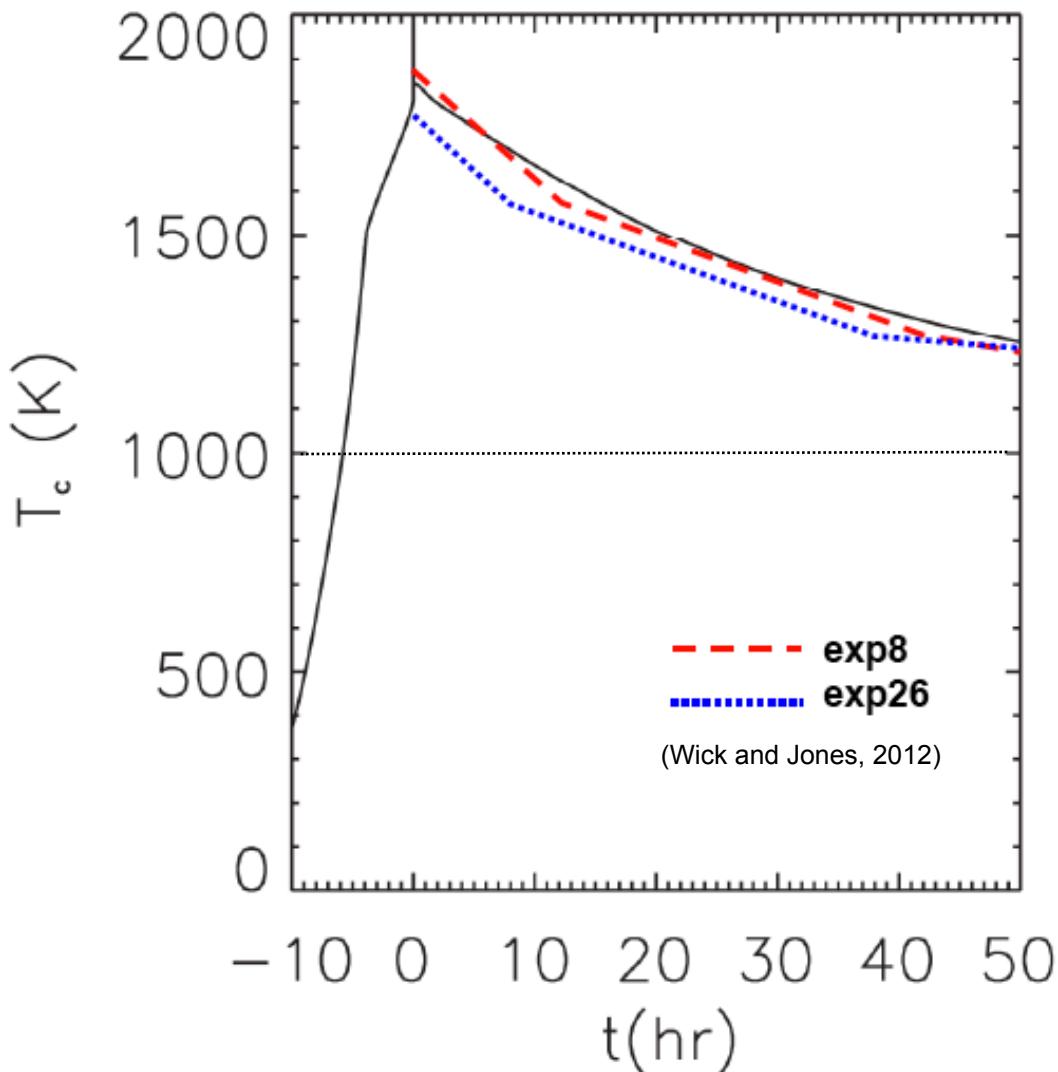


# Second Fa overgrowth

$$D(T(t)) = D_0 \times \exp\left(\frac{-E}{RT(t)}\right) \quad T(t) = T_0 - St \text{ (Lasaga, 1983)}$$



# Thermal histories for type I and type II PO chondrule formation



Shock wave model  
(Morris and Desch, 2010)

$$S = 10 - 10^3 \text{ K/h}$$

$$x = 2 \cdot (D_0 \cdot t')^{-1/2}$$

$t'$  = diffusion time

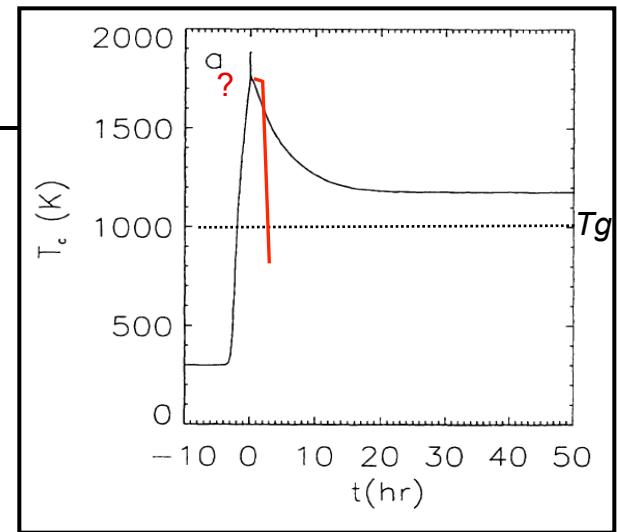
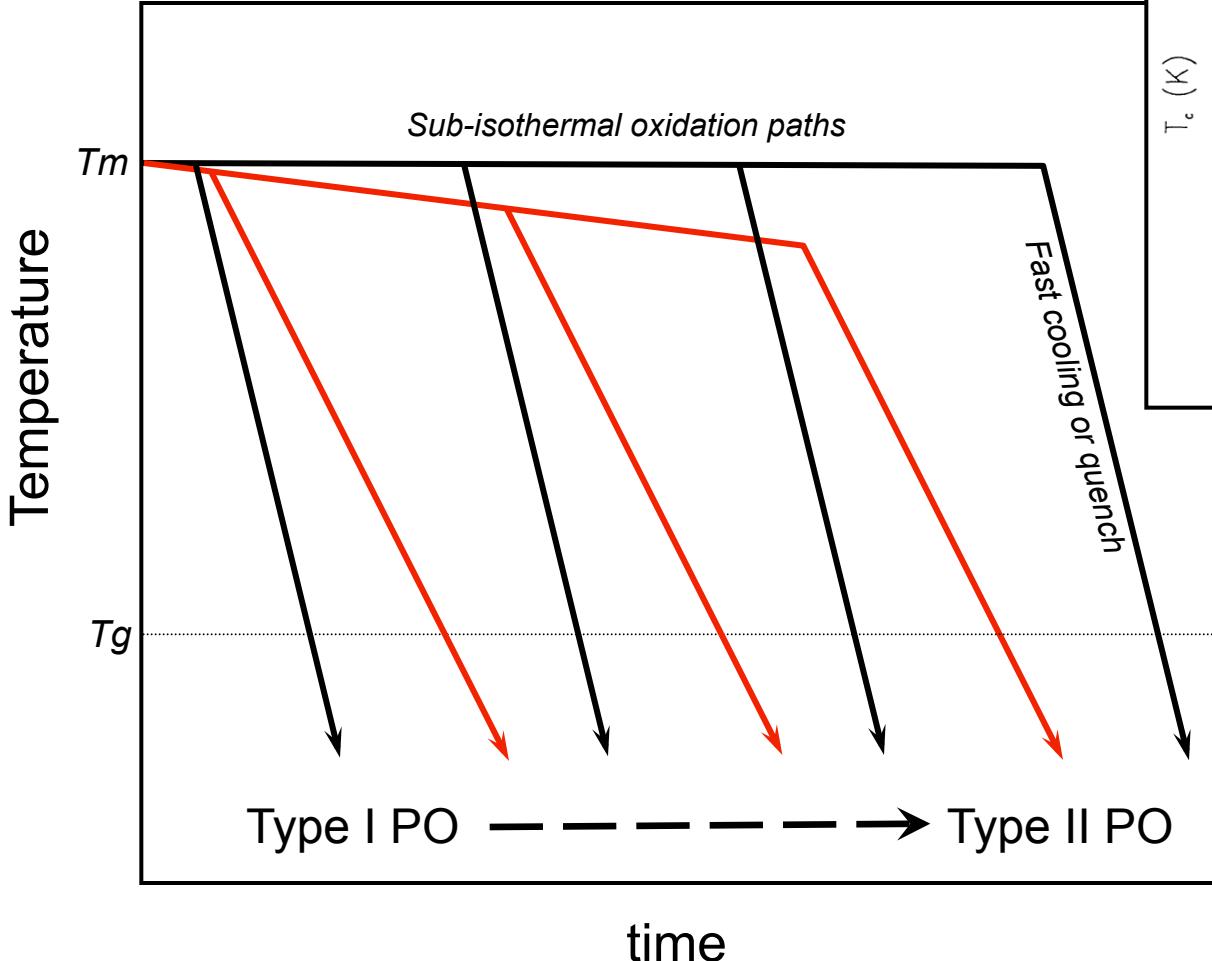
$$t' = R \cdot T_0^2 \cdot (E \cdot s)^{-1}$$

$$t' > 50 - 100 \text{ h}$$

**t' is well too long to match:**

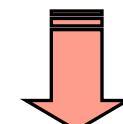
- Elements with fast and slow diffusion
- occurrence of glass

# Thermal histories for type I and type II PO chondrule formation



$5-10 \text{ min} < t' < 5 \text{ h}$

$S > 10^4 \text{ K/h}$

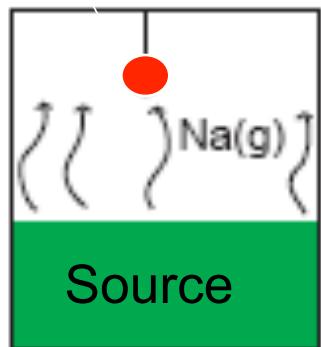


Chondrule formation:  
Quicker and faster

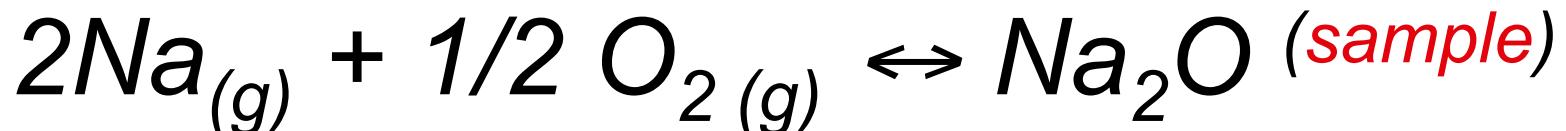
# Strategy: closed system experiments

Sample

Source (evaporation)



Sample (condensation)

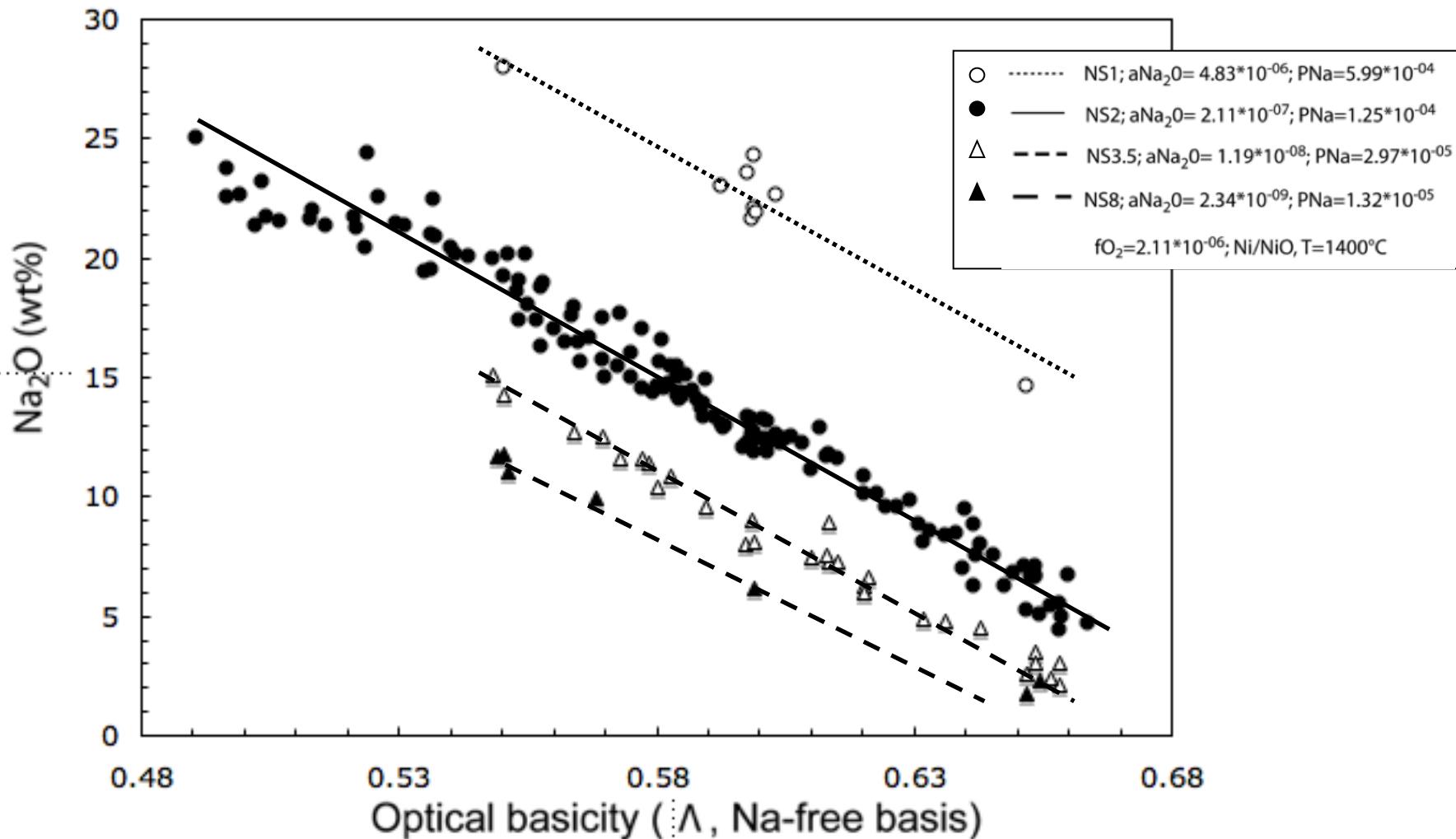


$$K_{eq(T,P)} = (P_{\text{Na}})^2 \cdot (P_{\text{O}_2})^{1/2} / (X_{\text{Na}_2\text{O}}^{\text{(sample)}} \cdot \gamma_{\text{Na}_2\text{O}}^{\text{(sample)}})$$

At equilibrium

$$a_{\text{Na}_2\text{O}}^{\text{(source)}} = a_{\text{Na}_2\text{O}}^{\text{(sample)}}$$

# Model of Na solubility



$$\text{Na}_2\text{O} (\text{wt}\%) = 106.84 - 110.87 * \Lambda + 4.06 * \log(a\text{Na}_2\text{O}) \quad (R^2=0.88)$$

## Model of Na solubility

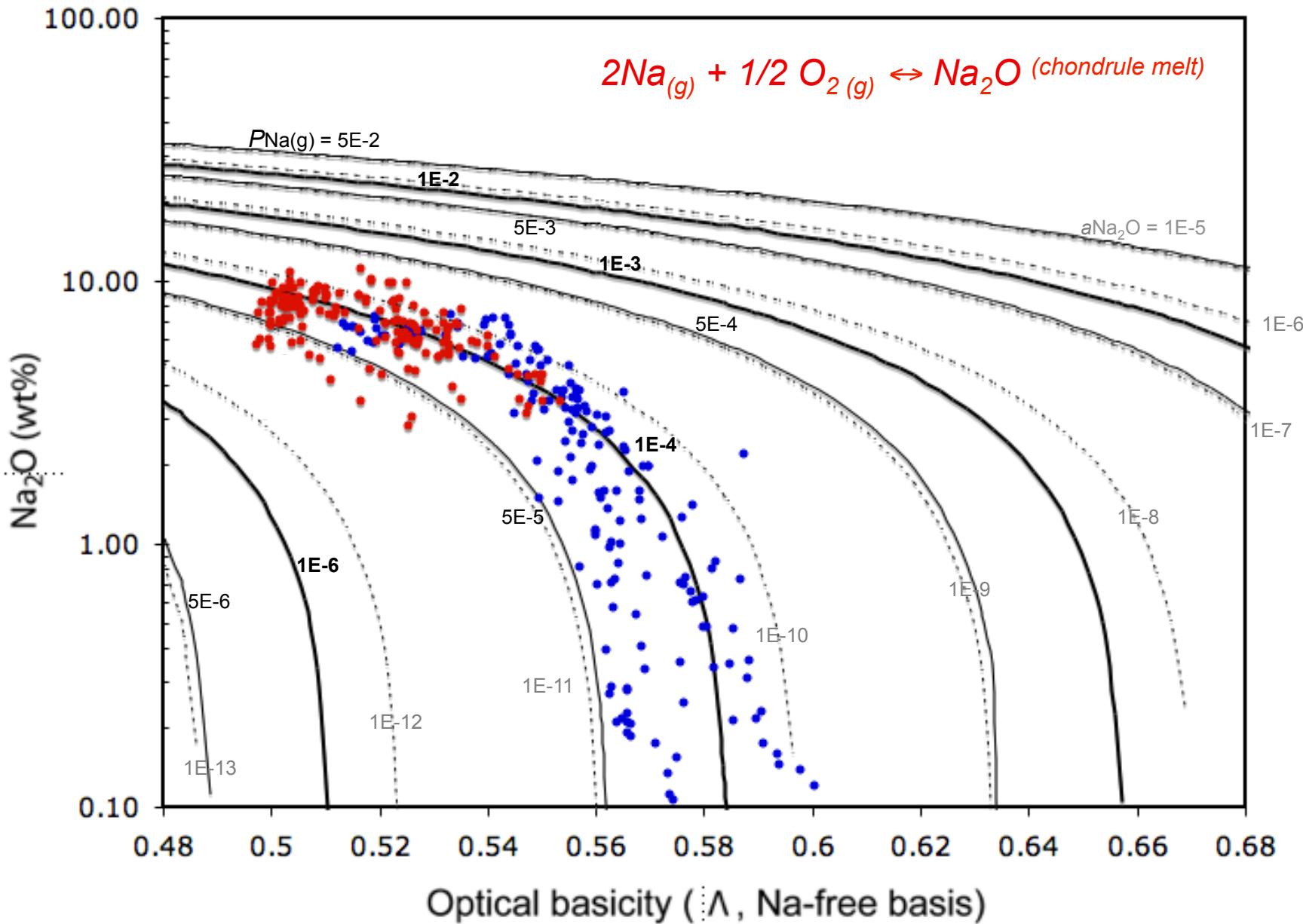


$$K_{eq(T)} = (P_{\text{Na}})^2 \cdot (P_{\text{O}_2})^{1/2} / a_{\text{Na}_2\text{O}}^{(liq)}$$

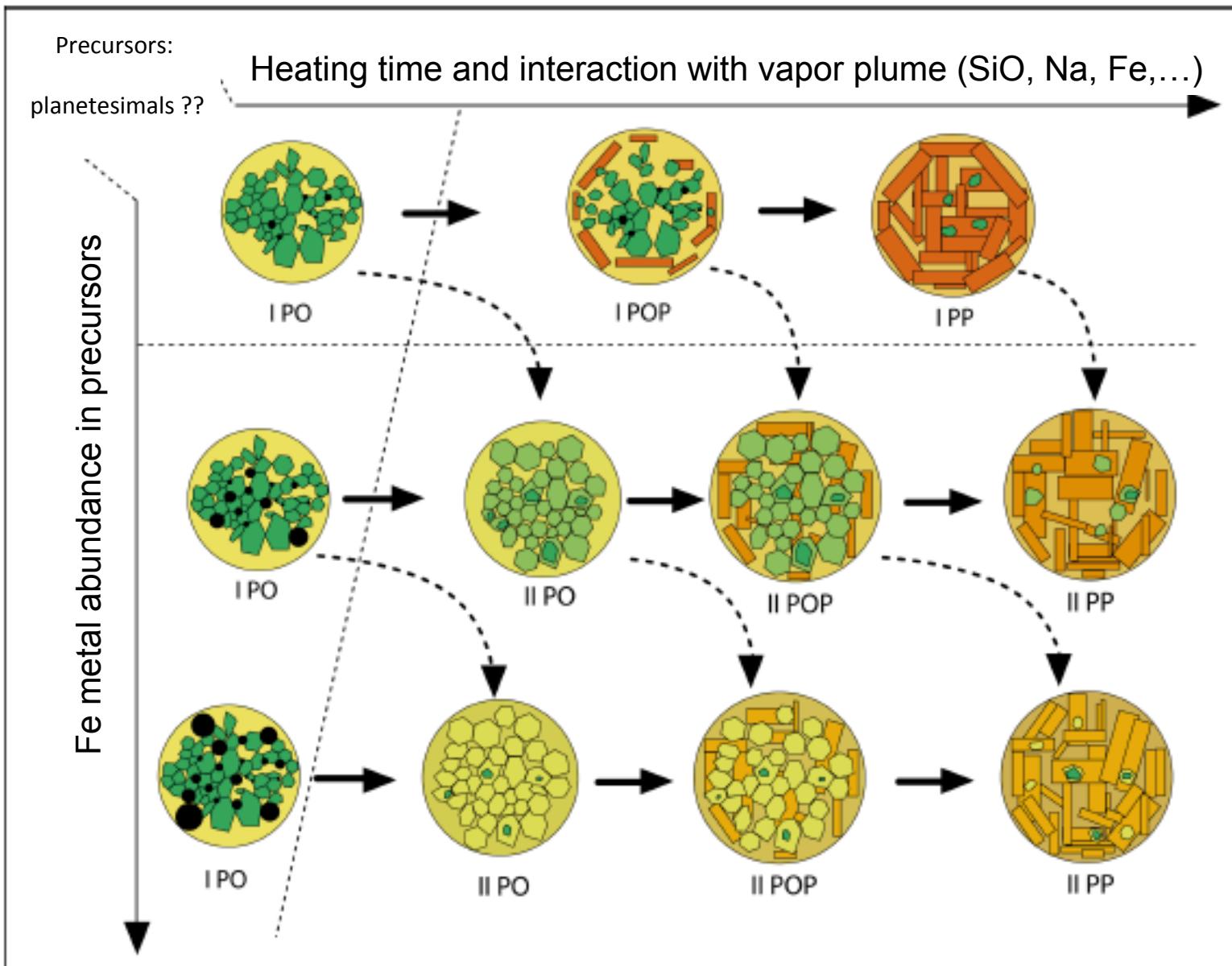
$$\log K_{eq(T)} = -2.6717 * 10000 / T^{(K)} + 12.522$$

$$\text{Na}_2\text{O (wt\%)} = 106.84 - 110.87 * \Lambda + 4.06 * \log(a_{\text{Na}_2\text{O}}) \quad (R^2=0.88)$$

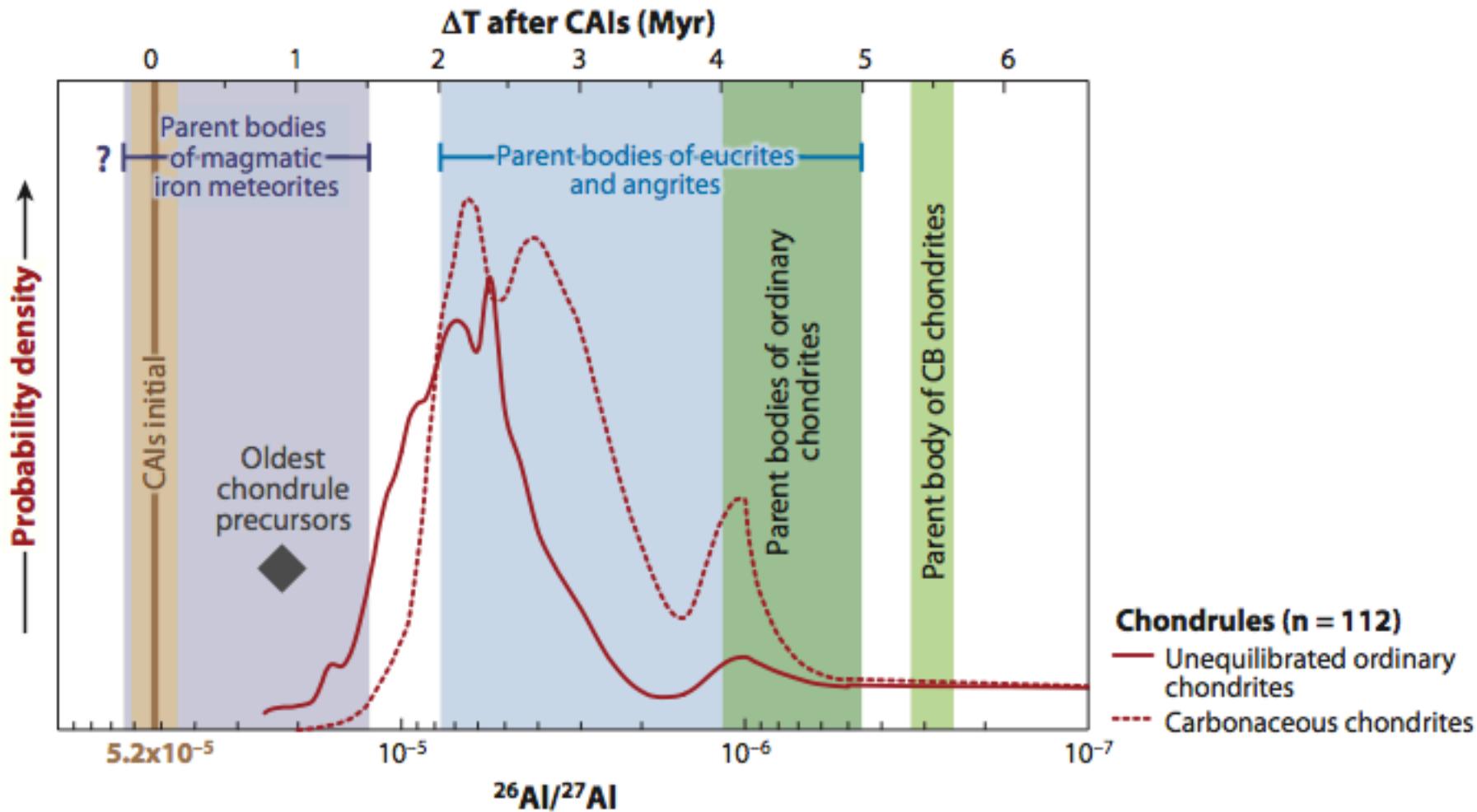
# Alkalies in chondrules



# Chondrule formation process



# Constraints from short-lived radionuclides on the timing of chondrule formation and primary accretion



Villeneuve et al. 2009

Dauphas and Chaussidon, 2011

# Chondrule formation process

1. The chemistry and the oxygen isotopic compositions indicate that Mg-rich olivines are unlikely to be of nebular origin (i.e., solar nebula condensates) but are more likely debris of broken differentiated planetesimals (each of them being characterized by a given  $\Delta^{17}\text{O}$ ).
2. Considering the very old age of chondrules, Mg-rich olivine grains or aggregates might be considered as millimeter-sized fragments from disrupted first-generation differentiated planetesimals.
3. The finding of only a small number of discrete  $\Delta^{17}\text{O}$  modes for Mg-rich olivines grains or aggregates in a given chondrite suggests that these shattered fragments have not been efficiently mixed in the disk and/or that chondrite formation occurred in the first vicinity of the breakup of these planetary bodies.

# Chondrule formation process

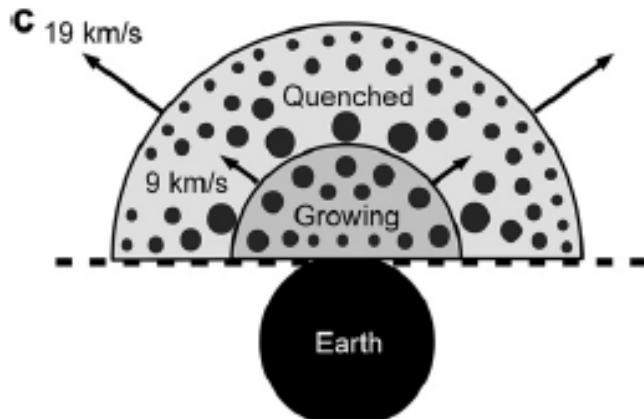
4. Type I chondrules or their fragments are very likely the main precursor material involved in the formation of Type II chondrules.
5. Chondrule formation must be preferentially the result of processes generating crystal growth by chemical disequilibrium at high temperature, i.e.,  $dC/dt$  as in our sub-isothermal open system behavior experiments, rather than processes generating crystallization by cooling rates, i.e.,  $dT/dt$  as in dynamical cooling rate experiments, questioning the reliability of cooling rate values hitherto inferred for producing porphyritic textures.
6. Last, PO chondrule formation is a very fast process. After periods of sub-isothermal heating as short as several tenths of minutes and no longer than few hundreds of minutes in the range of 1500 -1800°C, PO chondrules terminates their formation by a very fast cooling ( $>> 10^4$  K/h).

# Chondrule formation: quicker and faster

Chondrules are interpreted as resulting from various degrees of interaction of the ejected fragments of the collisions with the gas during their ballistic trajectory through the impact vapor plume;

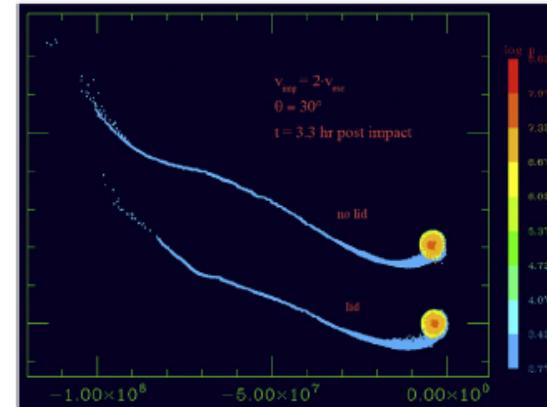
- The most reducing conditions recorded by type I PO chondrules are interpreted as remnant of the conditions of their parental planetimals from which they were ejected during the impact
- The most oxidizing conditions recorded in type II PO chondrules being very likely the closest to those imposed by the impact vapor plume.

High velocity impacts ( $>> 1\text{ km.s}^{-1}$ )

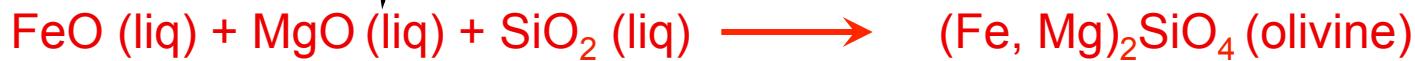
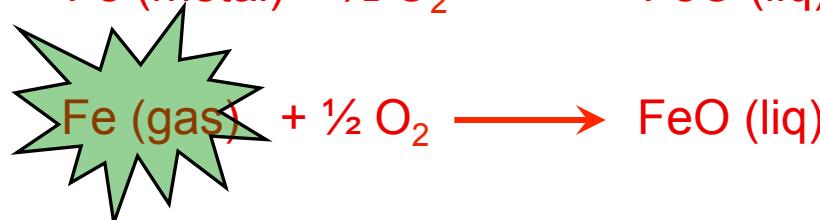
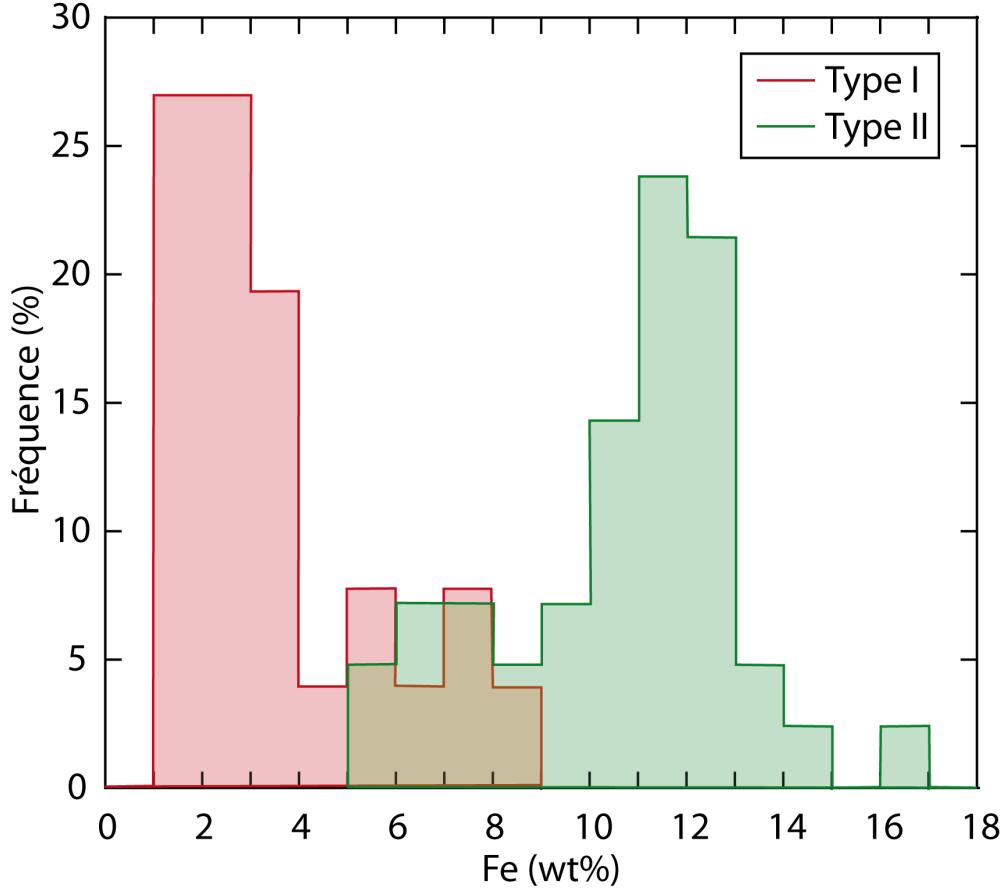


?

Low velocity impacts ( $< 1\text{ km.s}^{-1}$ )



# Semarkona PO chondrule



# Thermal model for type I and type II PO chondrules formation

