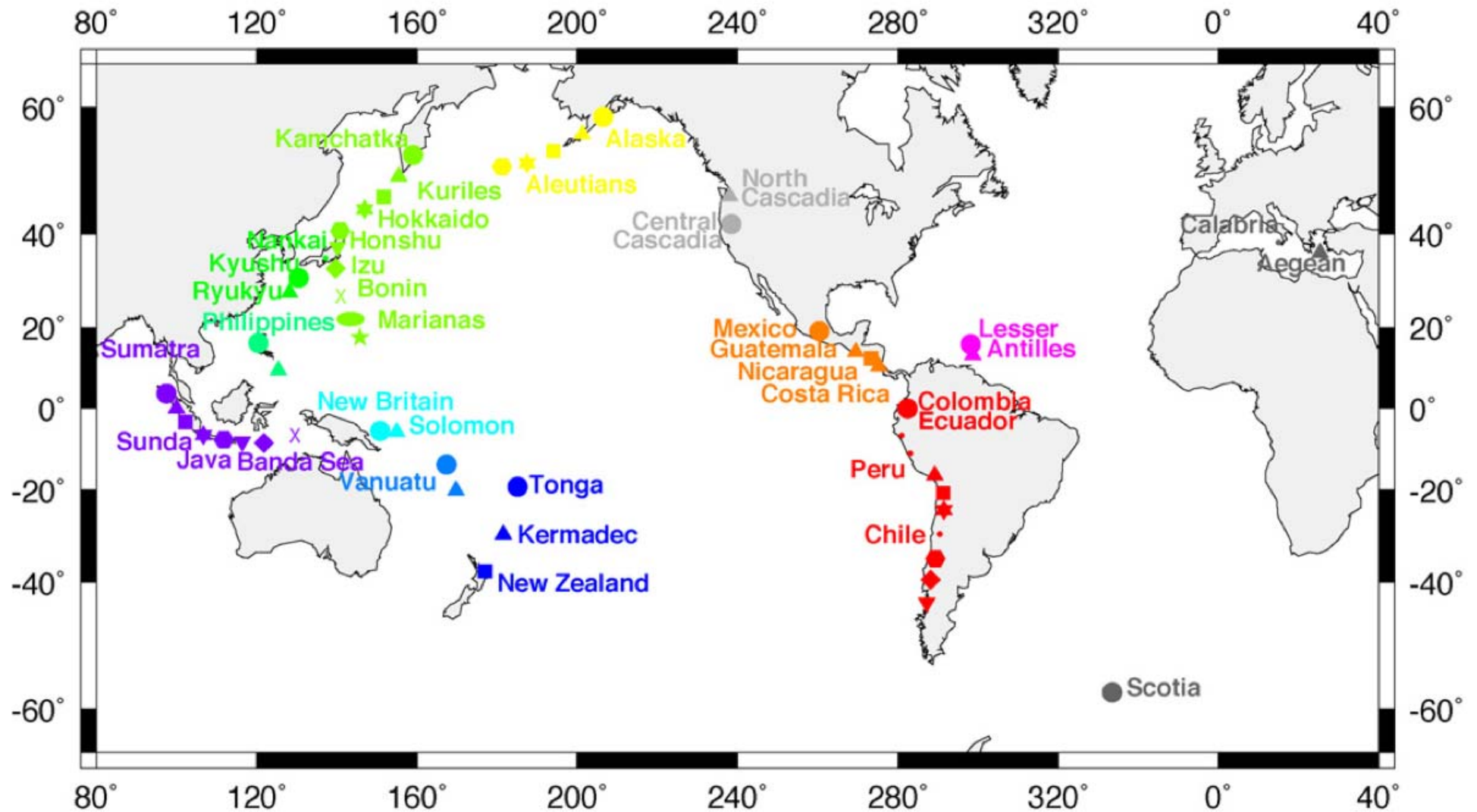


Petrologia sperimentale: uno sguardo ai processi orogenici

Stefano Poli

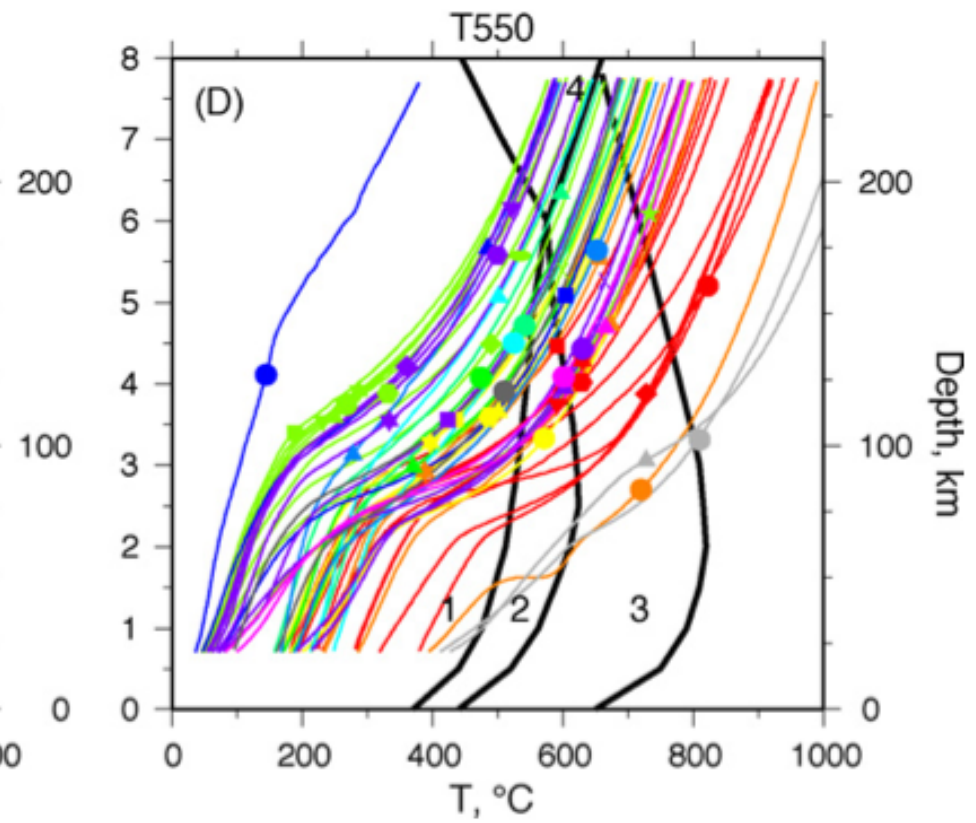
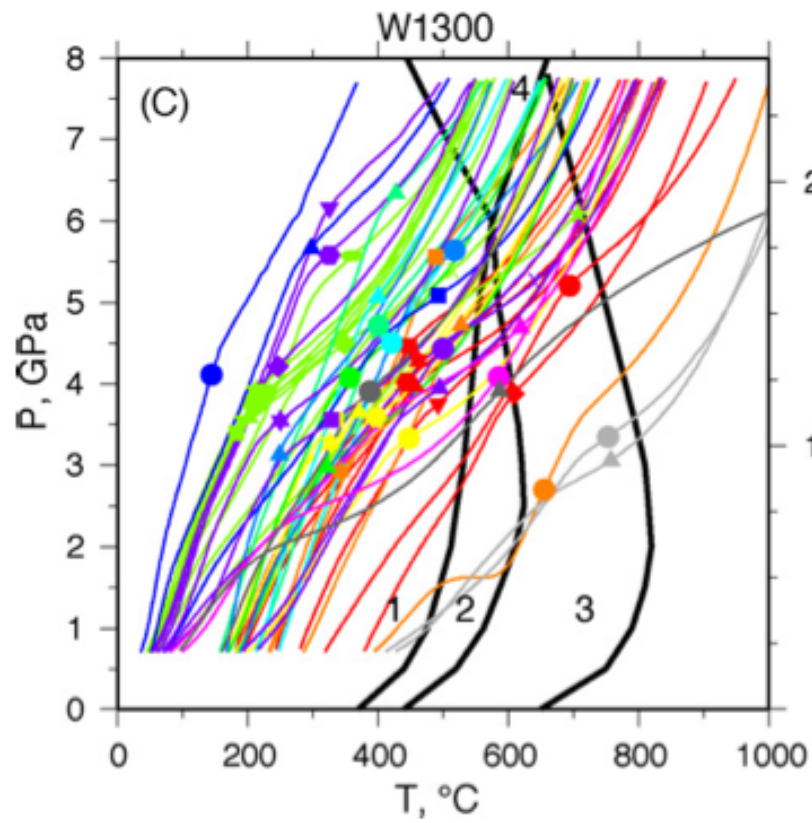
*Dipartimento di Scienze della Terra
Università degli Studi di Milano*

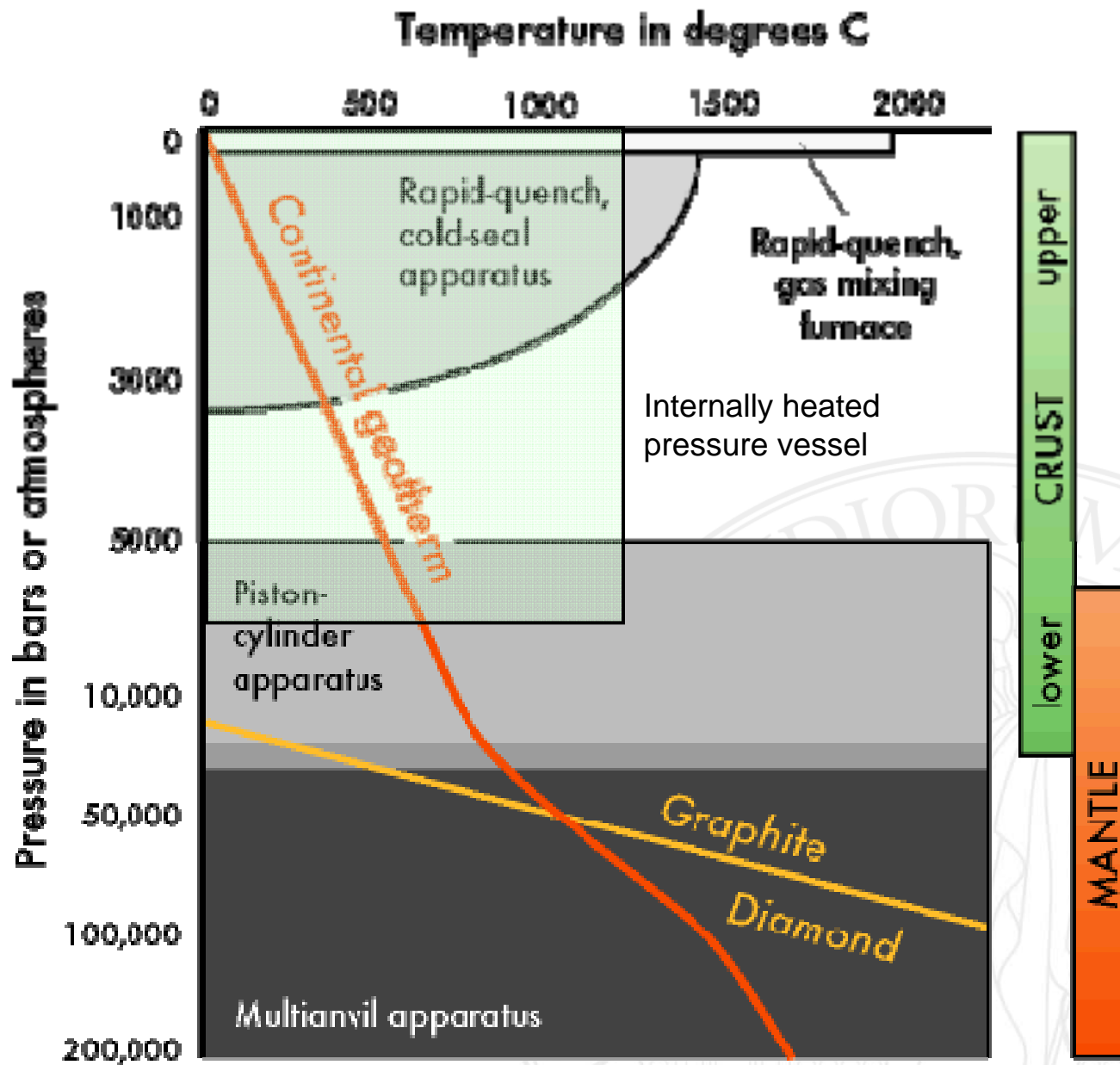




Syracuse et al. 2010







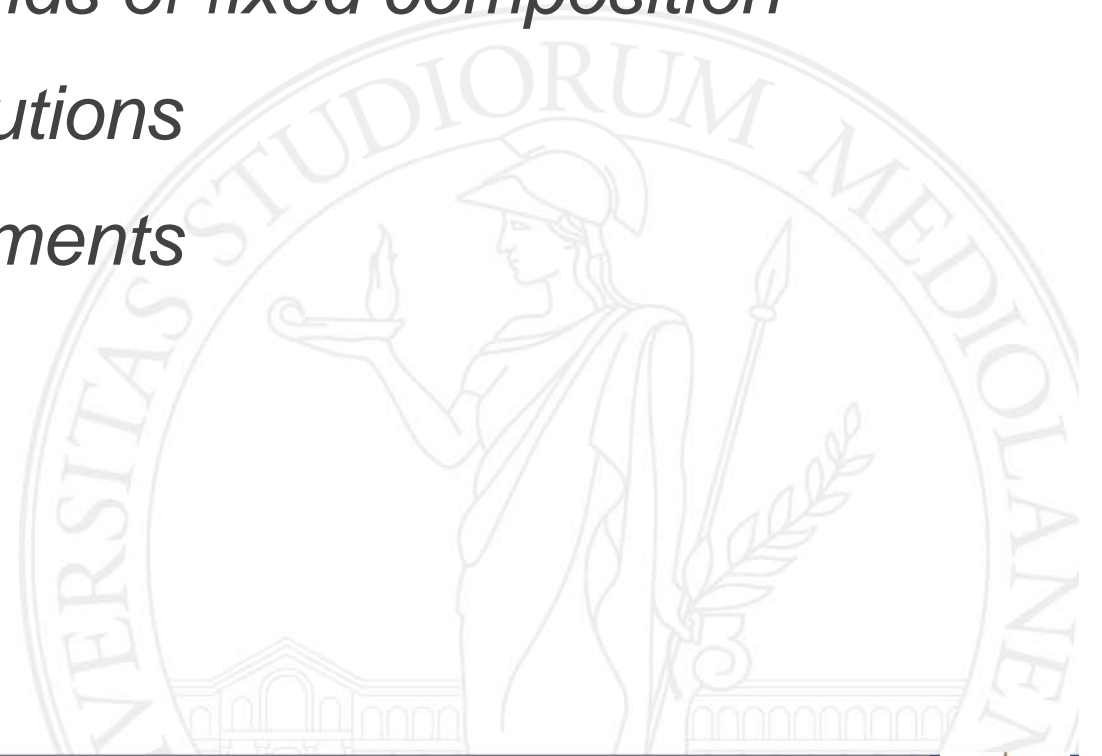
Simulating the natural world: what goes in?

Just solids, compounds of fixed composition

Just solids, solid solutions

Fluid bearing experiments

Just fluids



What goes in?

gels

glasses

“oxide” powders

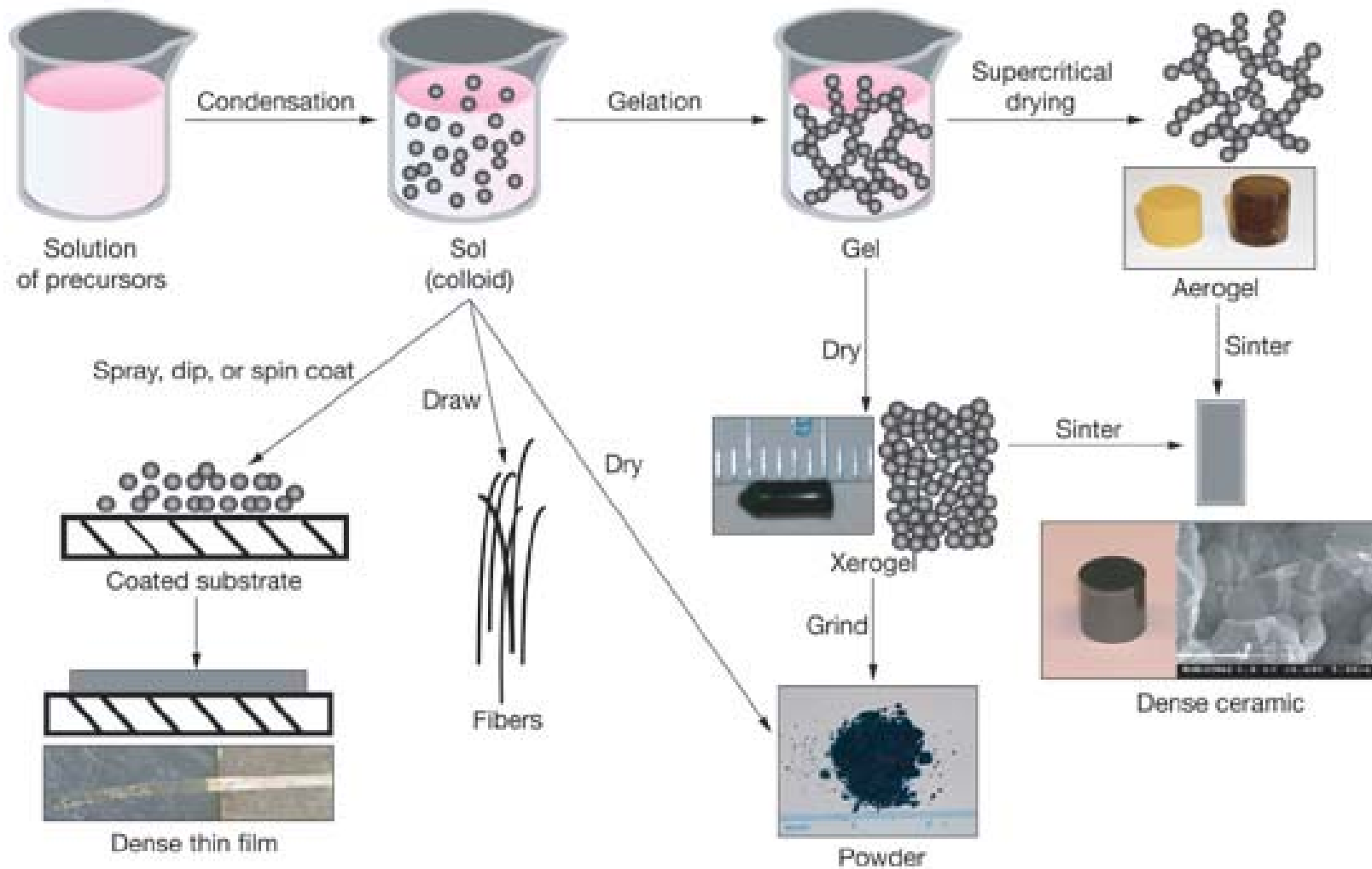
crystalline mixtures

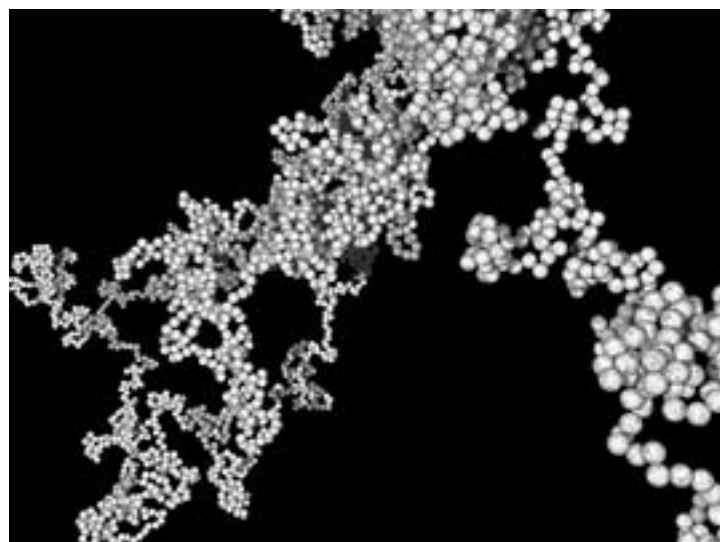
solid sources of volatiles

fluids

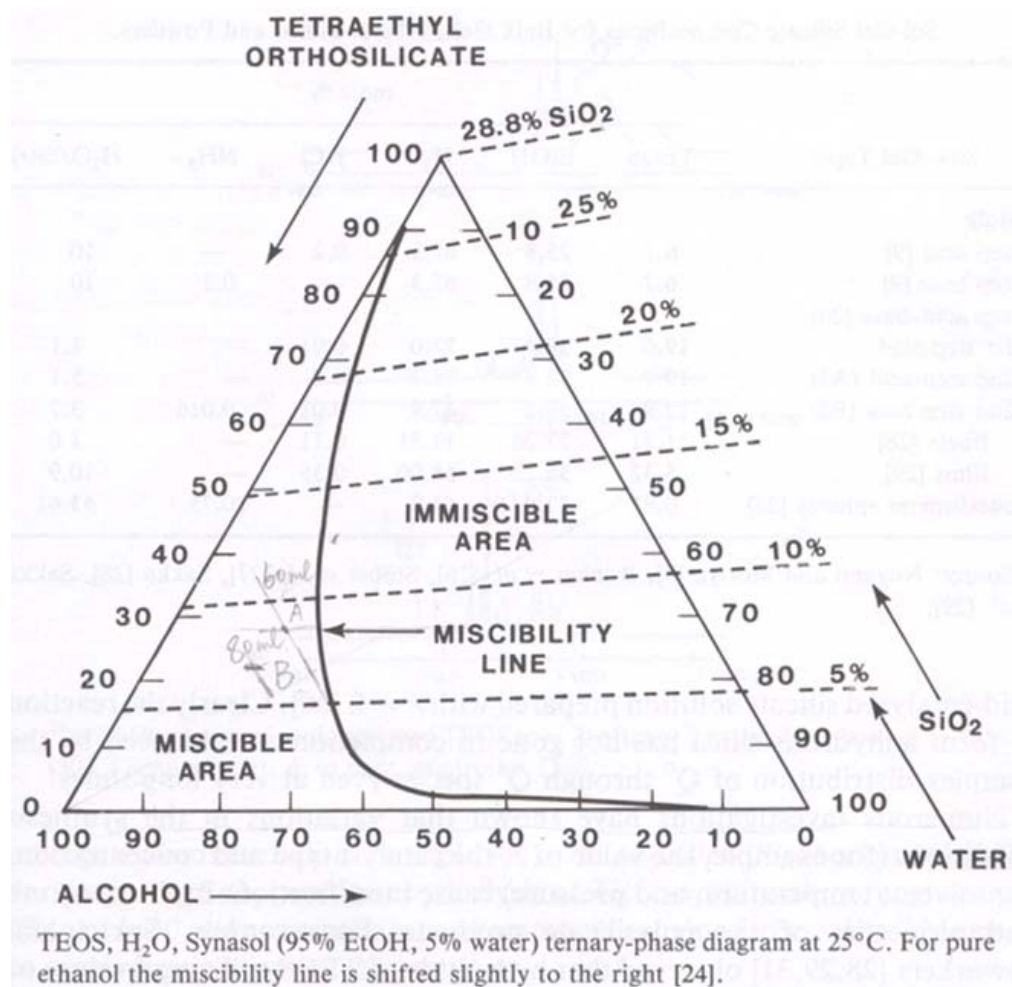


sol – gel techniques





TEOS: source of SiO_2



diluted aqueous nitric solutions:
source of most metals



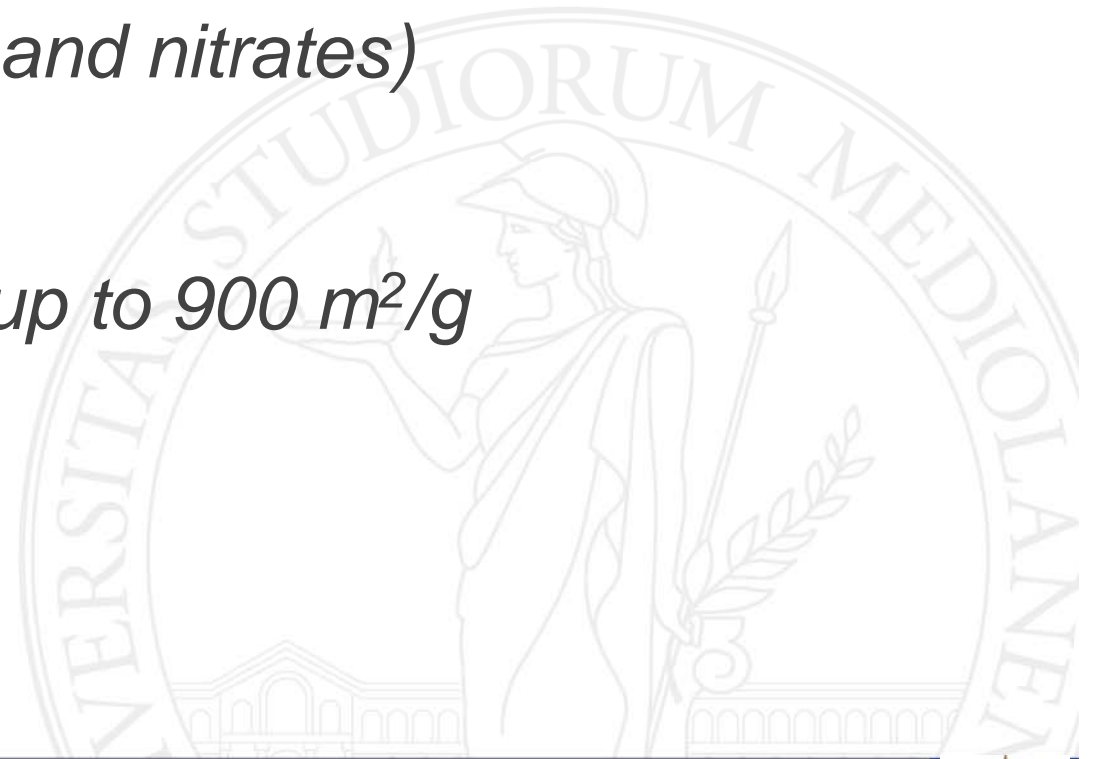
xerogel

gelation using ammonia

drying (remove H_2O and nitrates)

high active surface, up to $900 \text{ m}^2/\text{g}$

very reactive



glass

- *melting oxides/carbonates, quenching (H_2O , dry ice) and remelting powder pellets*
- *vertical furnace (“gas-mixing”)*
- *Fe-bearing glasses difficult to “handle” (Mo-crucibles, Pt-loops)*



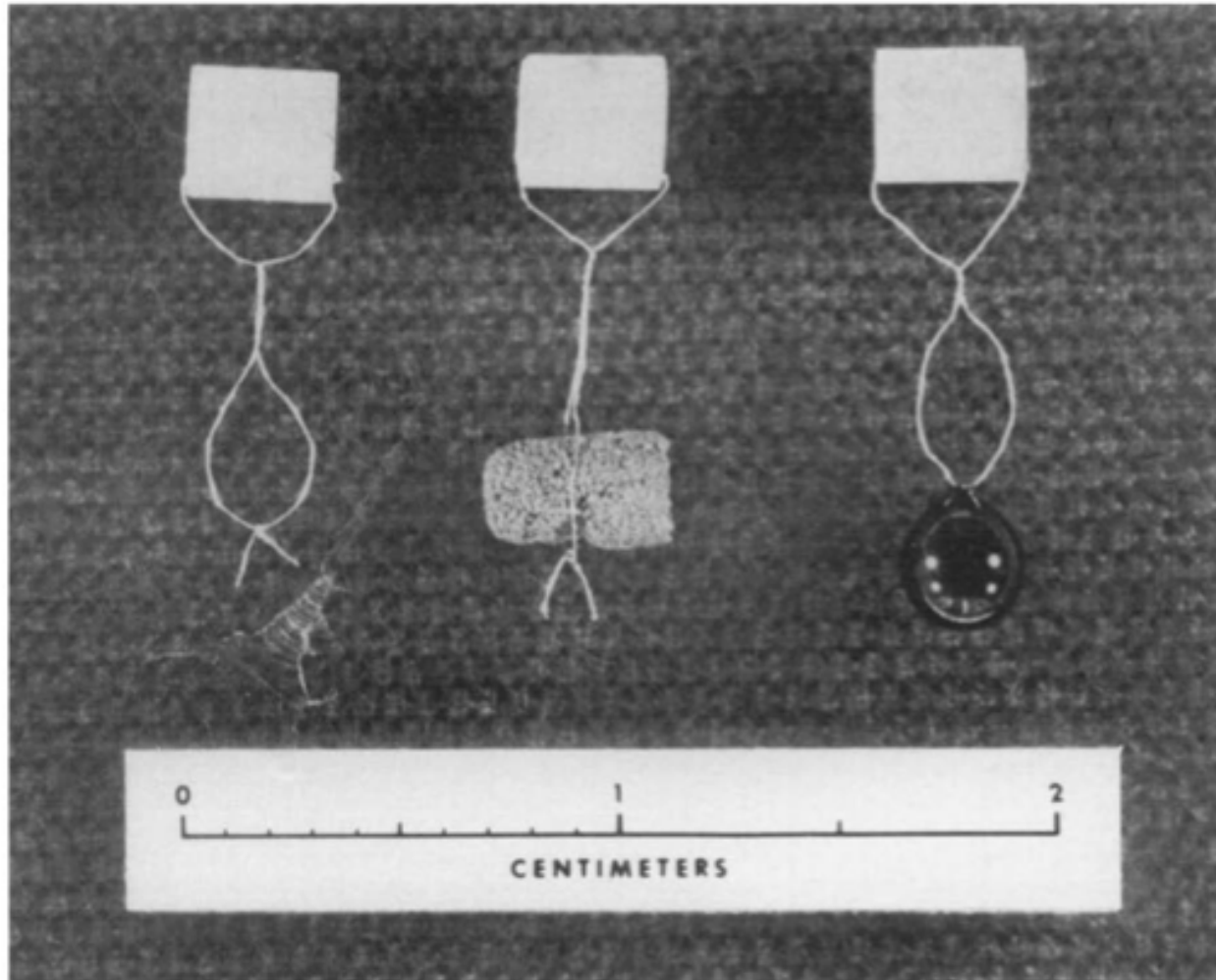


Fig. 1. Three stages of sample preparation. See text for explanation.

Presnall & Brenner, GCA, 1974



“oxides”

mostly crystalline materials, various forms

various sources for “oxides”

e.g. Al_2O_3 :

fused alumina (glassy)

calcined alumina (> 50 m²/g surface area)

tabular alumina (α - Al_2O_3 , sintered)

reactive alumina (nanometer sized)



“...gels may retain early formed metastable phases and the glasses may fail to nucleate stable phases.”

Biggar and O'Hara, Min. Mag. 1969

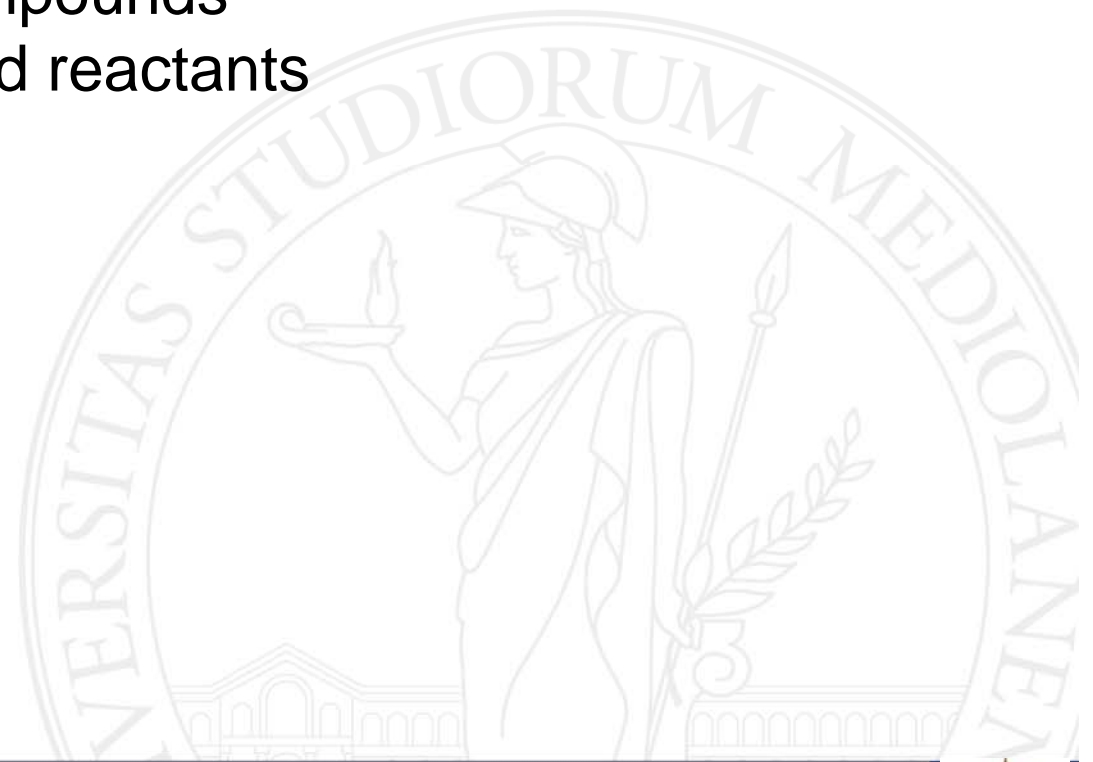
how successful crystalline material... ?



seed your starting material

- add “expected” stable phases only
- add end-member compounds
- add both products and reactants

- dissolution
- reprecipitation
- diffusion
- annealing-ripening



sources of volatiles

*H₂O: water, hydroxides – Mg(OH)₂, Al(OH)₃,
etc.*

CO₂: carbonates, silver oxalate

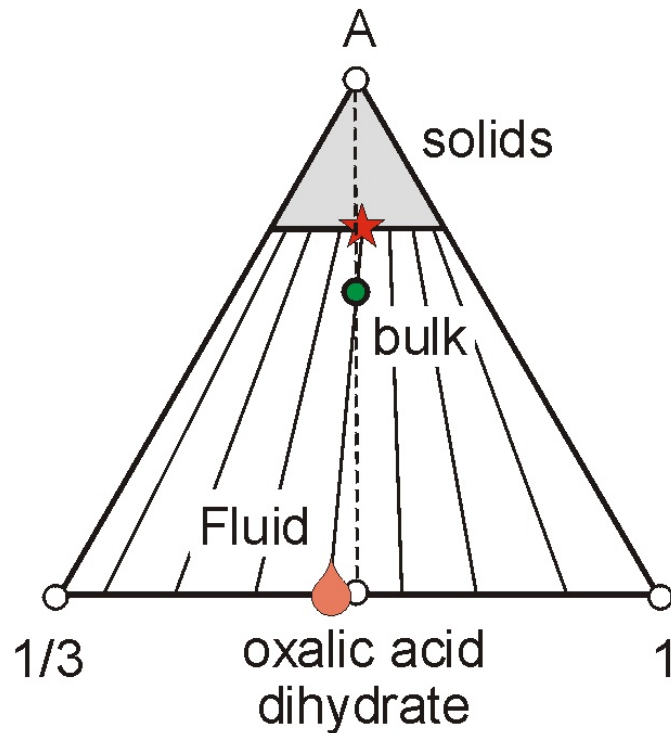
C-O-H: oxalic acid (di-hydrate)

C-O-H-N: guanidine nitrate, ammonium oxalate



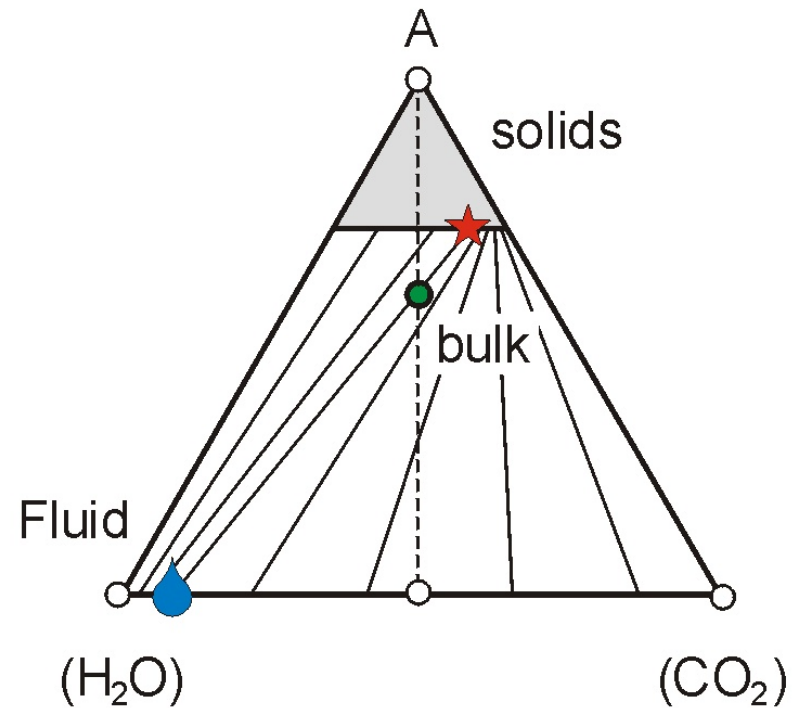
adding mixed fluids differs from adding pure H₂O (assuming at this point that solid dissolution is negligible)

Low pressure



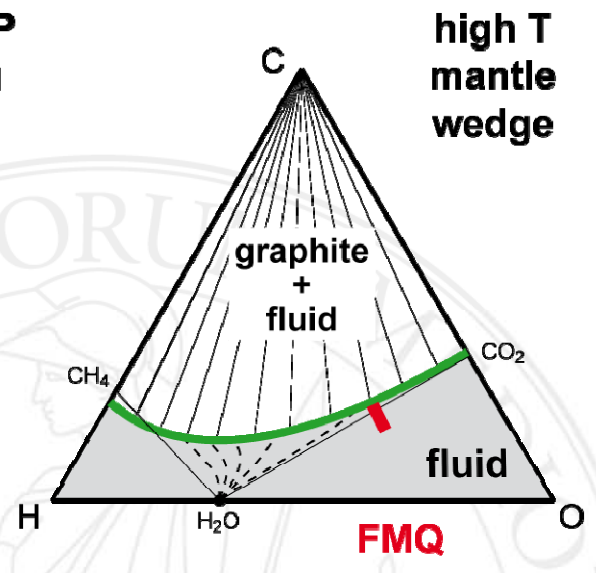
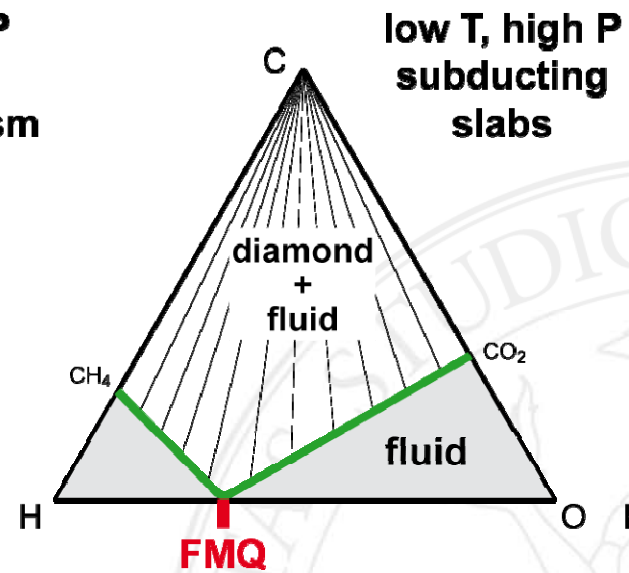
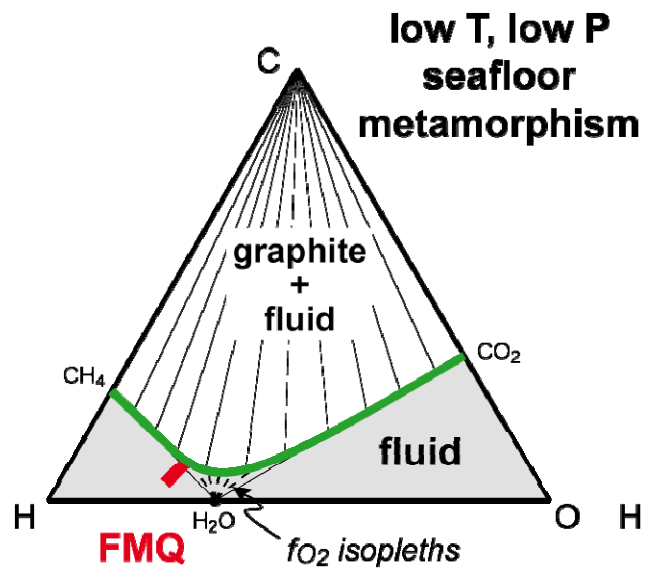
$$X(O) = nO / (nO + nH)$$

High pressure



Molina & Poli, EPSL, 2000





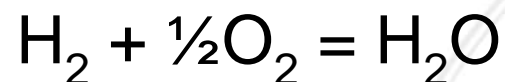
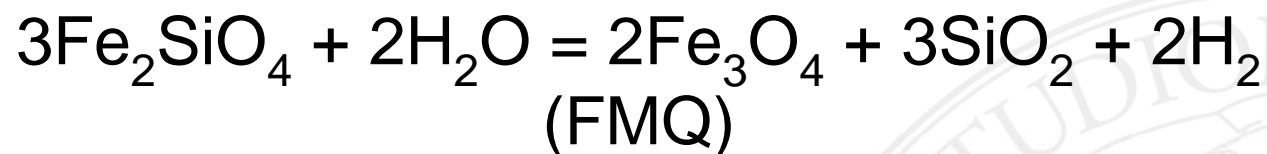
Schmidt & Poli, *Treatise in
Geochem.*, 2nd ed., 2012



Controlling redox conditions

double capsule techniques

“solid buffer” – outer capsule – e.g.



hydrogen membrane (noble metals)

inner capsule – charge + H_2O

$$f\text{O}_2 = (f\text{H}_2\text{O} / f\text{H}_2 \cdot K)$$

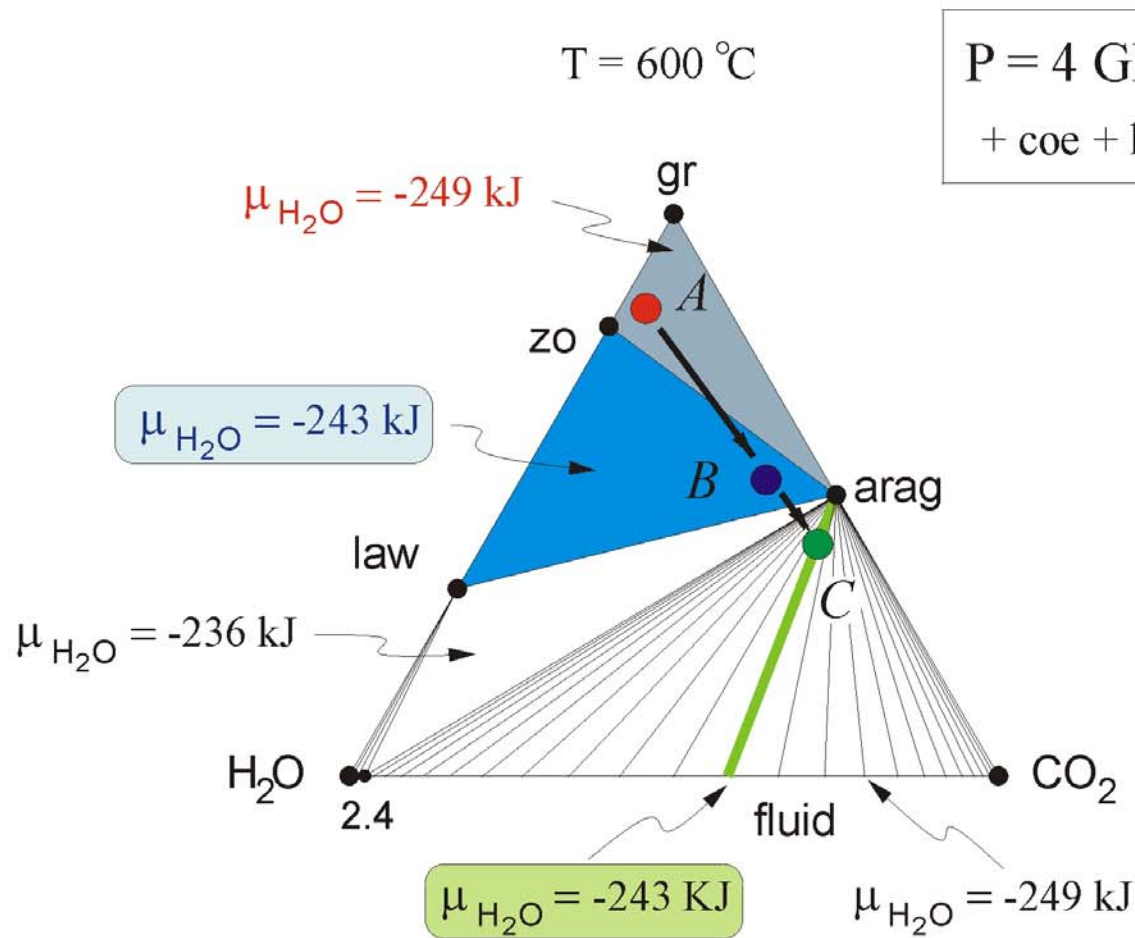


Warning - I

Does an increase in $n\text{CO}_2$ always imply an increase in μCO_2 ? and the appearance of a CO_2 fluid?

NO!





addition of CO₂ increase of $\mu_{\text{H}_2\text{O}}$

$$\mu_{\text{H}_2\text{O}}^{\text{arag-fluid}} = \mu_{\text{H}_2\text{O}}^{\text{law-zo-arag}}$$

"a_{H2O}" in inverse models ?

Poli & Schmidt, CMP 1997

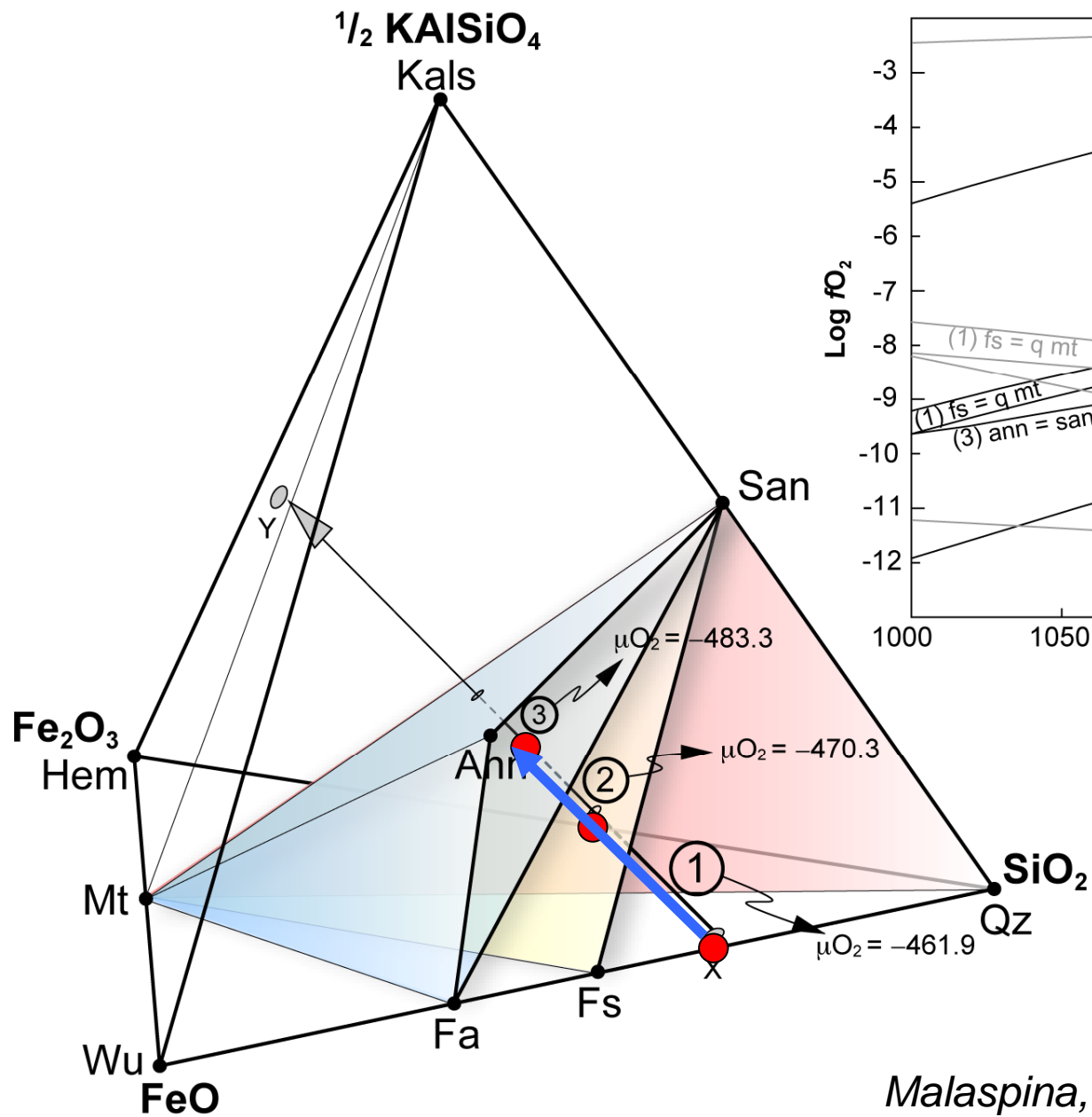


Warning - II

Does an increase in nO_2 always imply an increase in μO_2 ? and therefore do more “oxidized” materials necessarily show higher oxygen fugacities ?

NO!





Malaspina, Poli, Fumagalli J Pet 2009



Approach to equilibrium:

“reversibility”
and
“compositional bracketing”
VS
synthesis



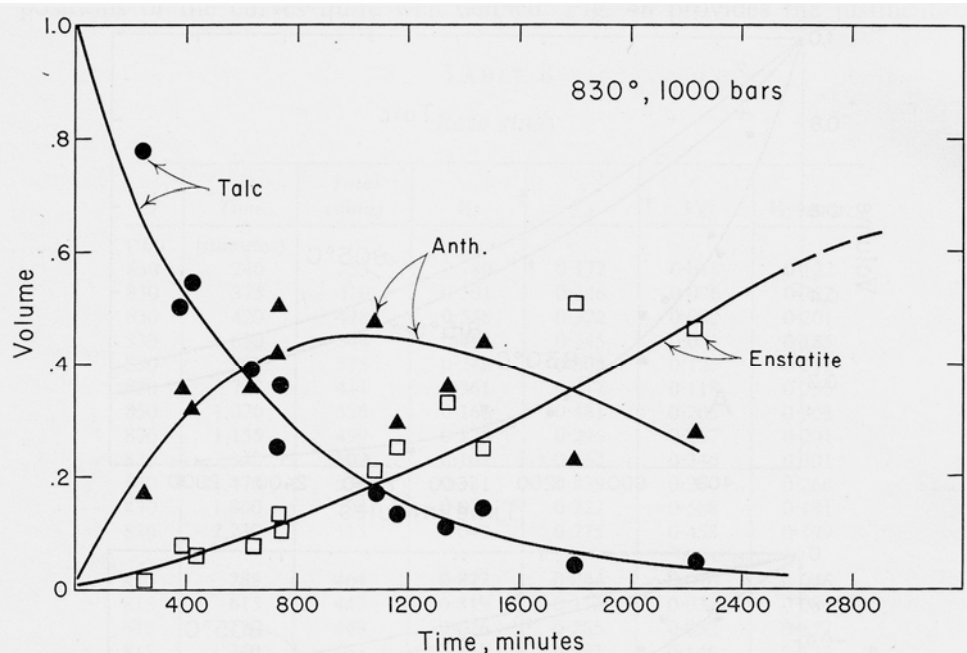


FIG. 5. Volumes of talc, anthophyllite, and enstatite as functions of time at 830°C and 1,000 bars

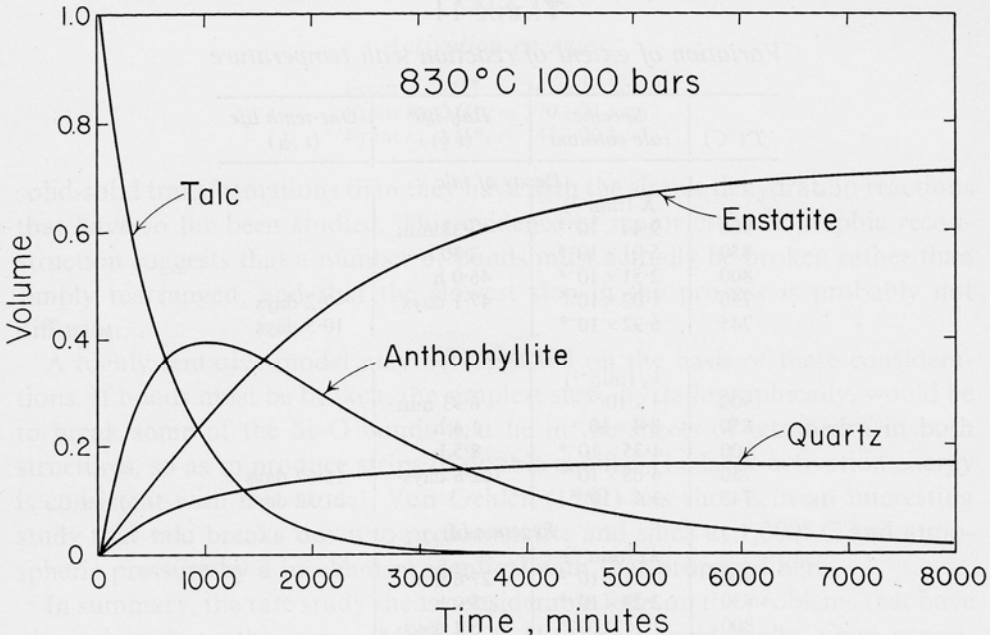
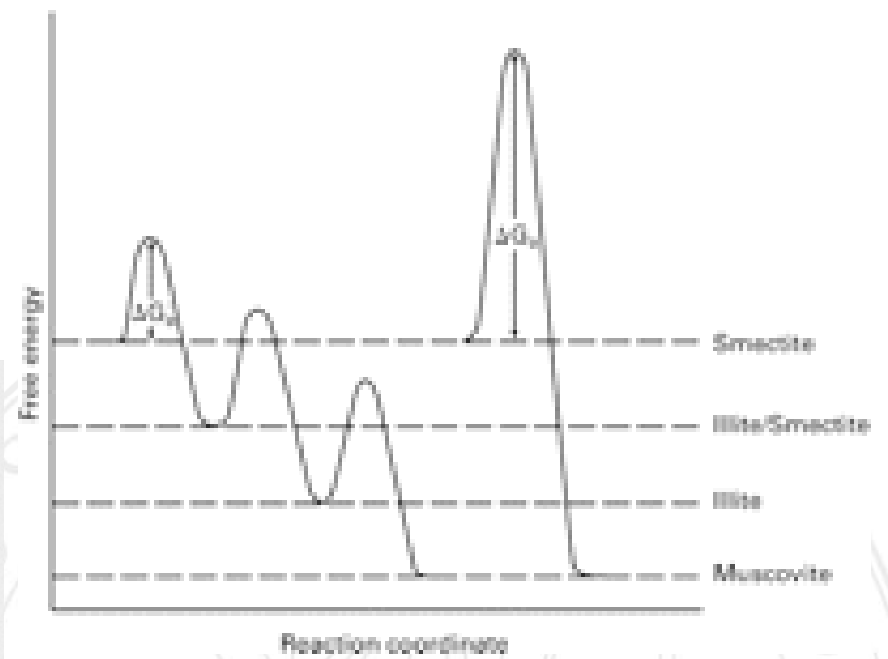


FIG. 7. Volumes of talc, anthophyllite, enstatite, and quartz as functions of time at 830°C and 1,000 bars. Calculated from measured rate constants. The stable assemblage is enstatite plus quartz, but anthophyllite is the most abundant phase between times of 1,000 and 1,500 min.

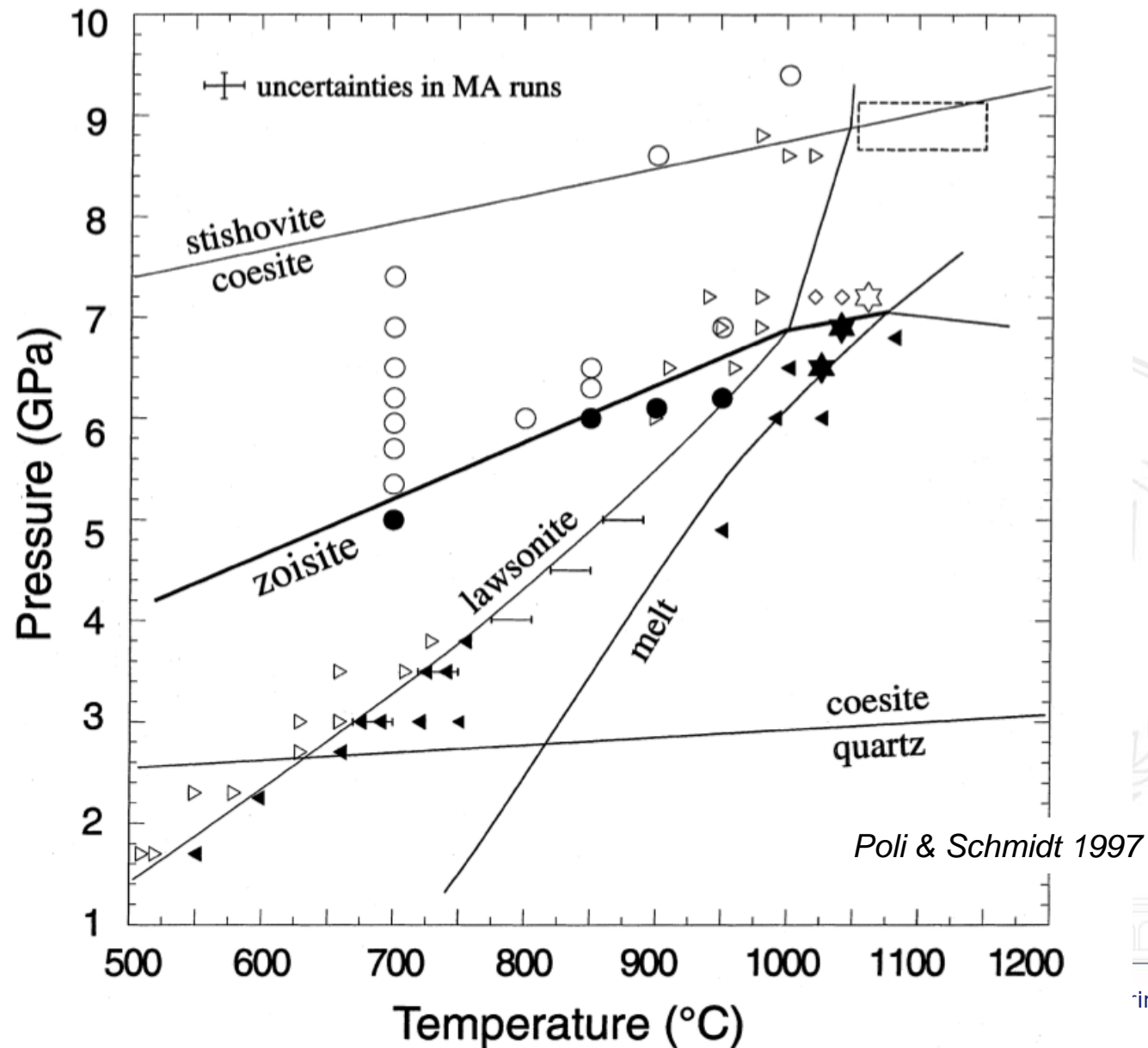
Ostwald step rule



Greenwood JPet 1963



“bracketing” phase-fields for compounds having **fixed** composition.

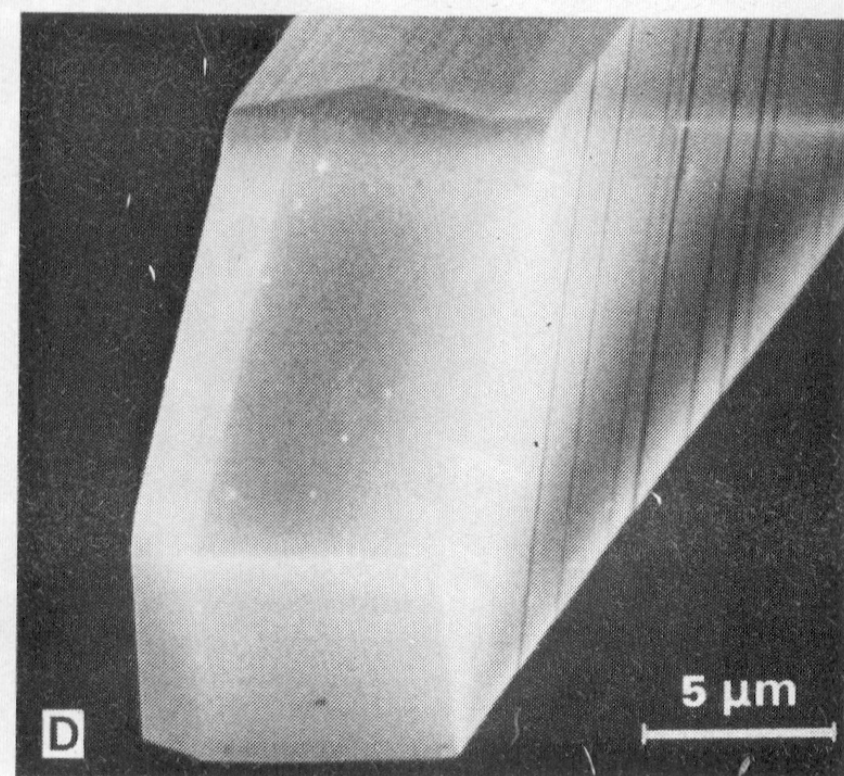
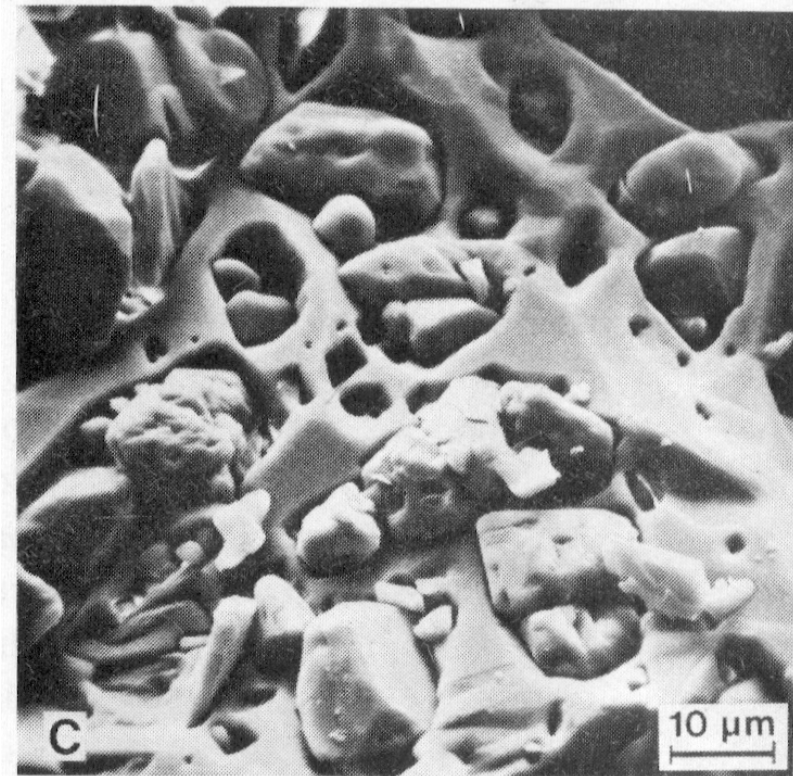


imentale



UNIVERSITÀ
DIPARTIMENTO

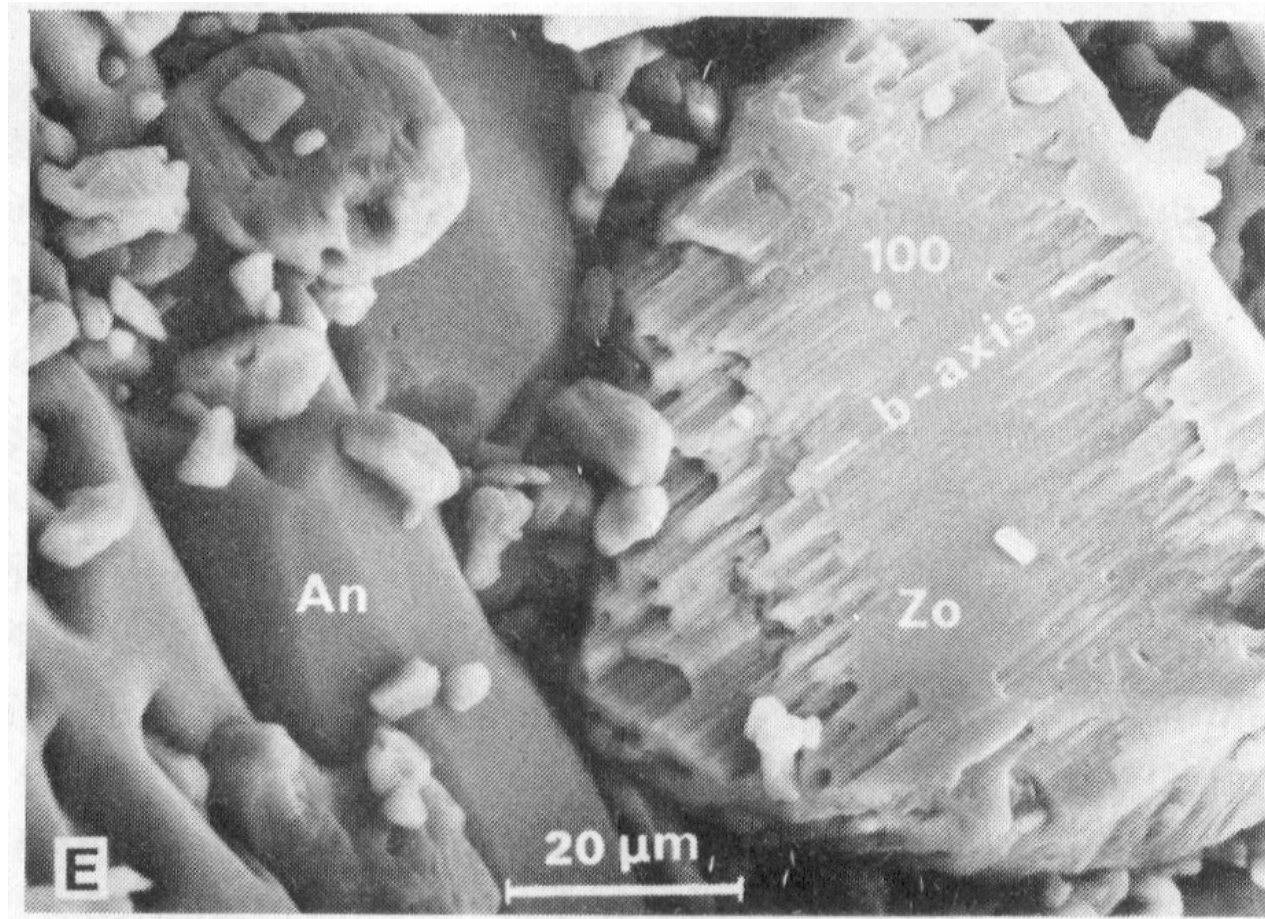
growth features



Allen & Fawcett 1982



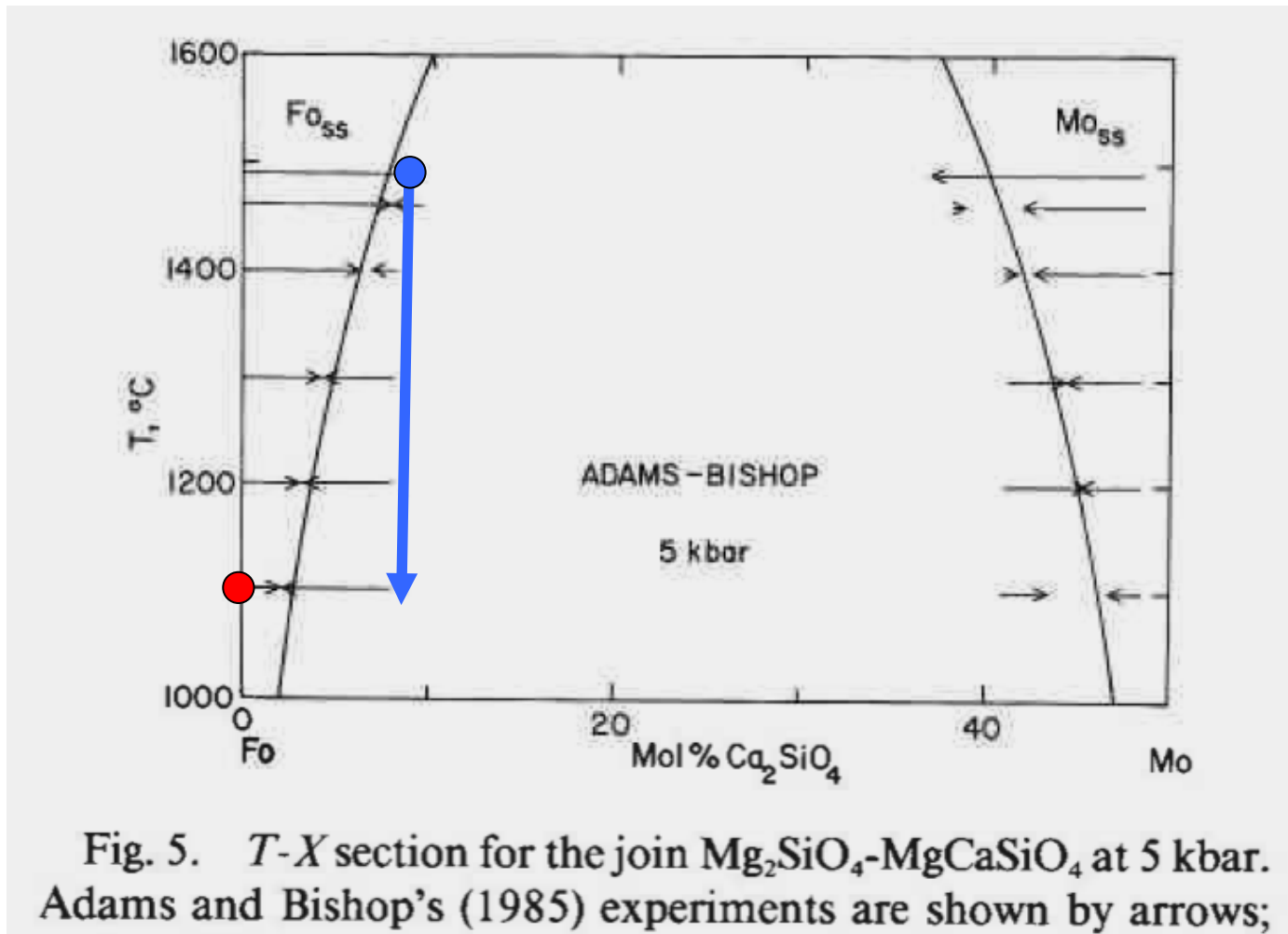
dissolution - etch striae



Allen & Fawcett 1982



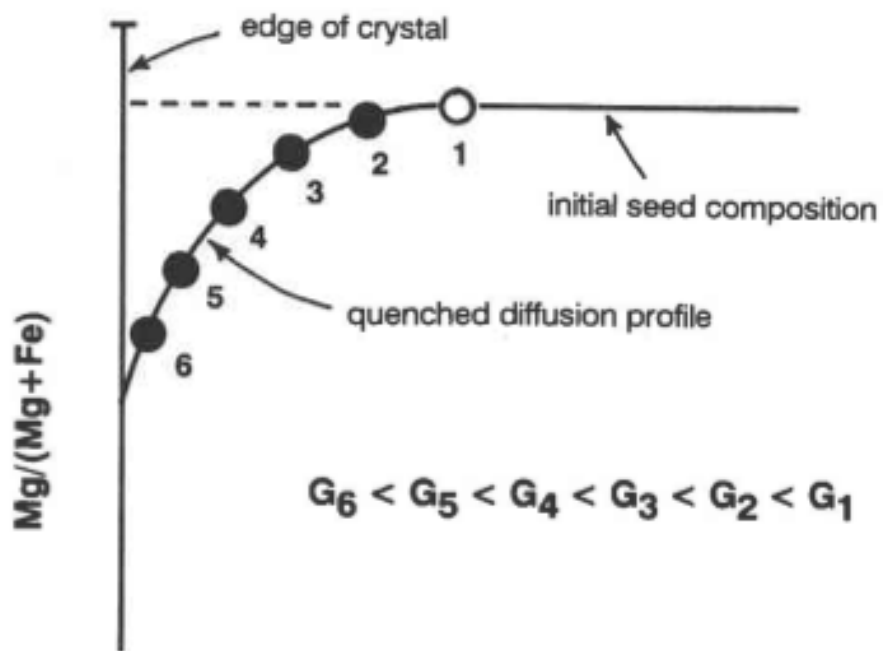
working with solid **solutions**...



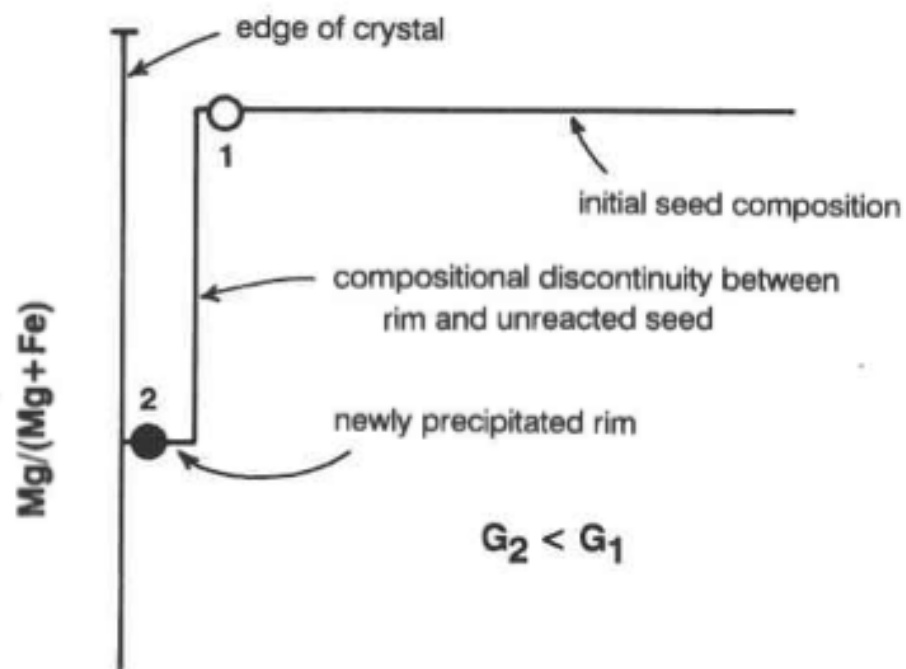
Davidson & Lindsley, Am Min 1989



A. DIFFUSION



B. SOLUTION-PRECIPITATION



“synthesis”



“Dirty systems”

large number of chemical components

phase relationships dominated by solid solutions

continuous reactions >> discontinuous reactions

sensitive to variable oxidation state

sensitive to variable amounts of volatiles



Disadvantages

models are semi-quantitative or qualitative

intrinsic difficulty in “bracketing”

low reaction rates

poorly known fluid speciation



Advantages

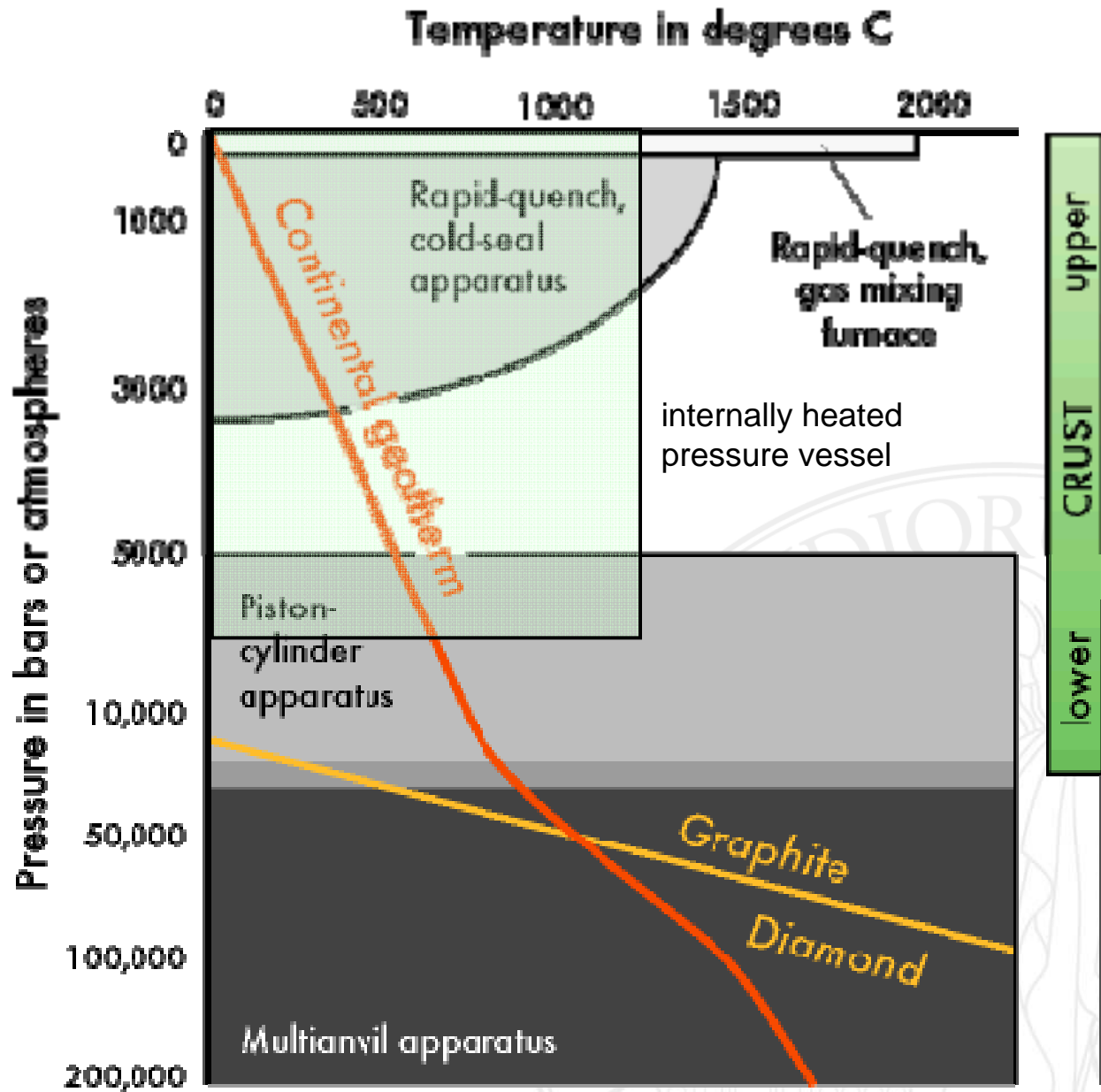
approach to natural systems

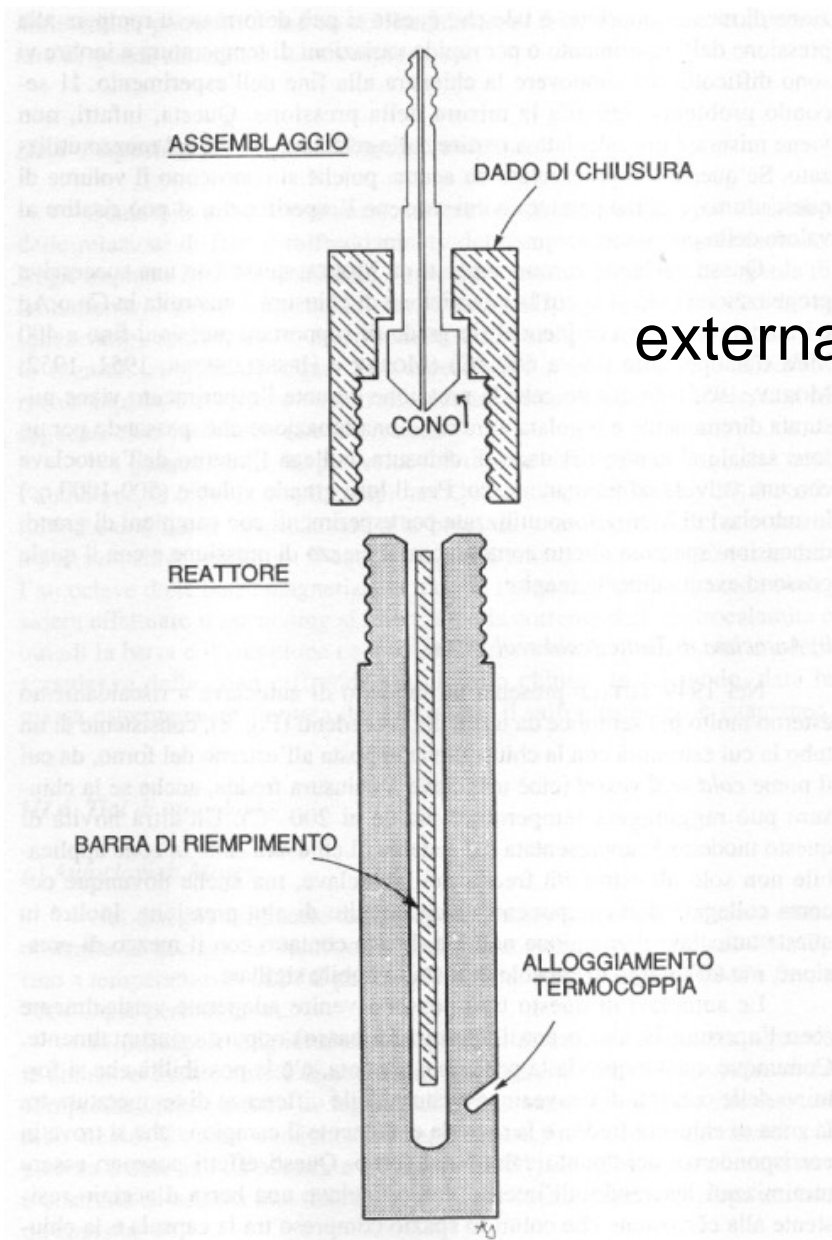
phase assemblages and phase compositions

textural information

*fill the gap between phase diagrams based on
“evaluated” thermodynamic data (e.g. mica-,
chlorite-, amphibole-bearing) and experimentally
determined diagrams in simple systems*



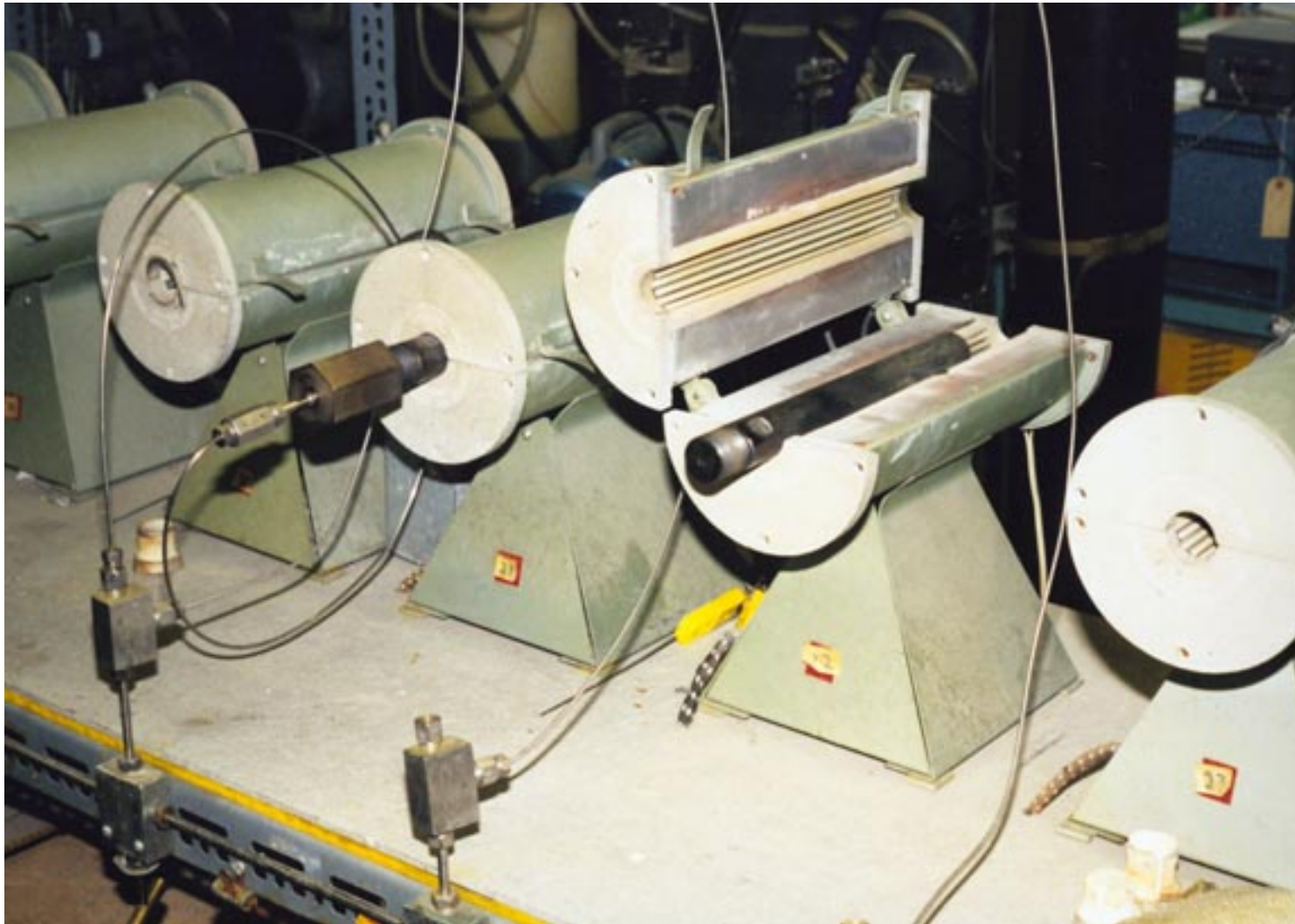




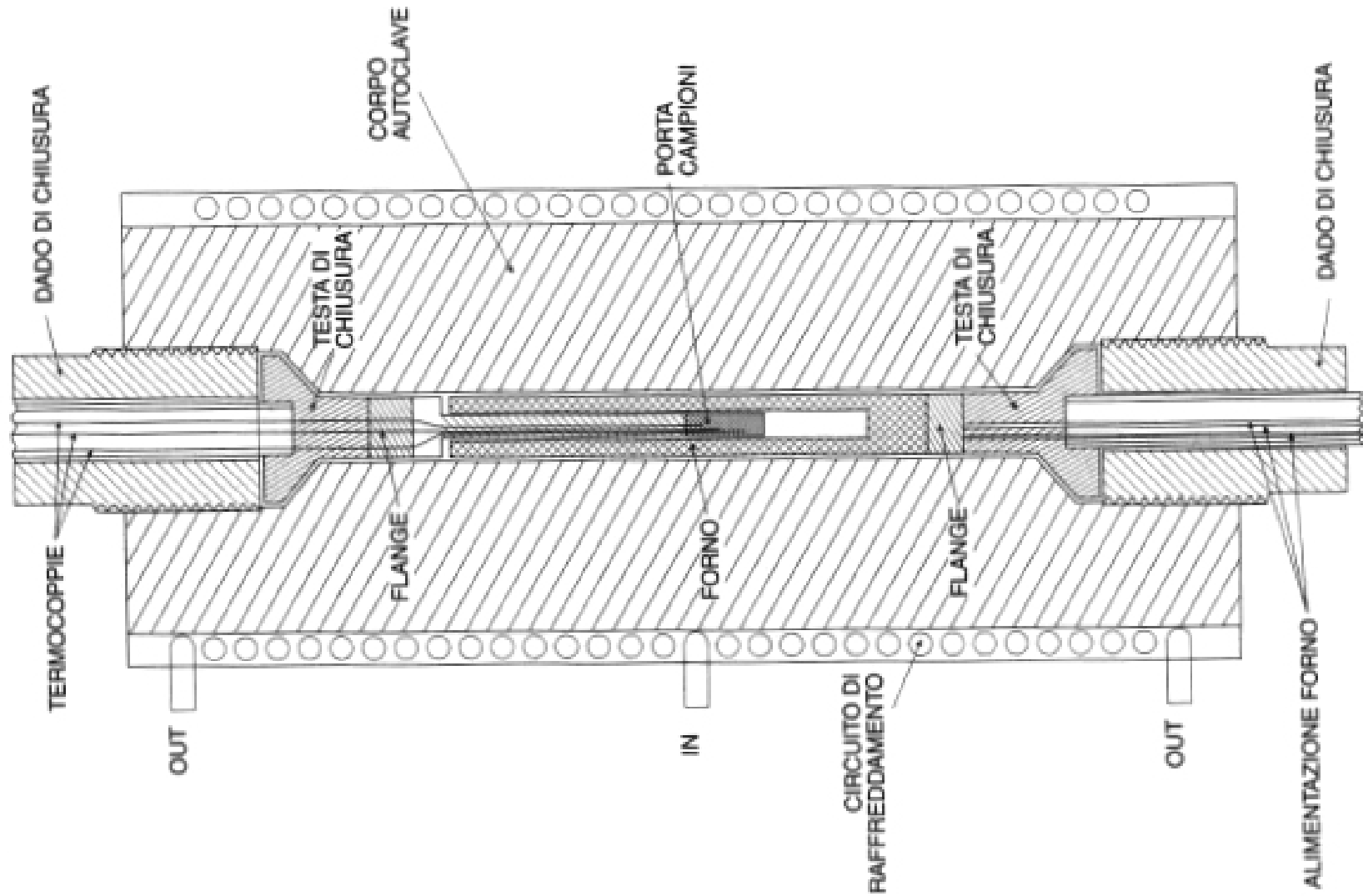
externally heated pressure vessel
“cold-seal”

Figura 8. Autoclave a riscaldamento esterno tipo Tuttle. Sezione trasversale e dispositivo di chiusura.





internally heated pressure vessel “cold-seal”

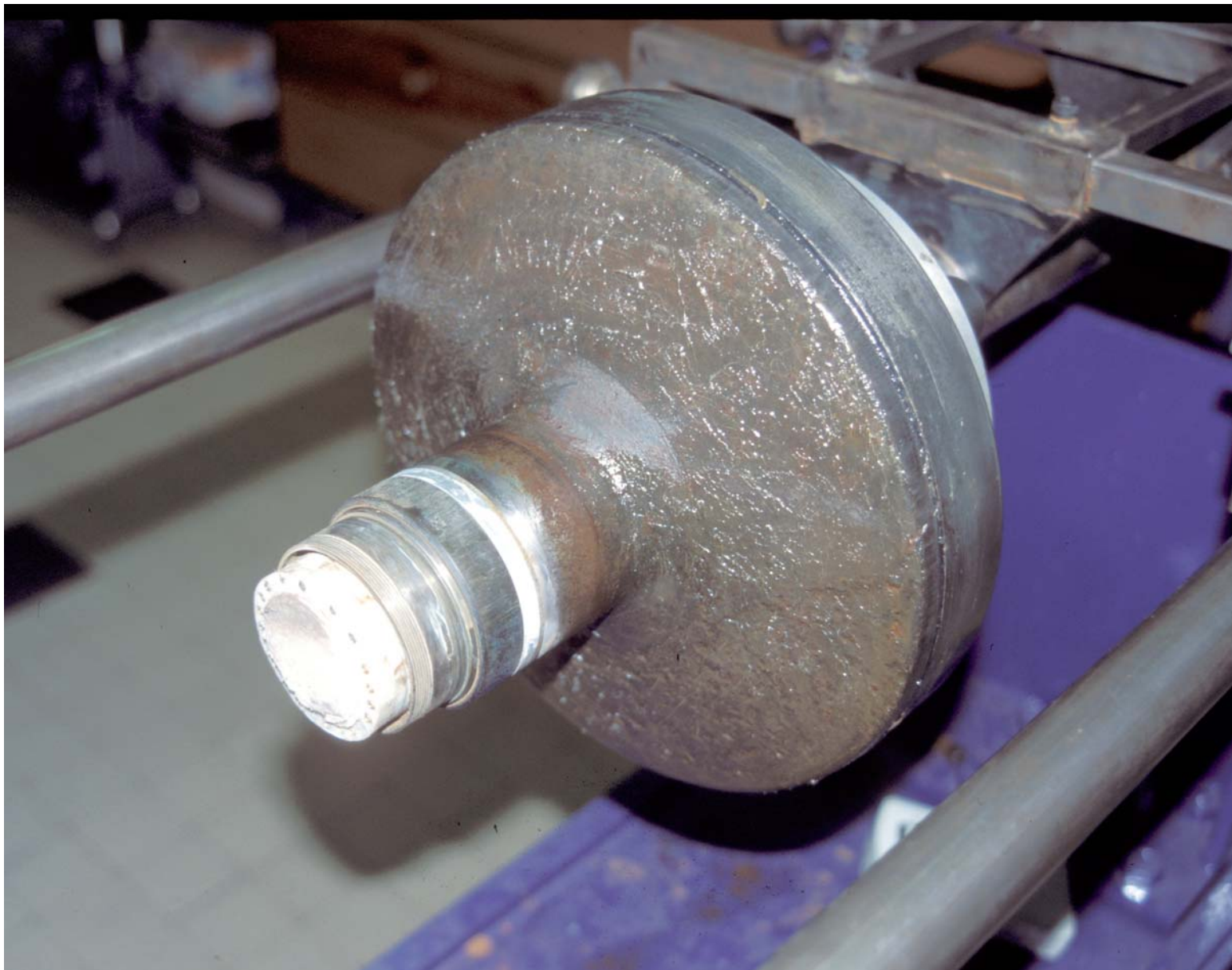




UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO SCIENZE DELLA TERRA

Laboratorio di Petrologia Sperimentale



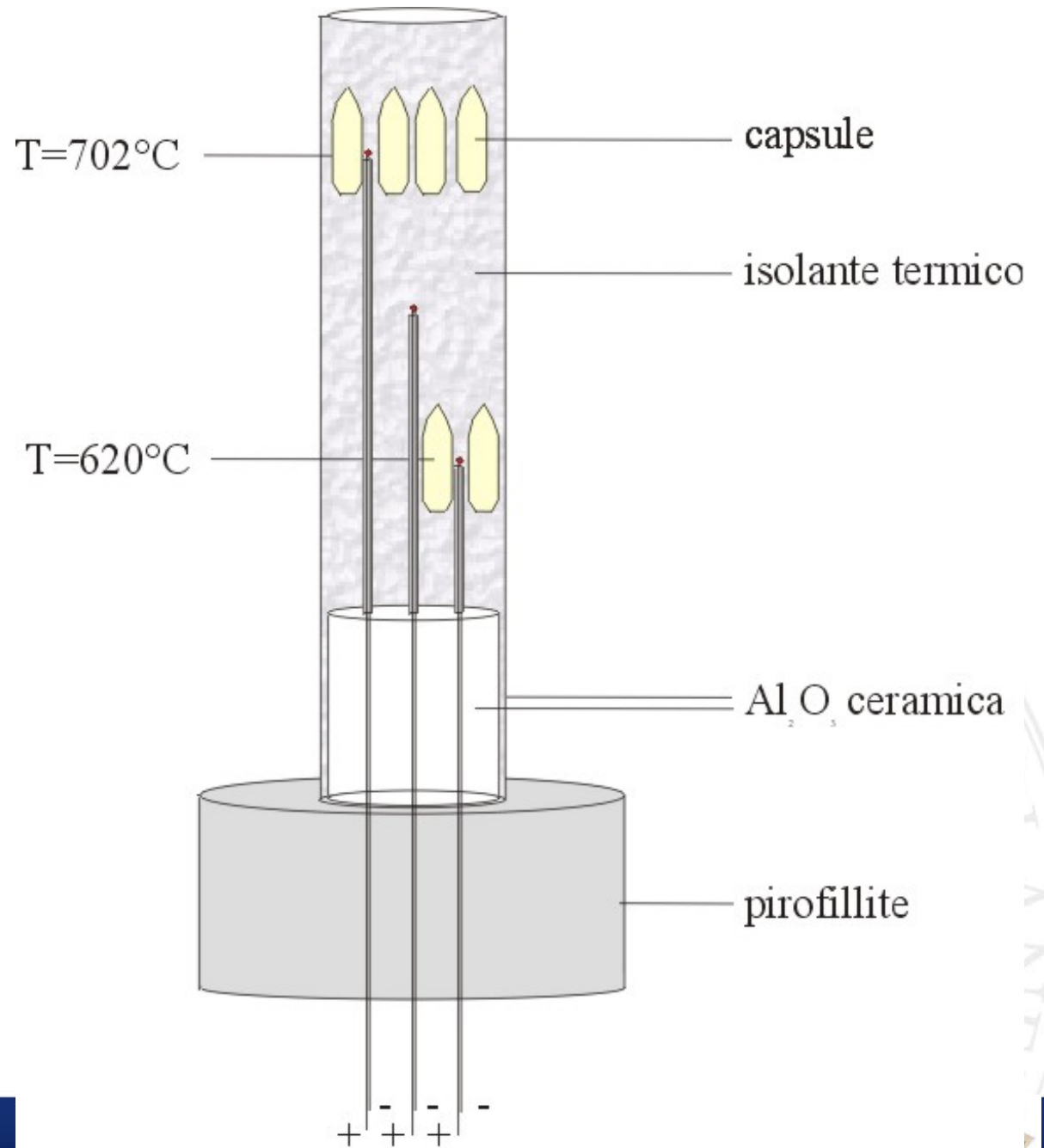
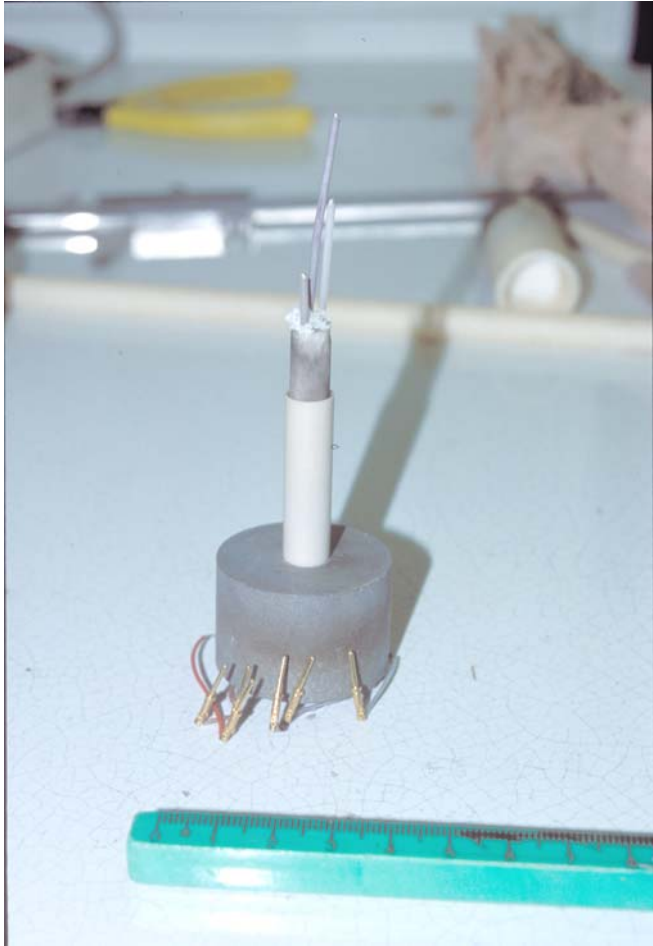


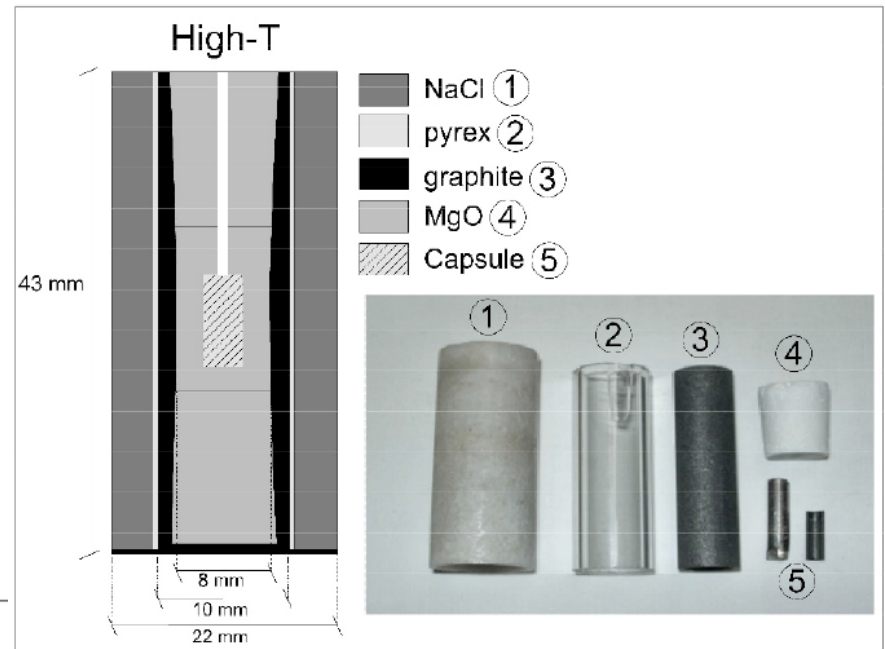
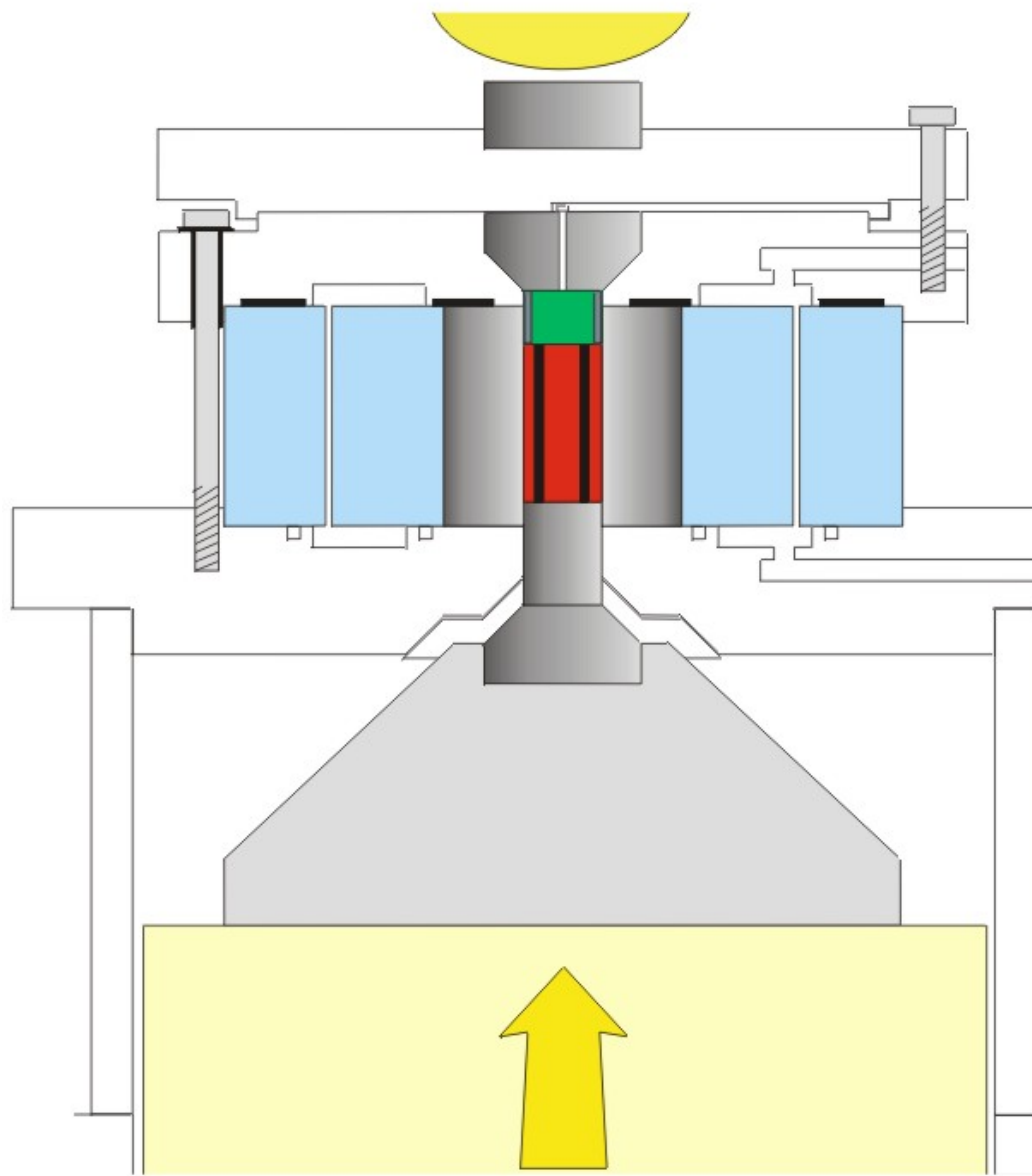
UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO SCIENZE DELLA TERRA

Laboratorio di Petrologia Sperimentale





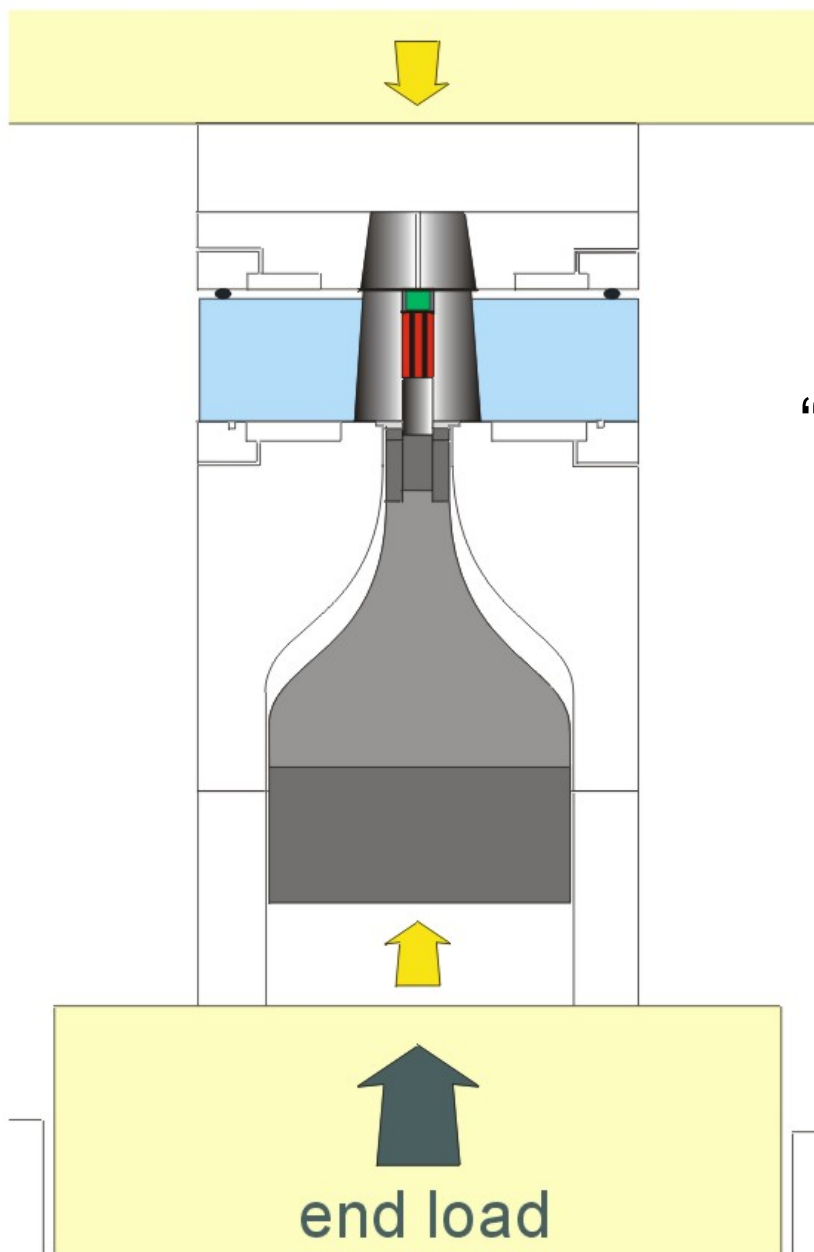




“single-stage” piston cylinder

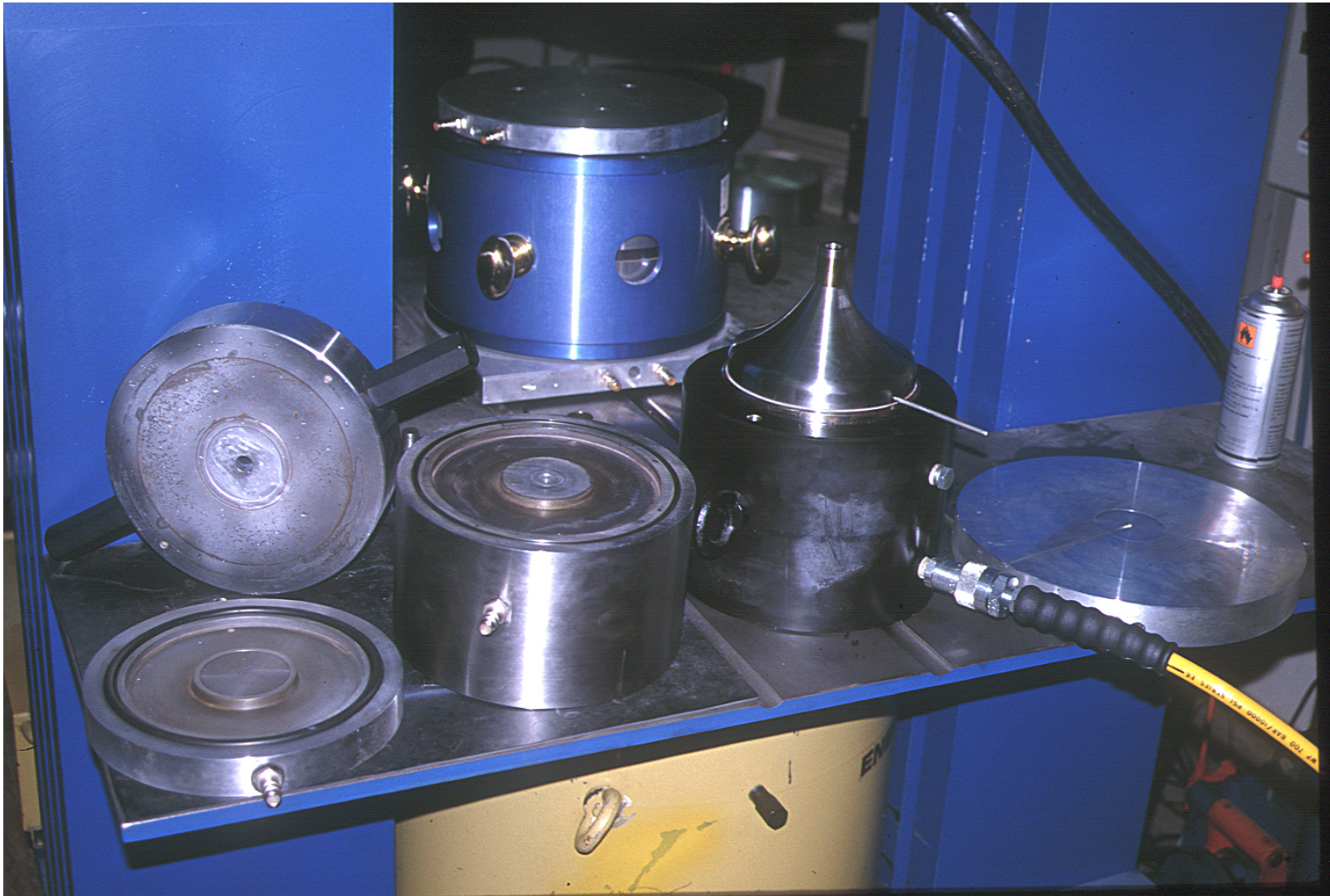






“end-loaded” piston cylinder





UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO SCIENZE DELLA TERRA

Laboratorio di Petrologia Sperimentale

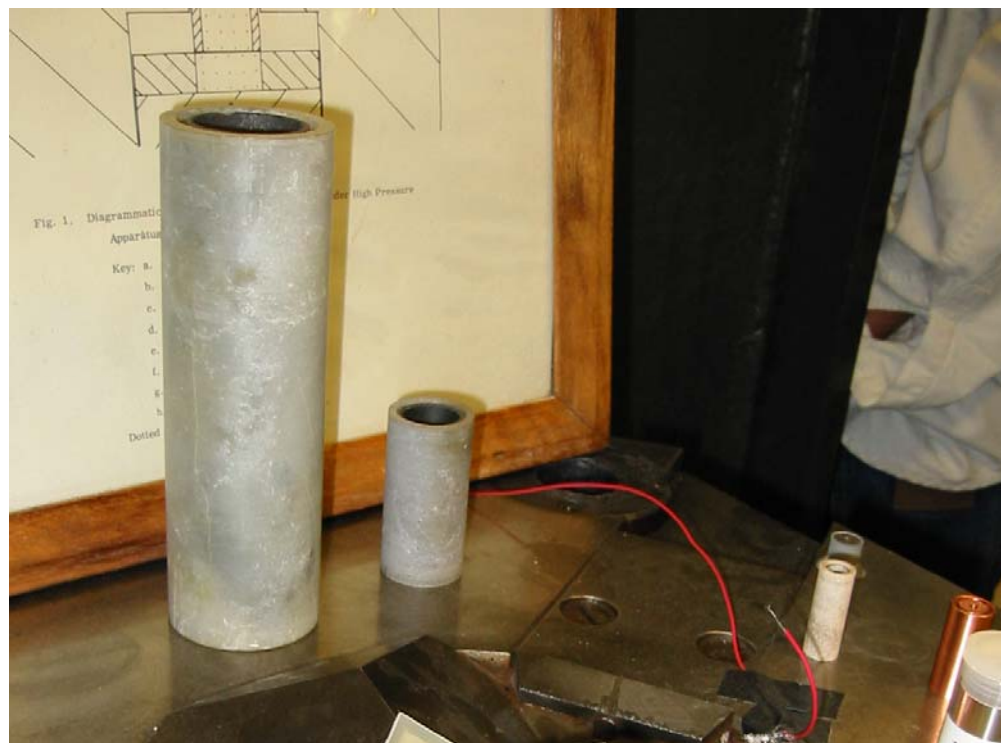




UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO SCIENZE DELLA TERRA

Laboratorio di Petrologia Sperimentale



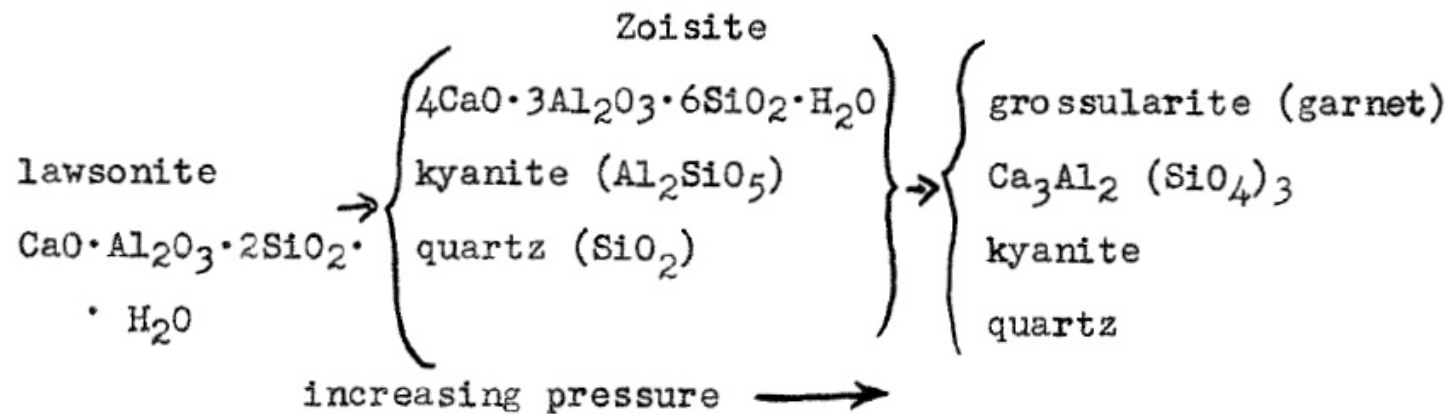


H. Tracy Hall, General Electric, 1954

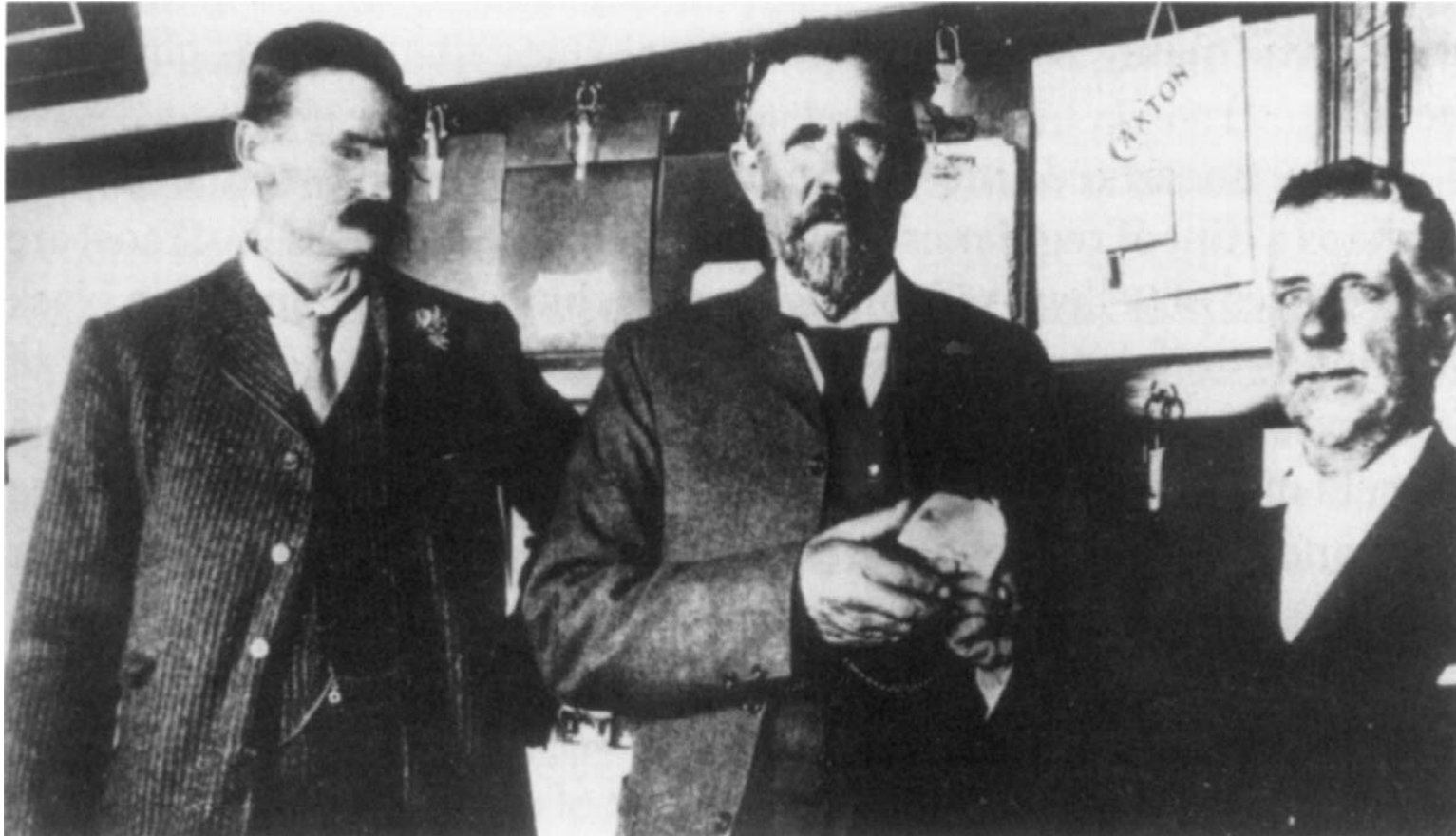
This is a Class 4 technical report. Its distribution in the General Electric Company is highly restricted. It may not be sent outside the United States.

Coes said that he didn't wish to discuss the high-pressure, high-temperature equipment because of intention to publish that information soon.

Coes avoided questioning by not appearing until time for his paper to start and by "having to catch a plane to Worcester" as soon as it was over.



il diamante Cullinan: 3106 carati



Hazen 1999



UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO SCIENZE DELLA TERRA

Laboratorio di Petrologia Sperimentale



Baltzar von Platen, Erik Lundblad ed il progetto QUINTUS ad ASEA, Svezia

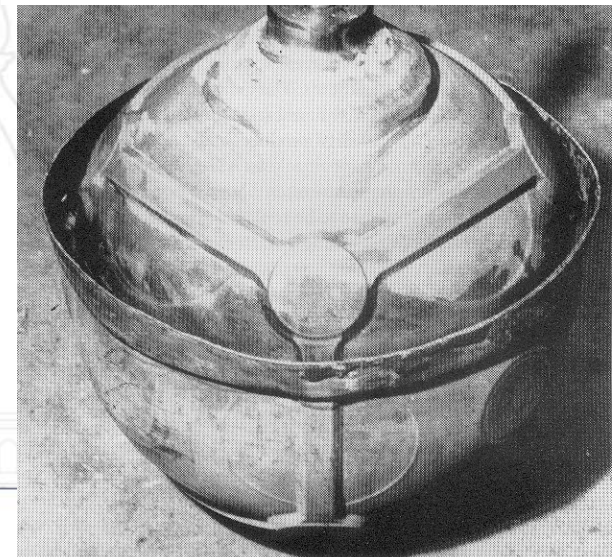
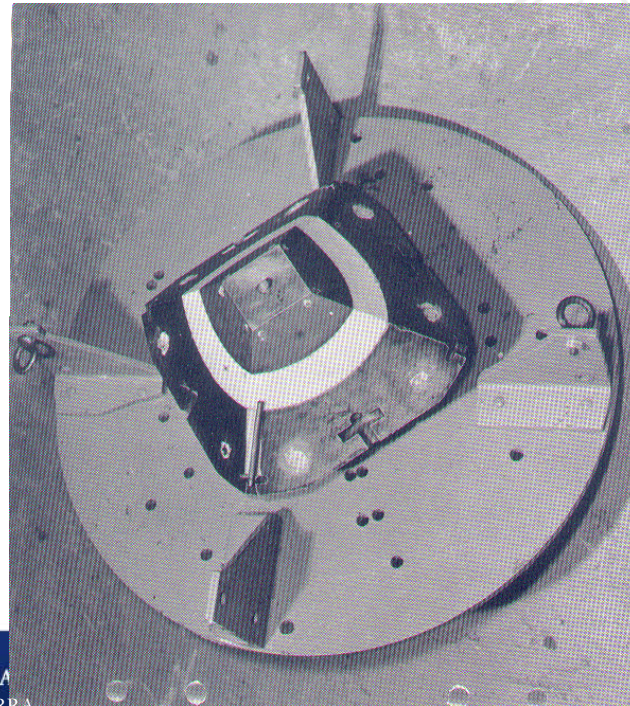




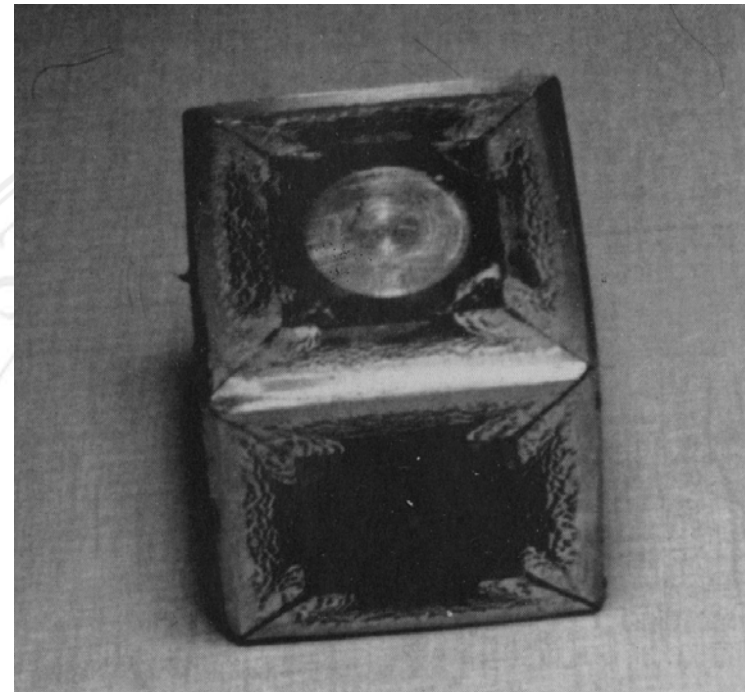
dal frigorifero a gas ...



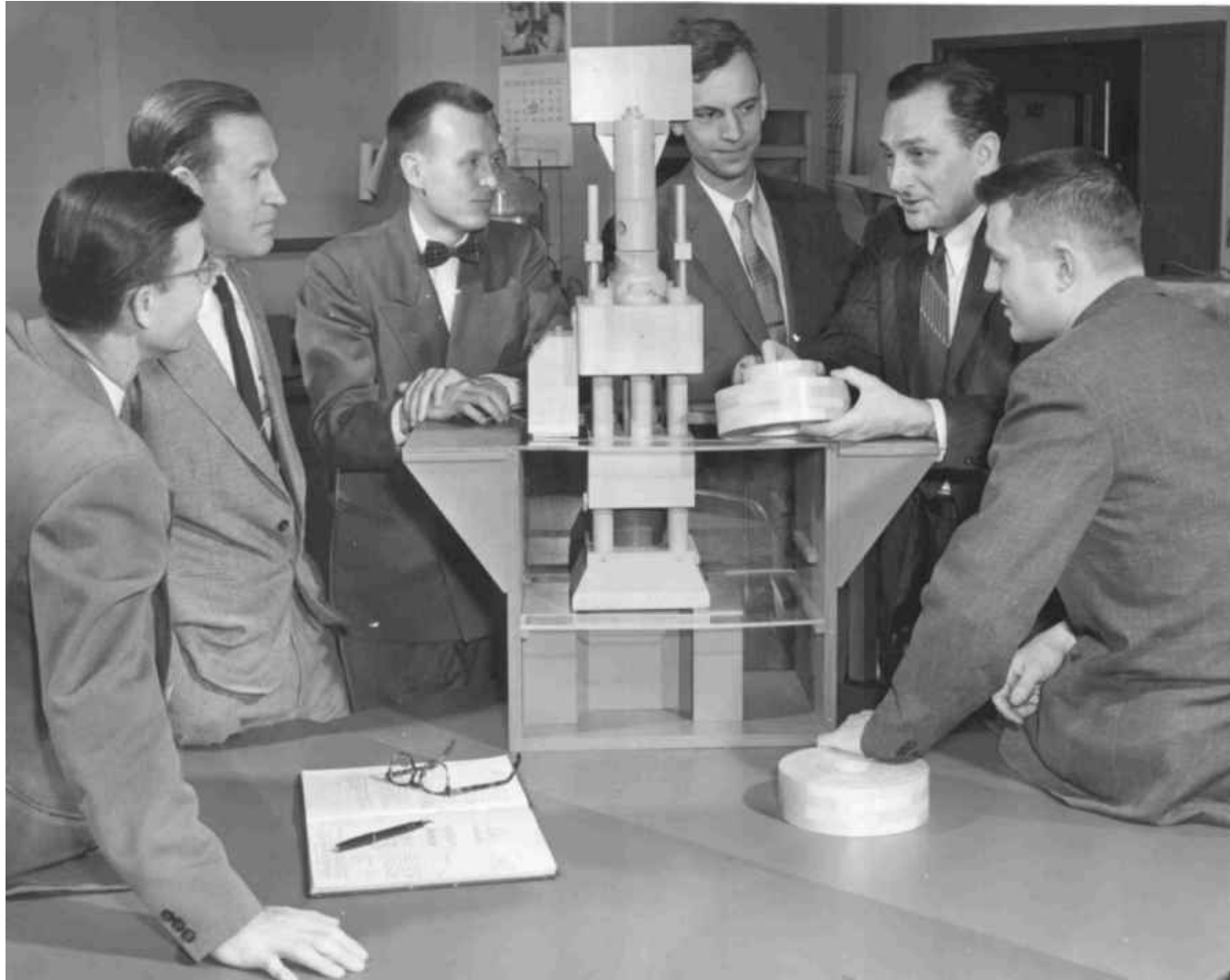
... all'incudine sferica



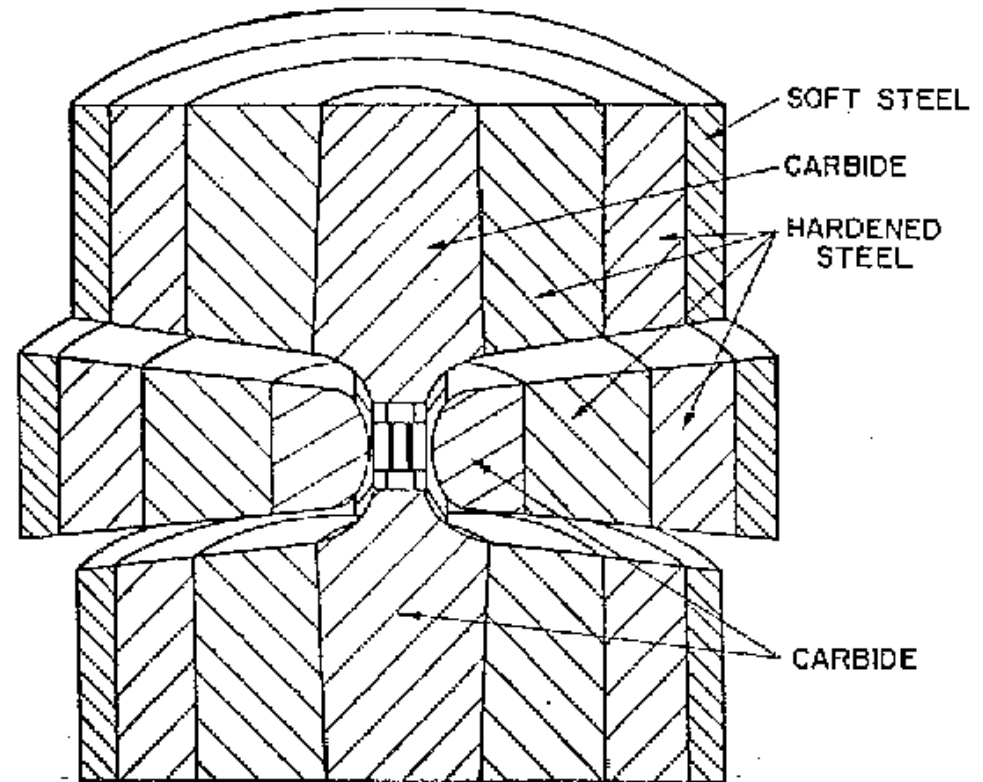
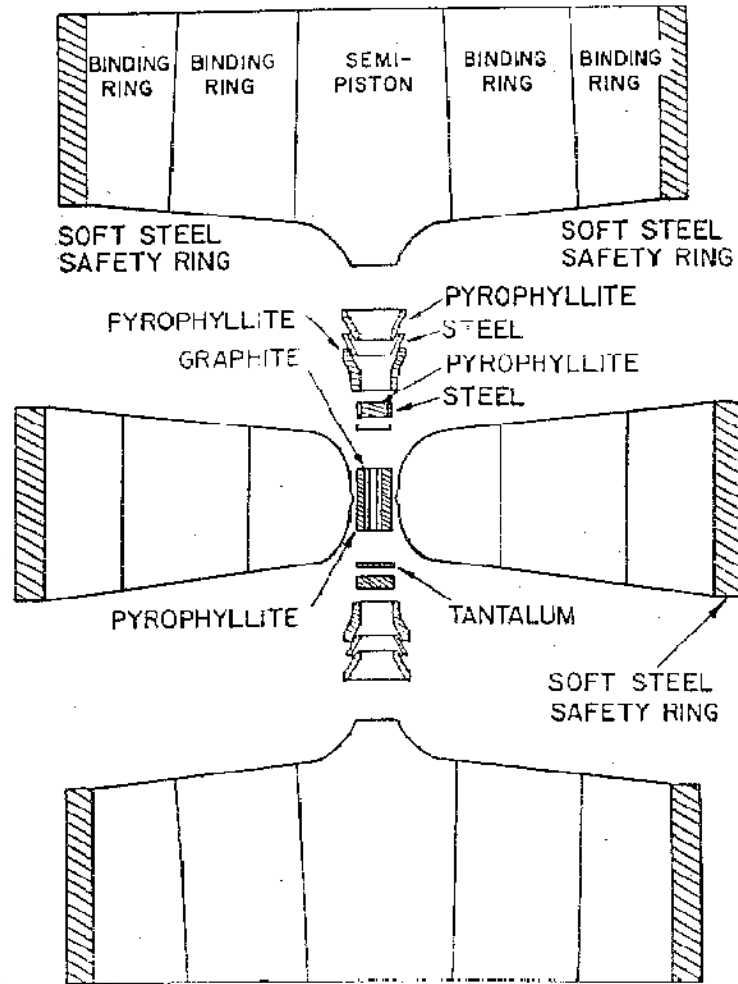
16 Febbraio 1953
50000 bar,
“fuoco” di thermite



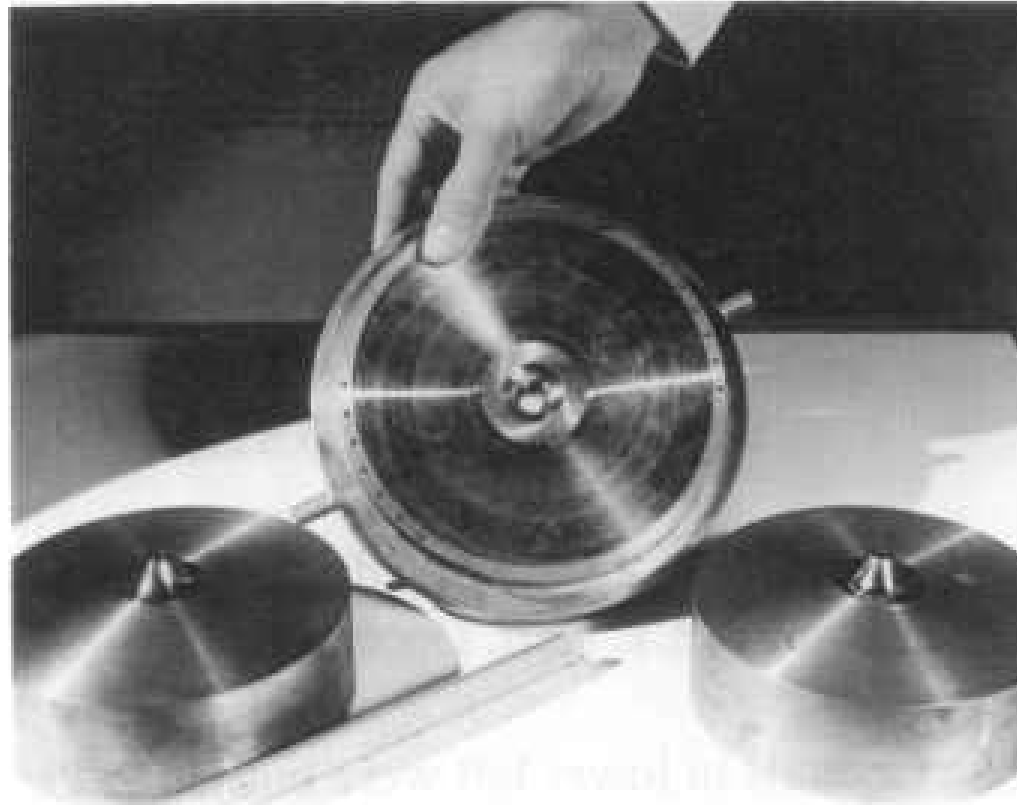
“DIAMOND MAKERS” General Electric, 1955



L'apparato BELT

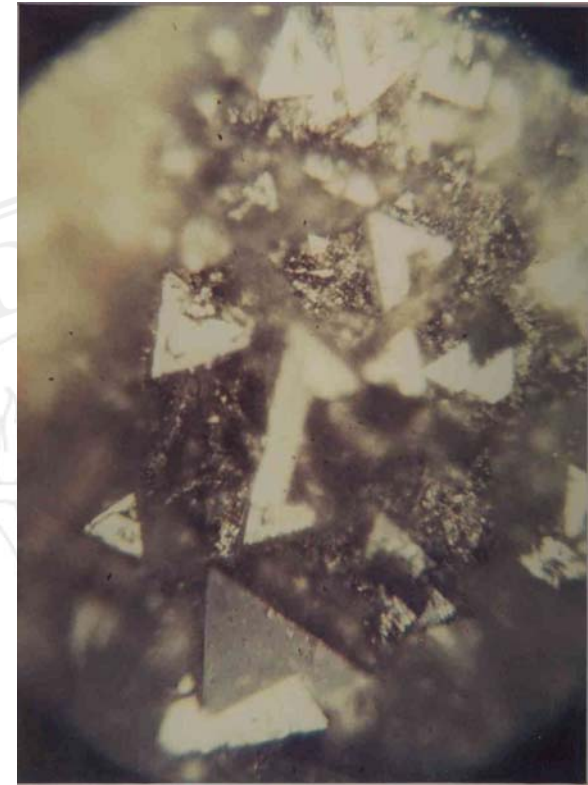


L'apparato BELT

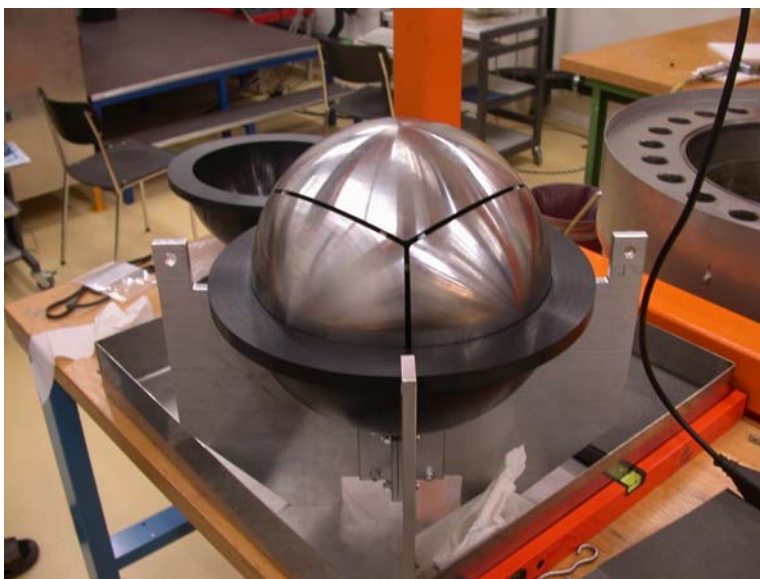
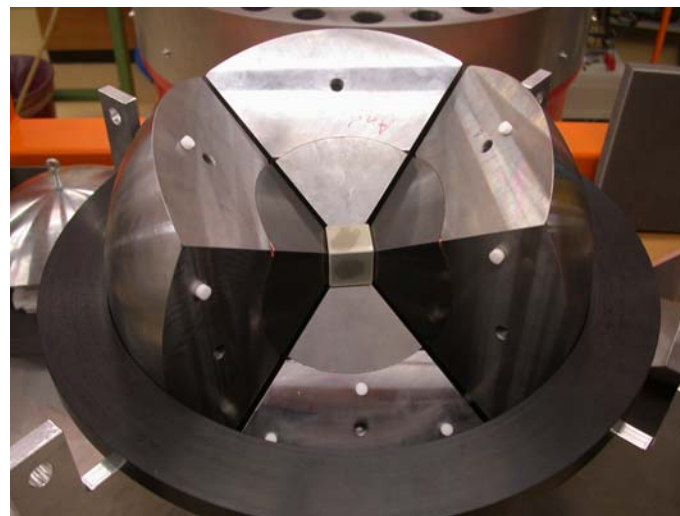
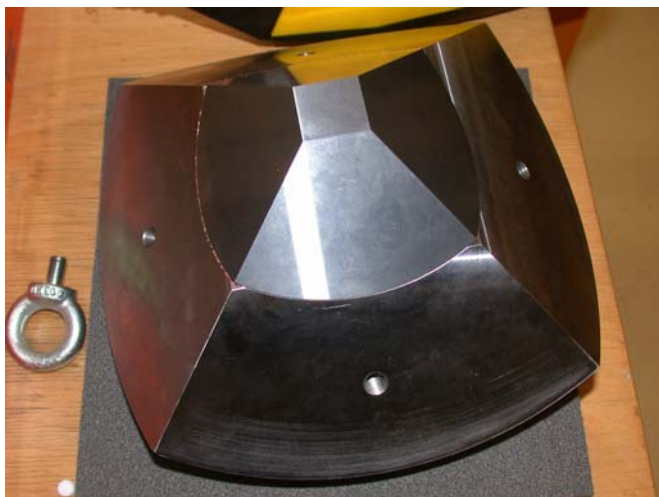




16 Dicembre 1954



La multi-incudine “split-sphere” a IMP-ETH, Zurigo

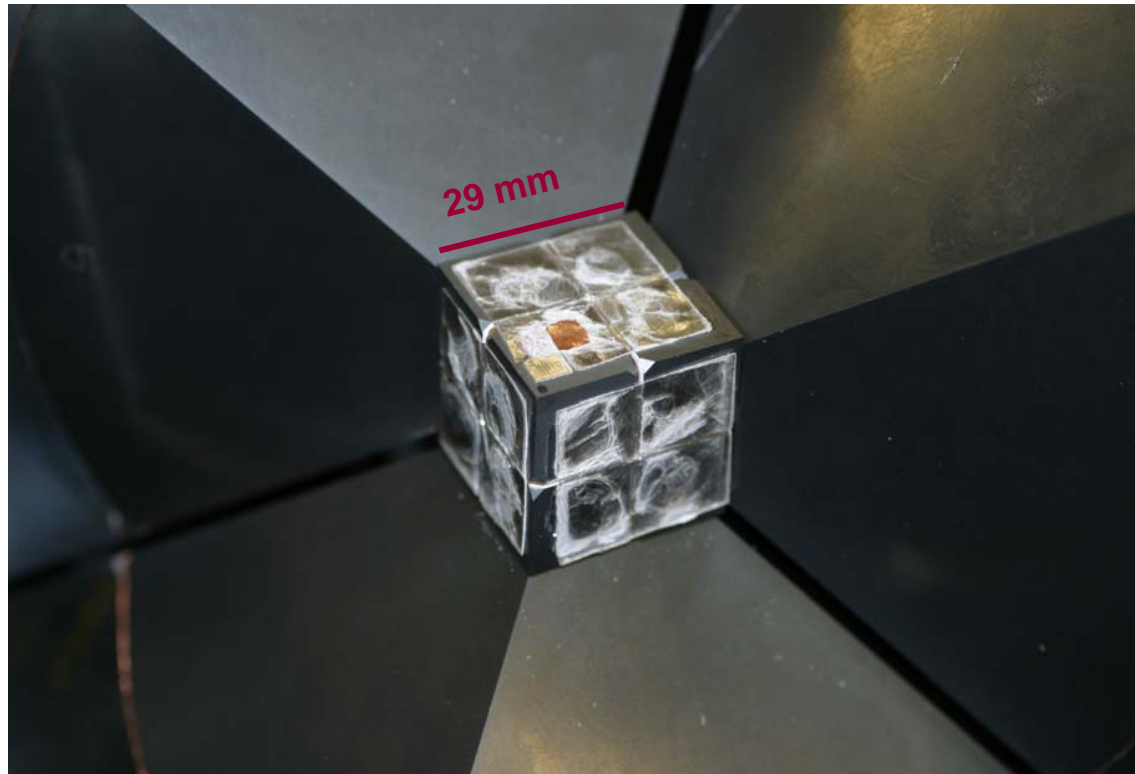
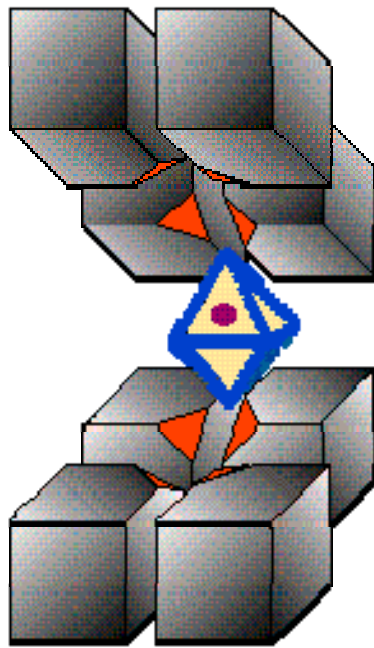


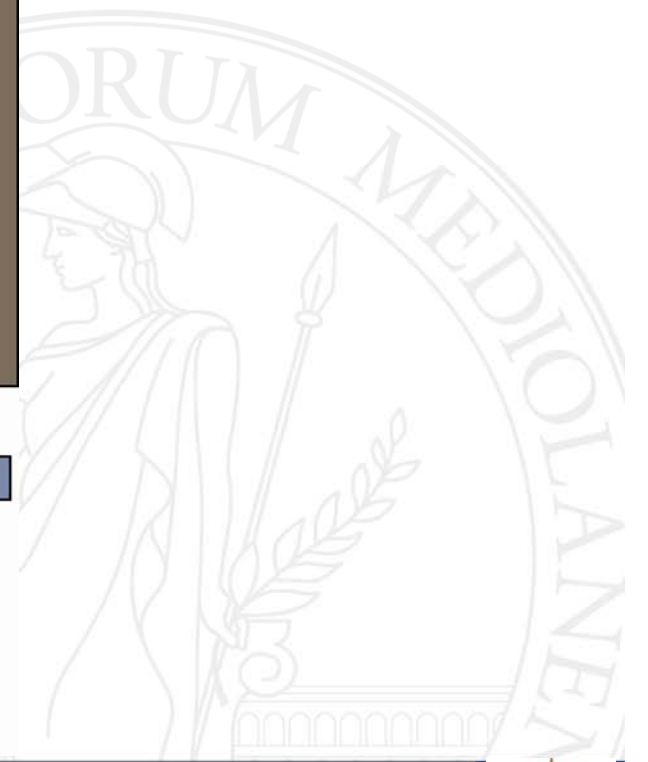
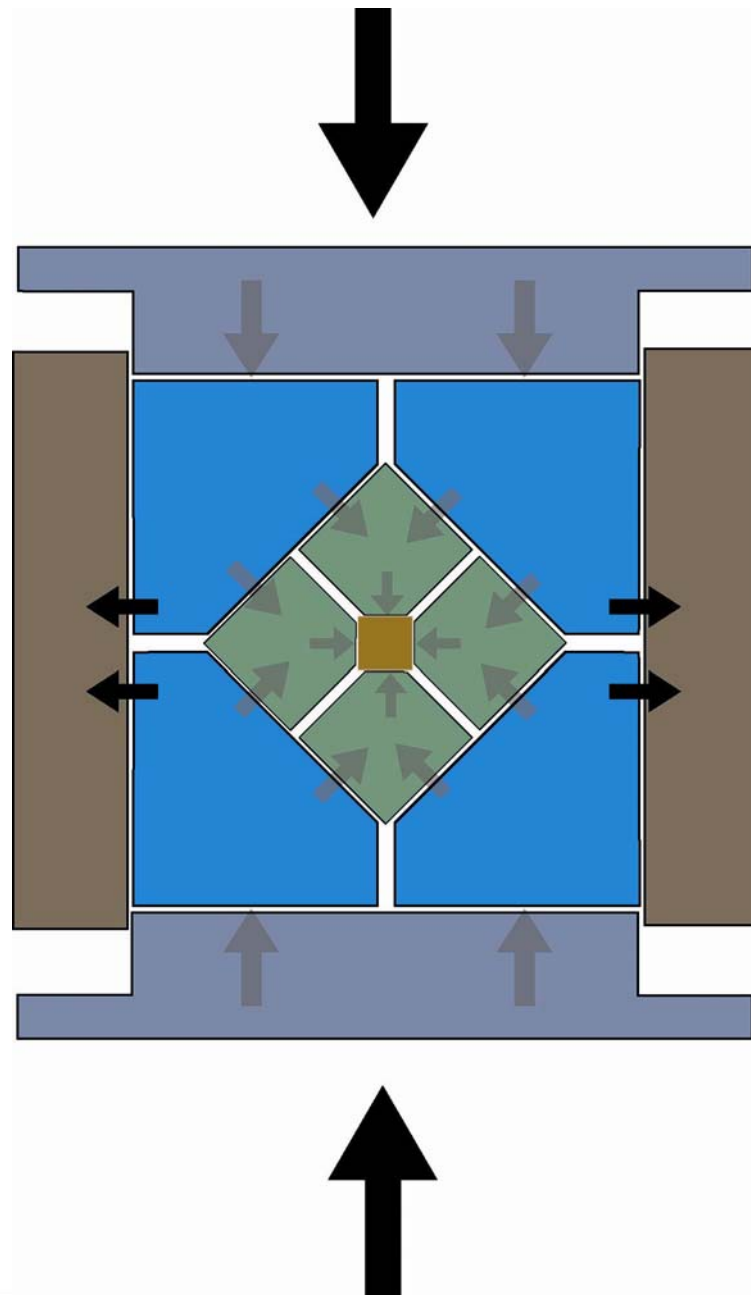


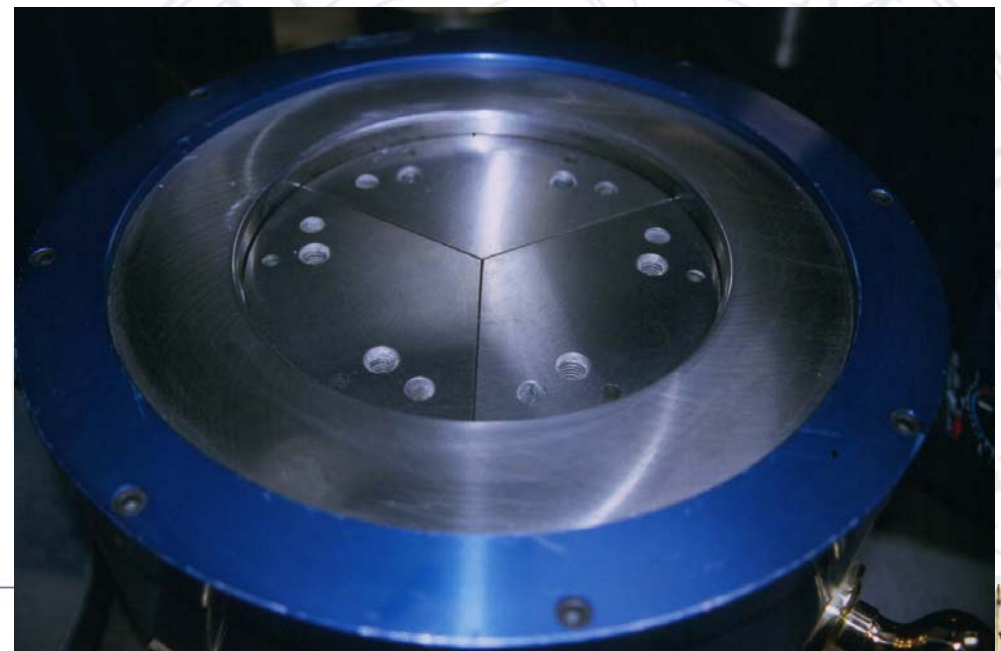
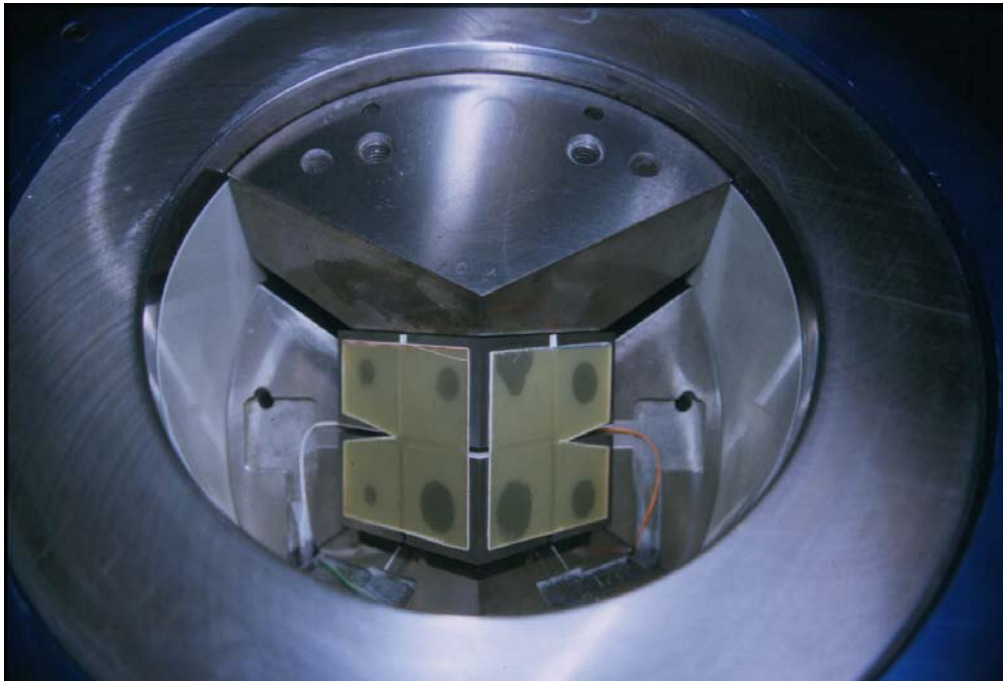
UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO SCIENZE DELLA TERRA

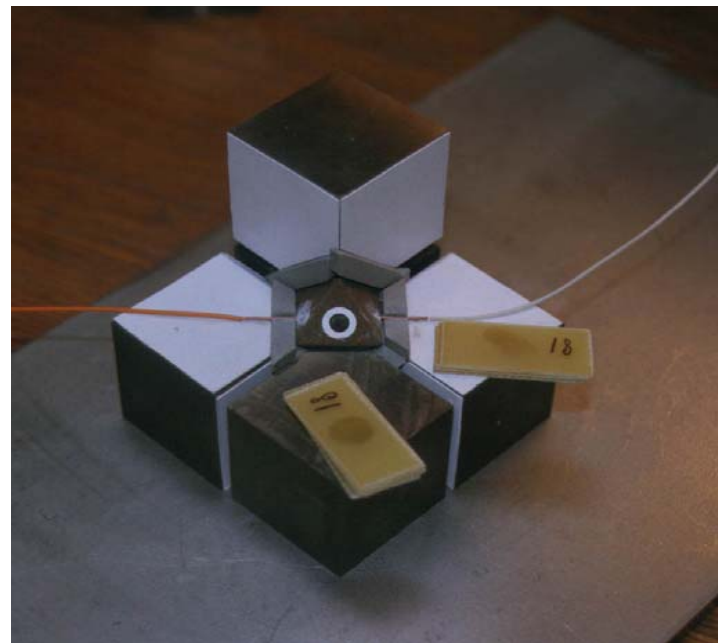
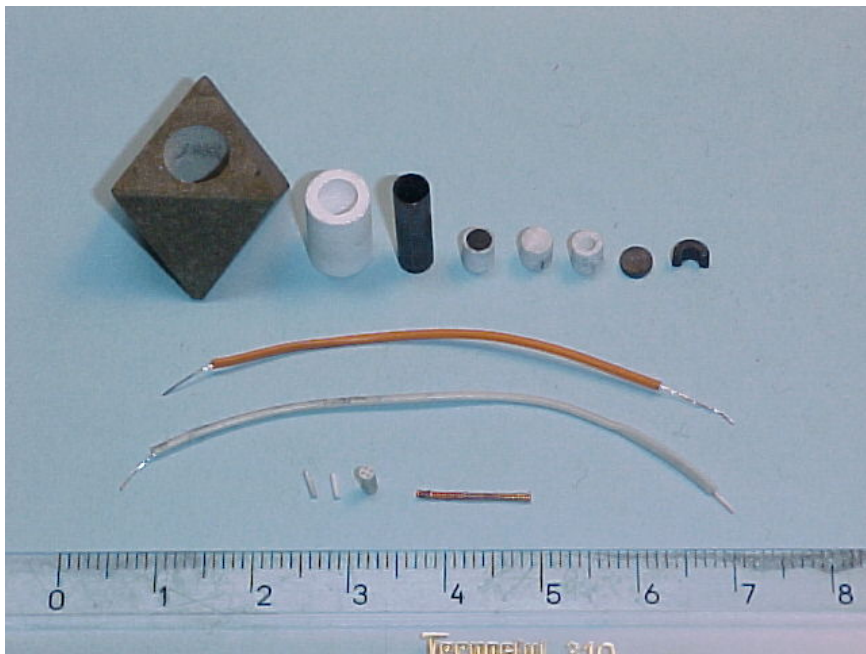
Laboratorio di Petrologia Sperimentale



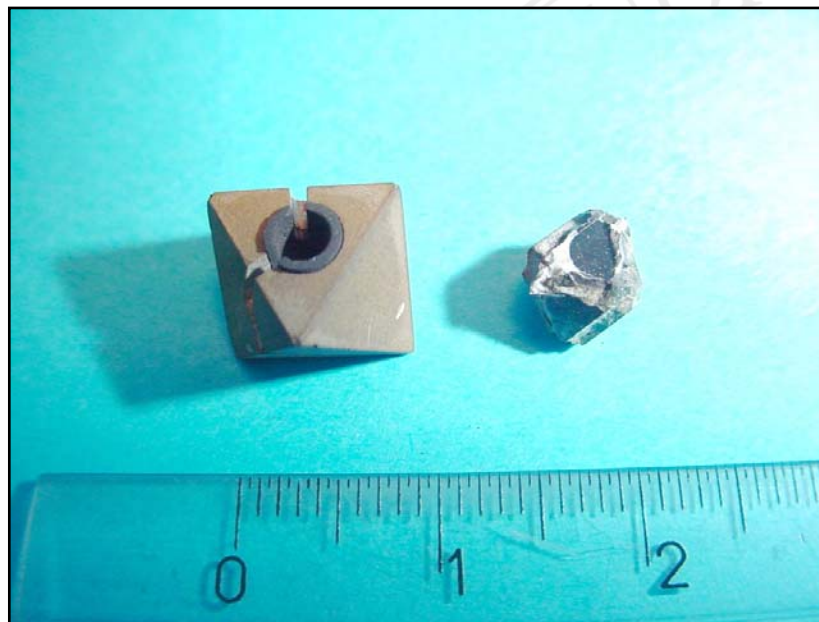








prima ...

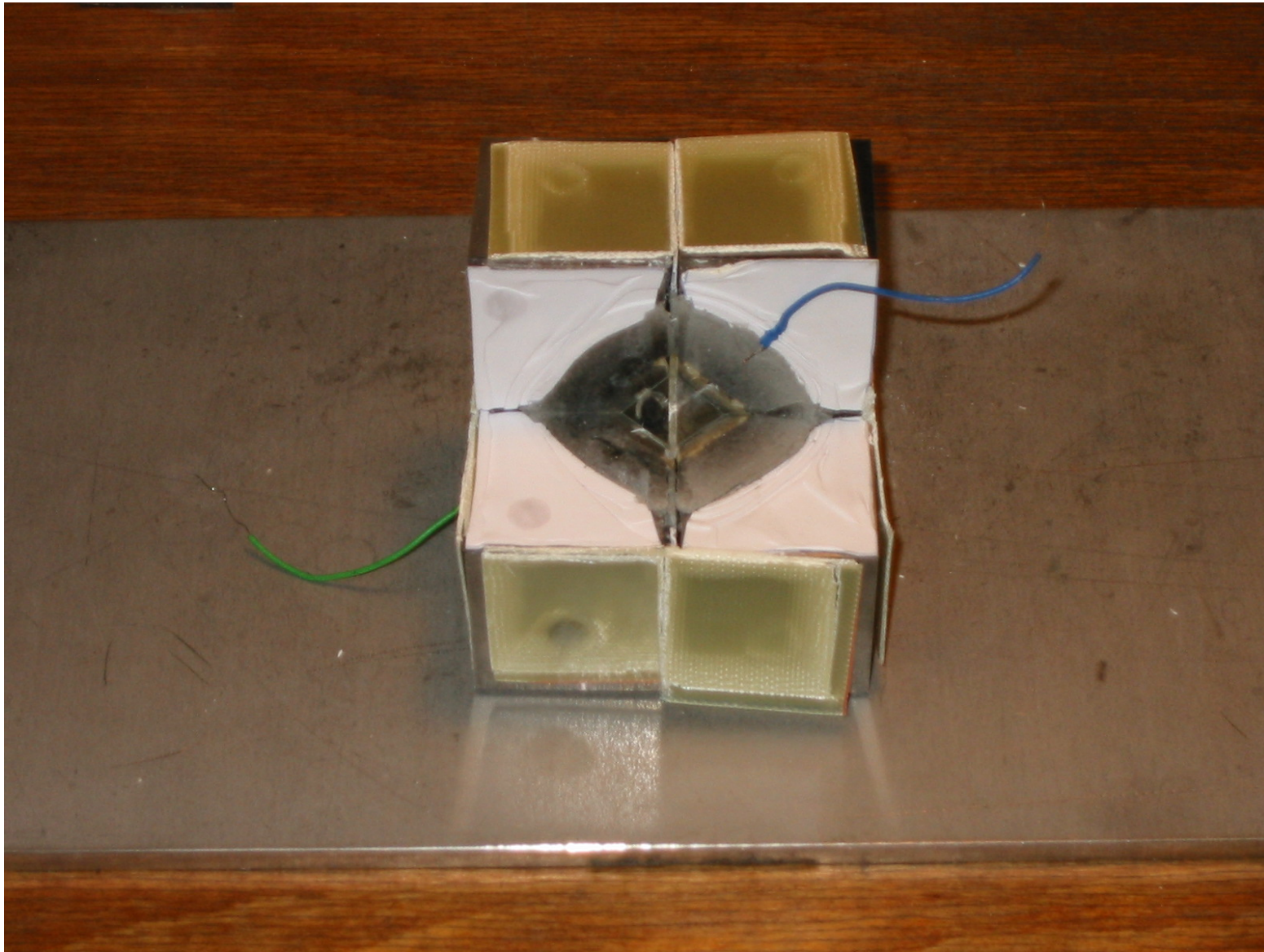


... dopo



La cella di pressione



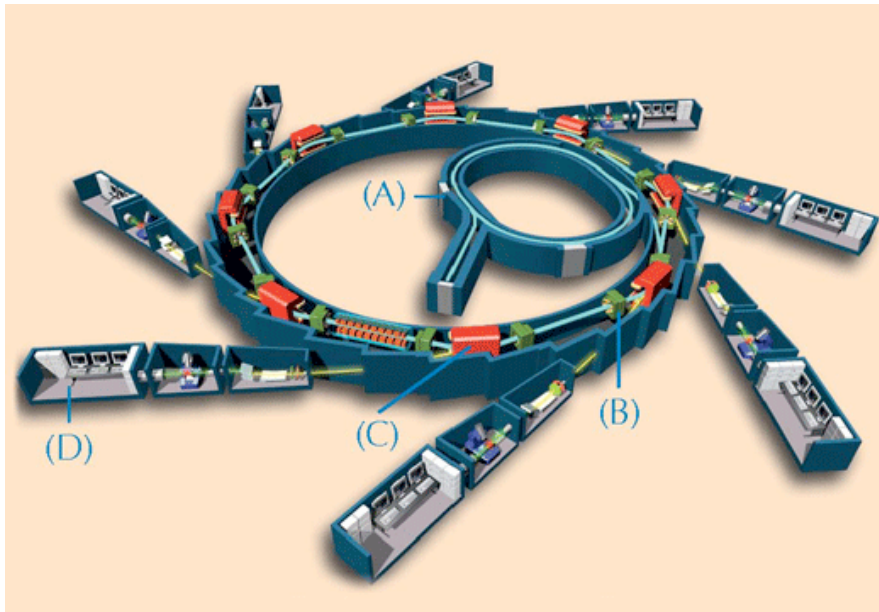


Laboratorio di Petrologia Sperimentale @ UniMi

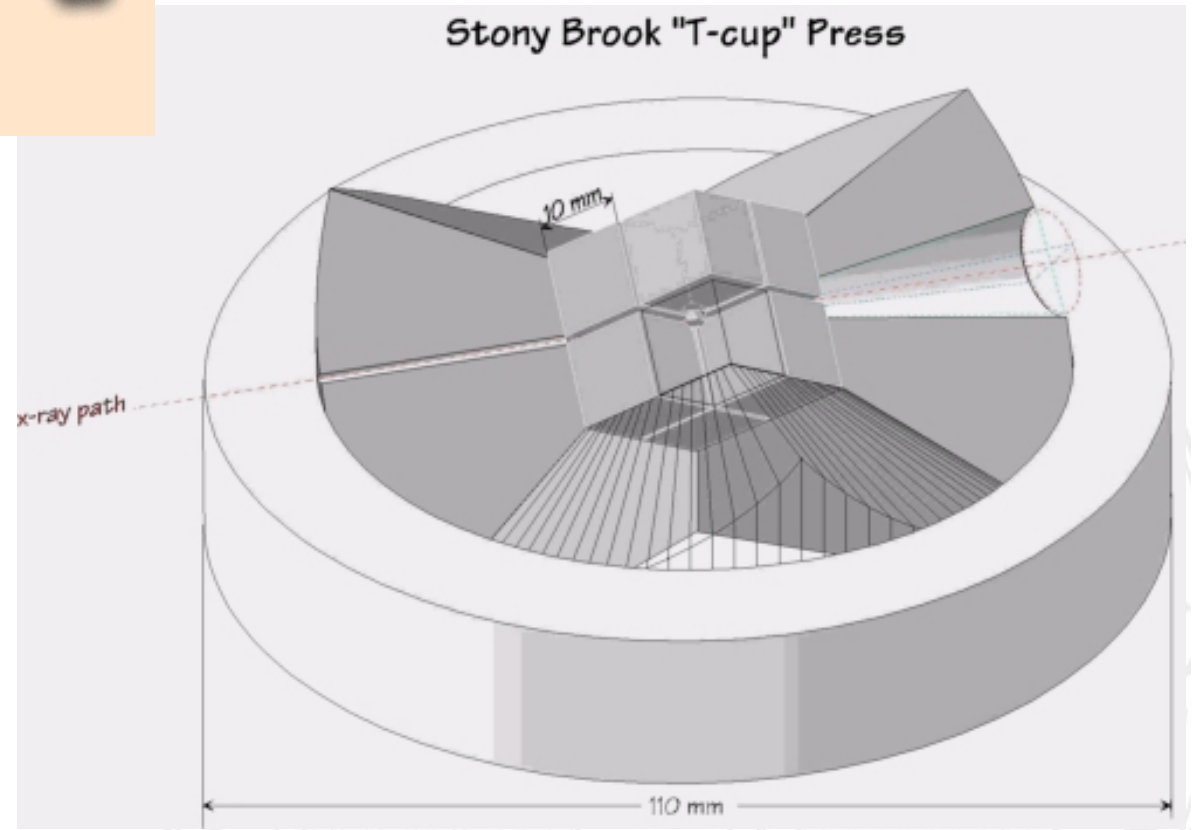


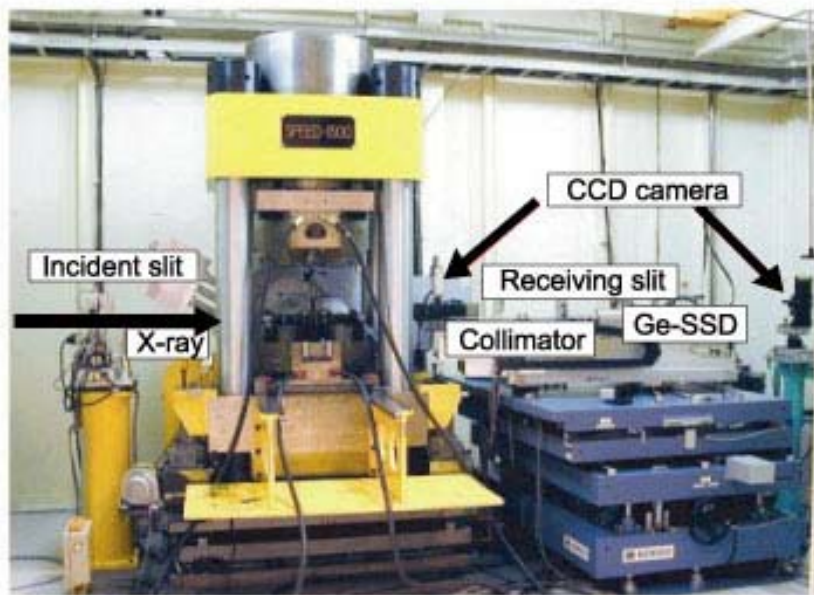
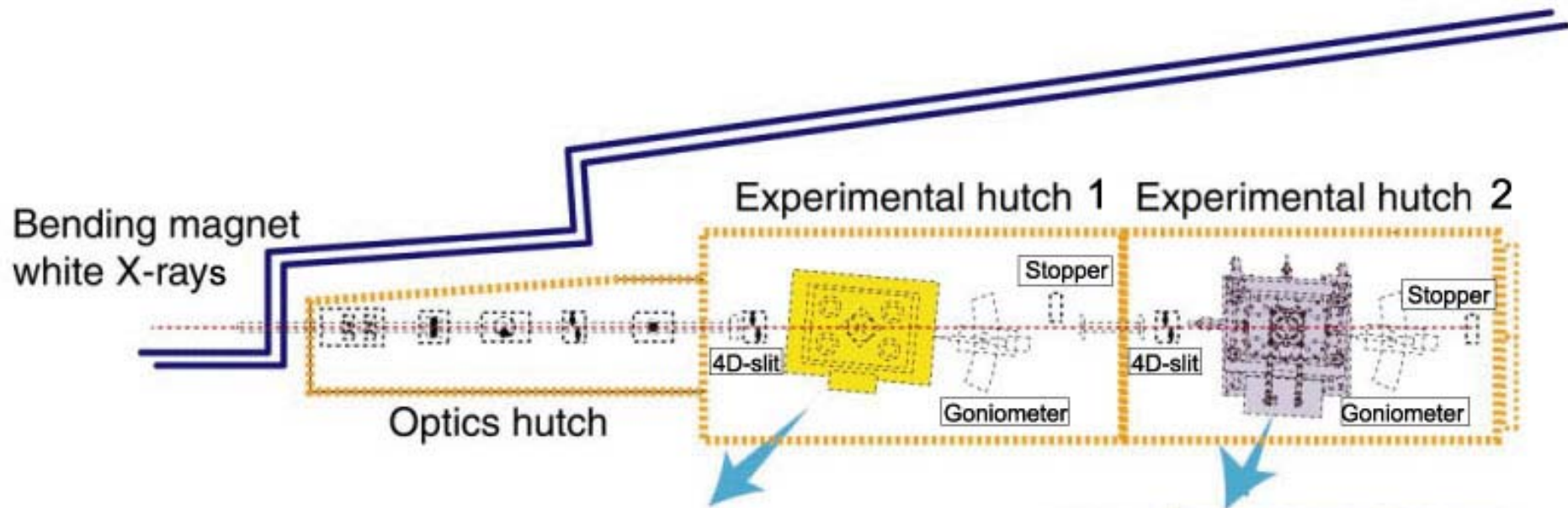
“Rocking-press”



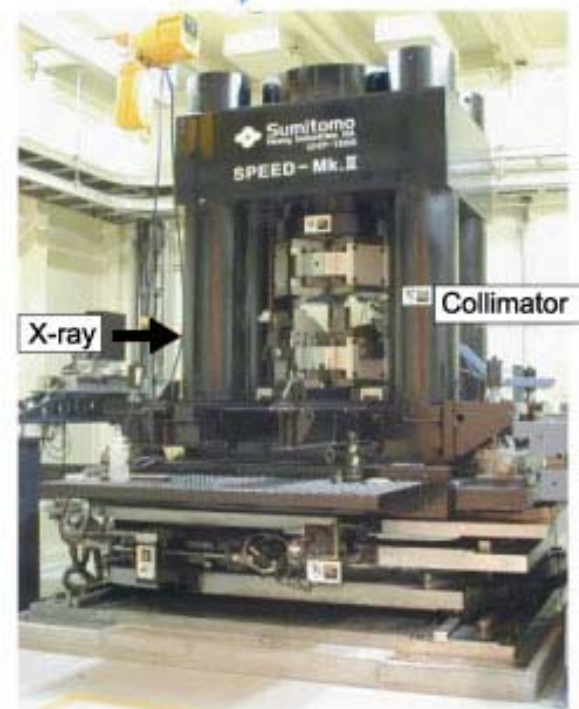


High-pressure machines for “*in-situ*” applications



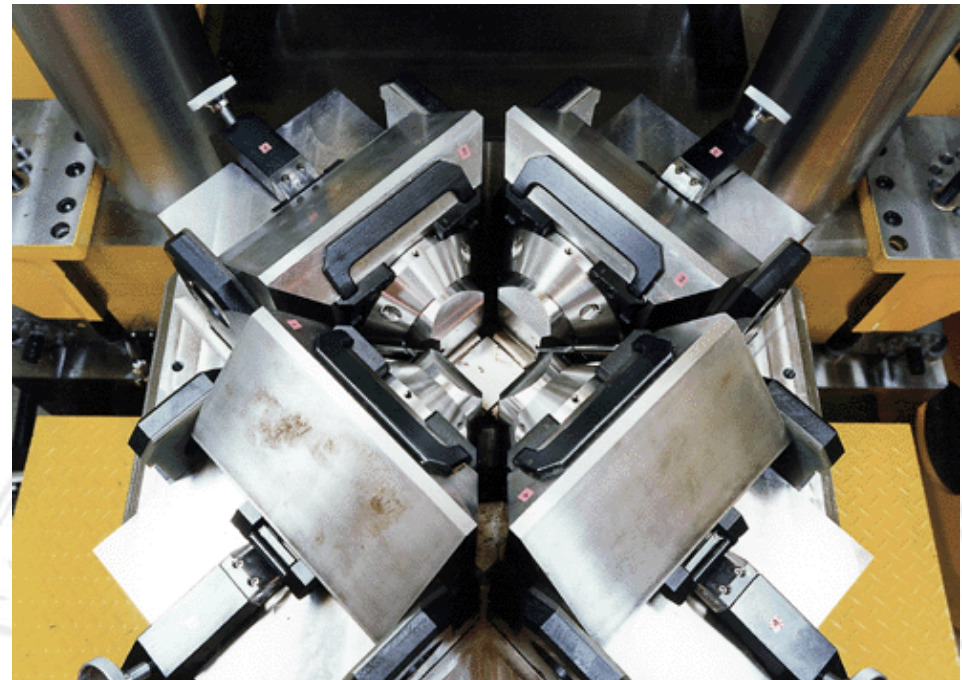
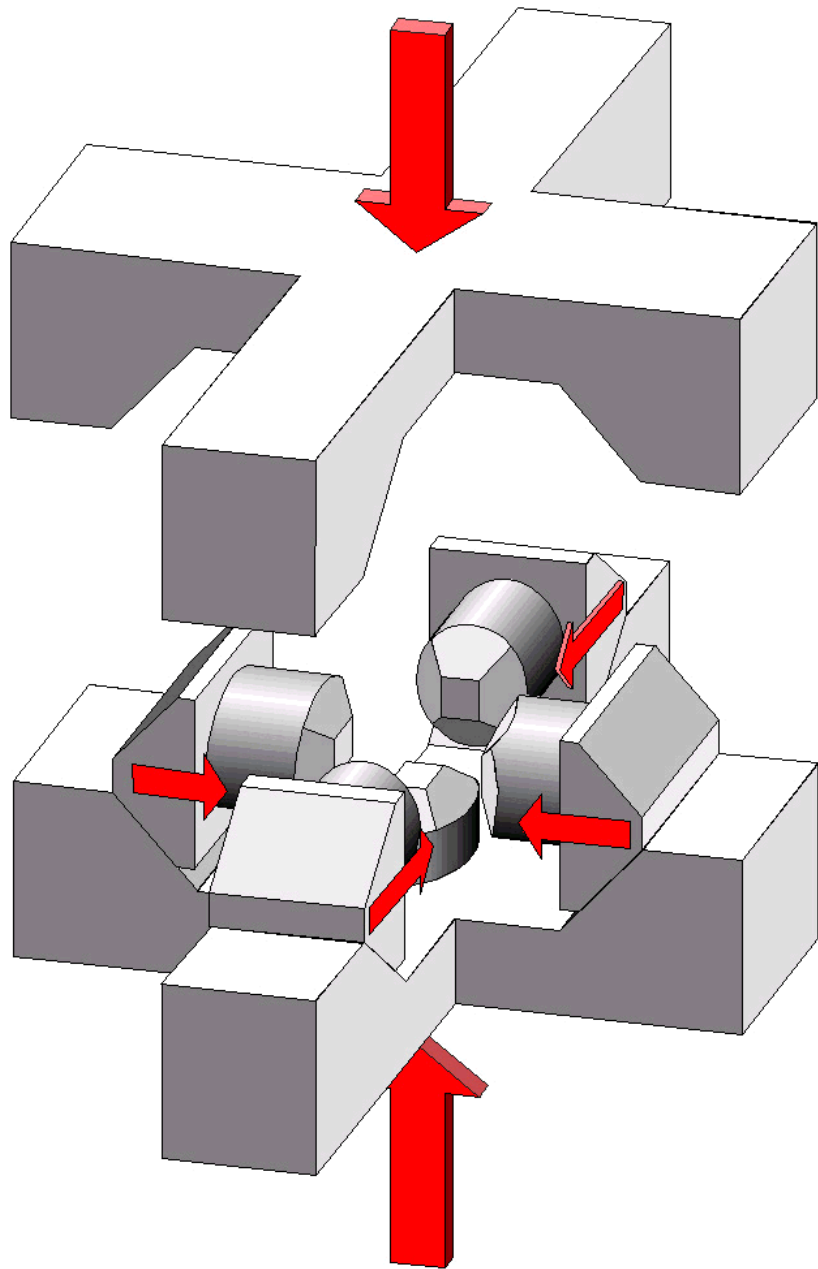


SPEED-1500

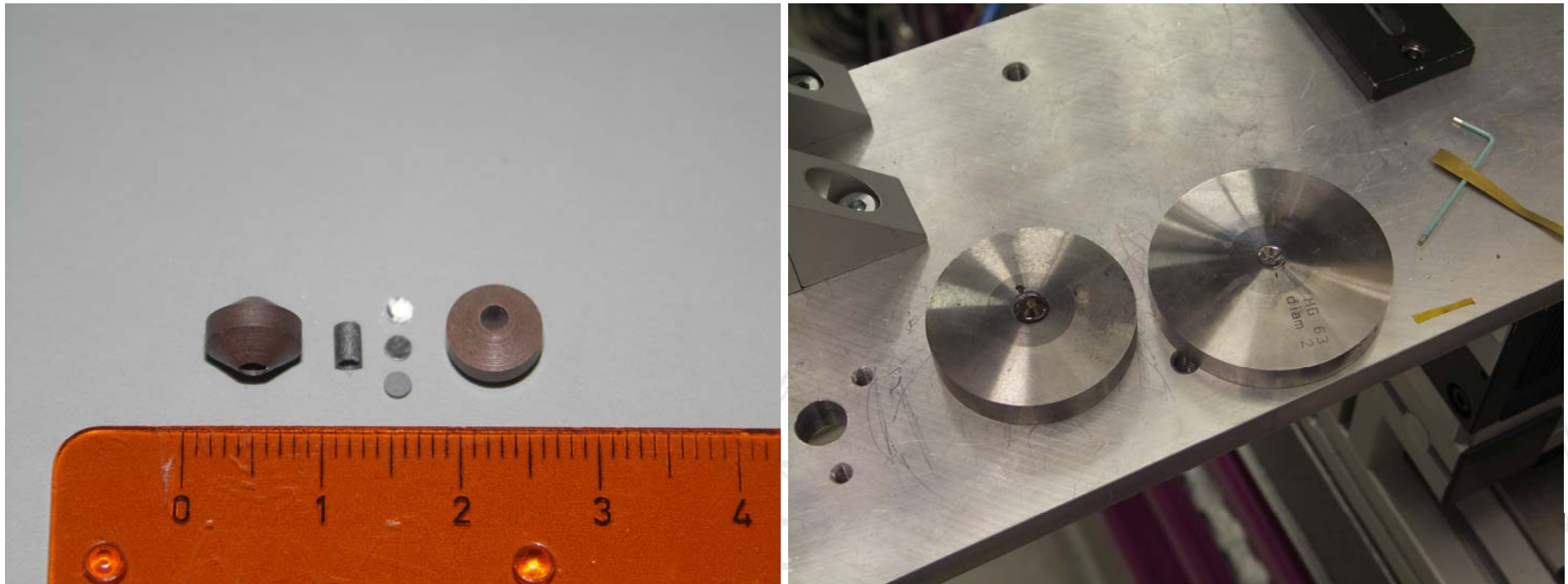


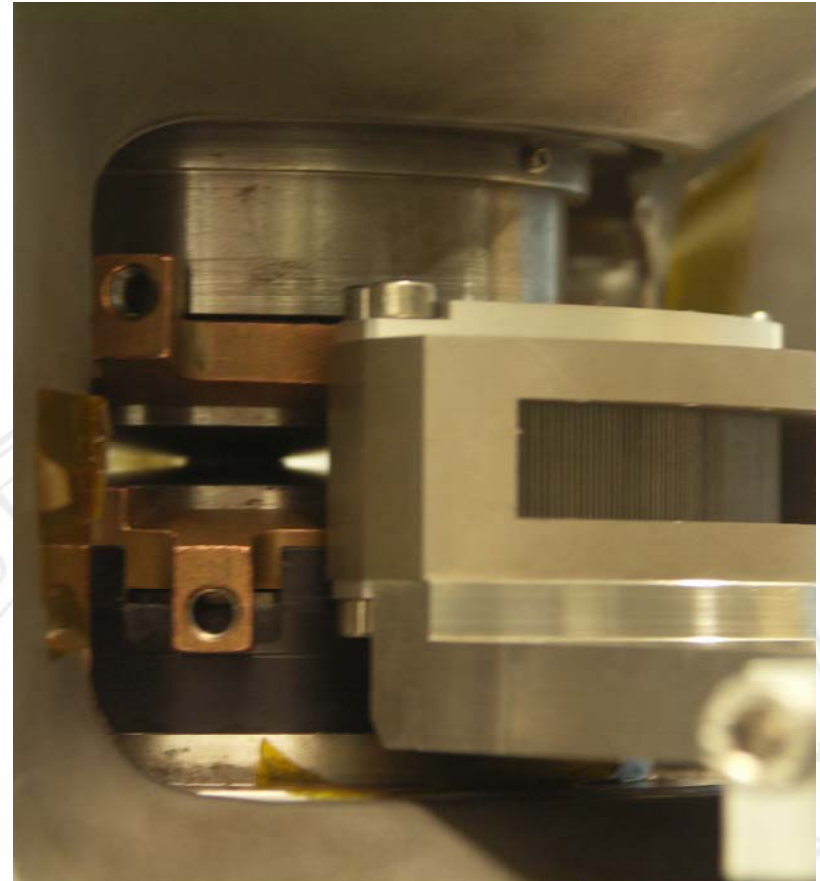
SPEED-Mk.II

“DIA-type” 6/8 multianvil



Paris-Edinburgh apparatus

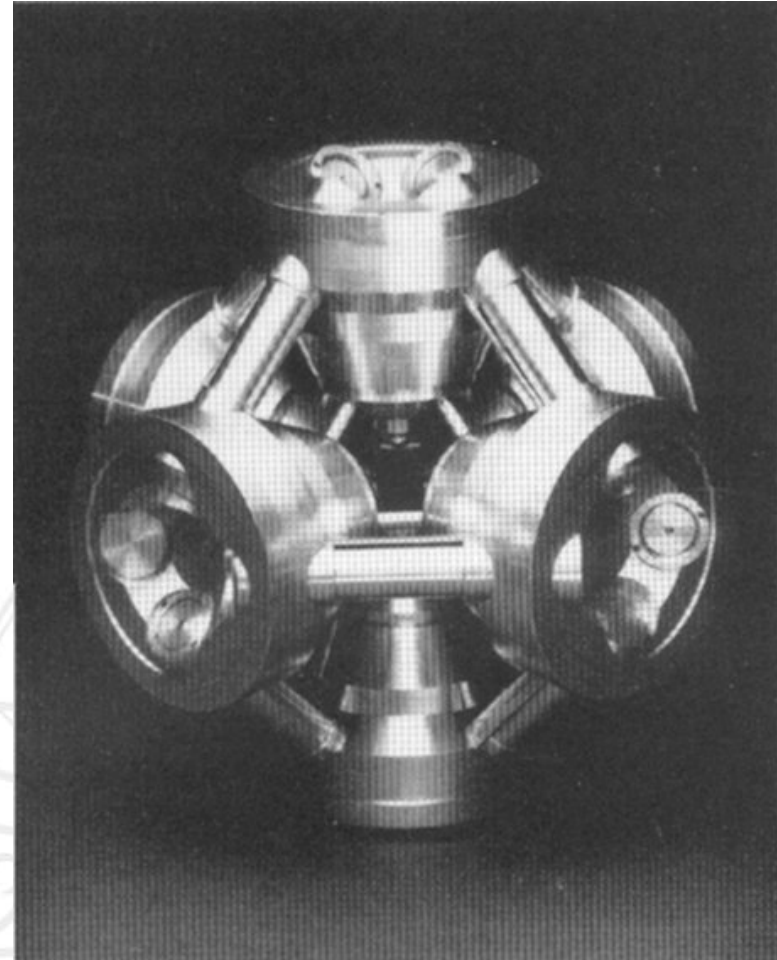
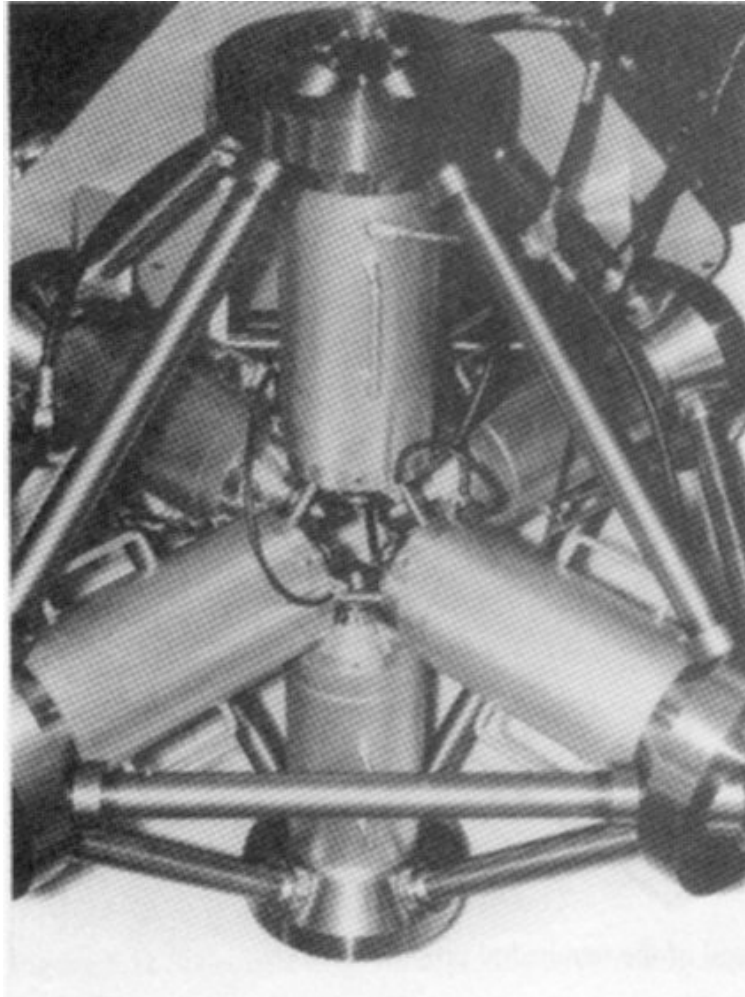




UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO SCIENZE DELLA TERRA

Laboratorio di Petrologia Sperimentale

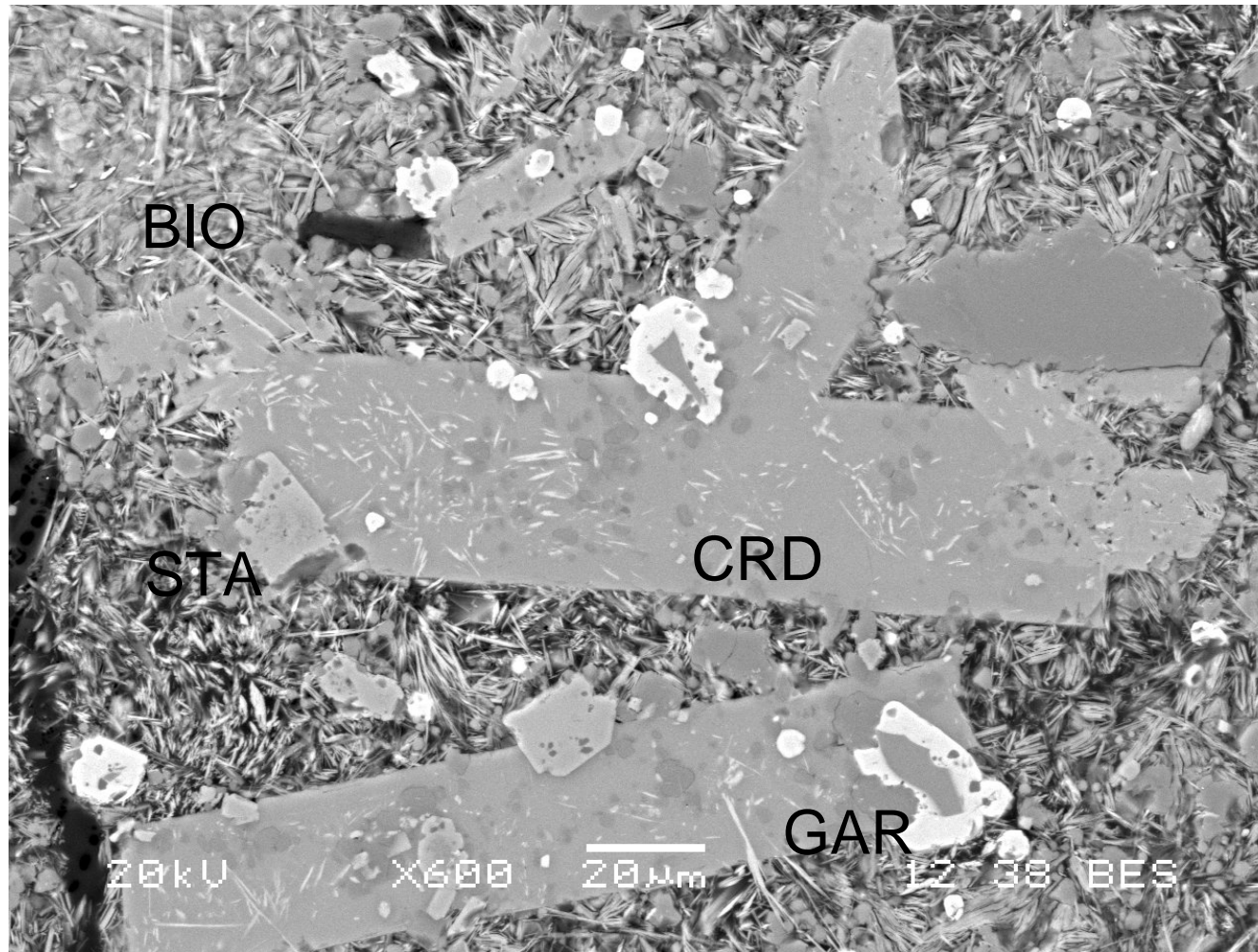




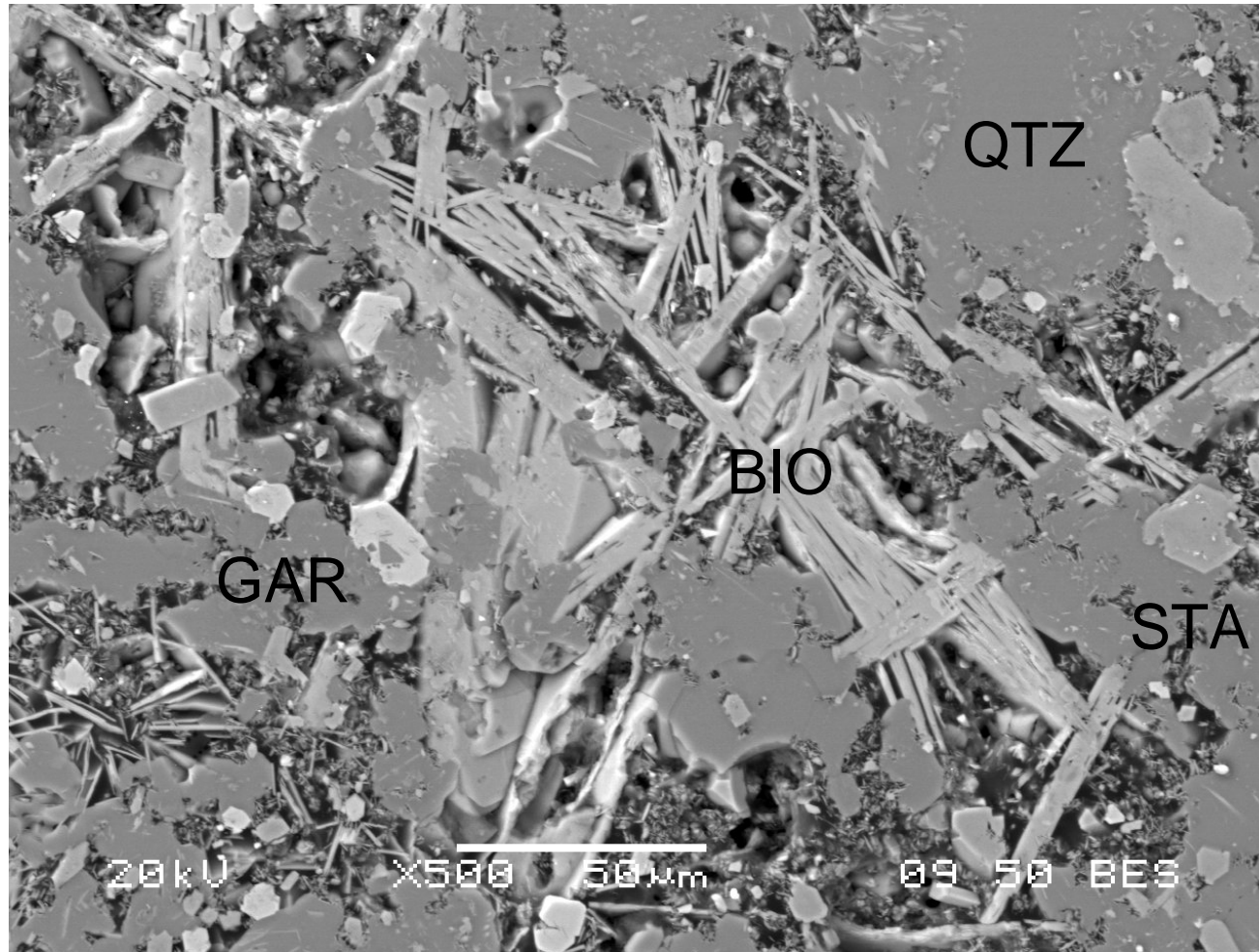
The fabric of experimental products



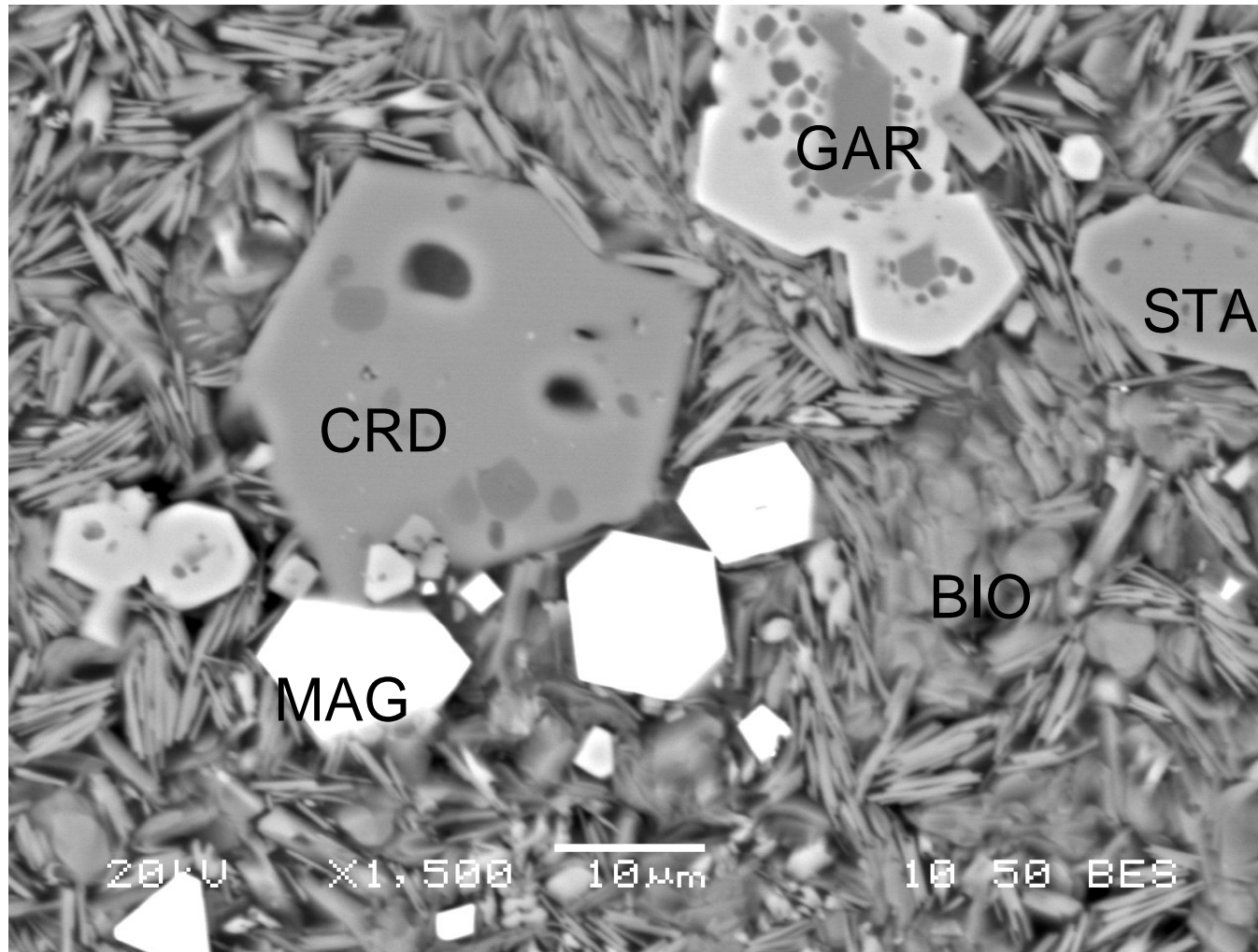
Metapelites and metagreywackes CKFMASH @ 1.0 GPa, 700°C, NNO



Metapelites and metagreywackes CKFMASH @ 0.8 GPa, 730°C, GCOH

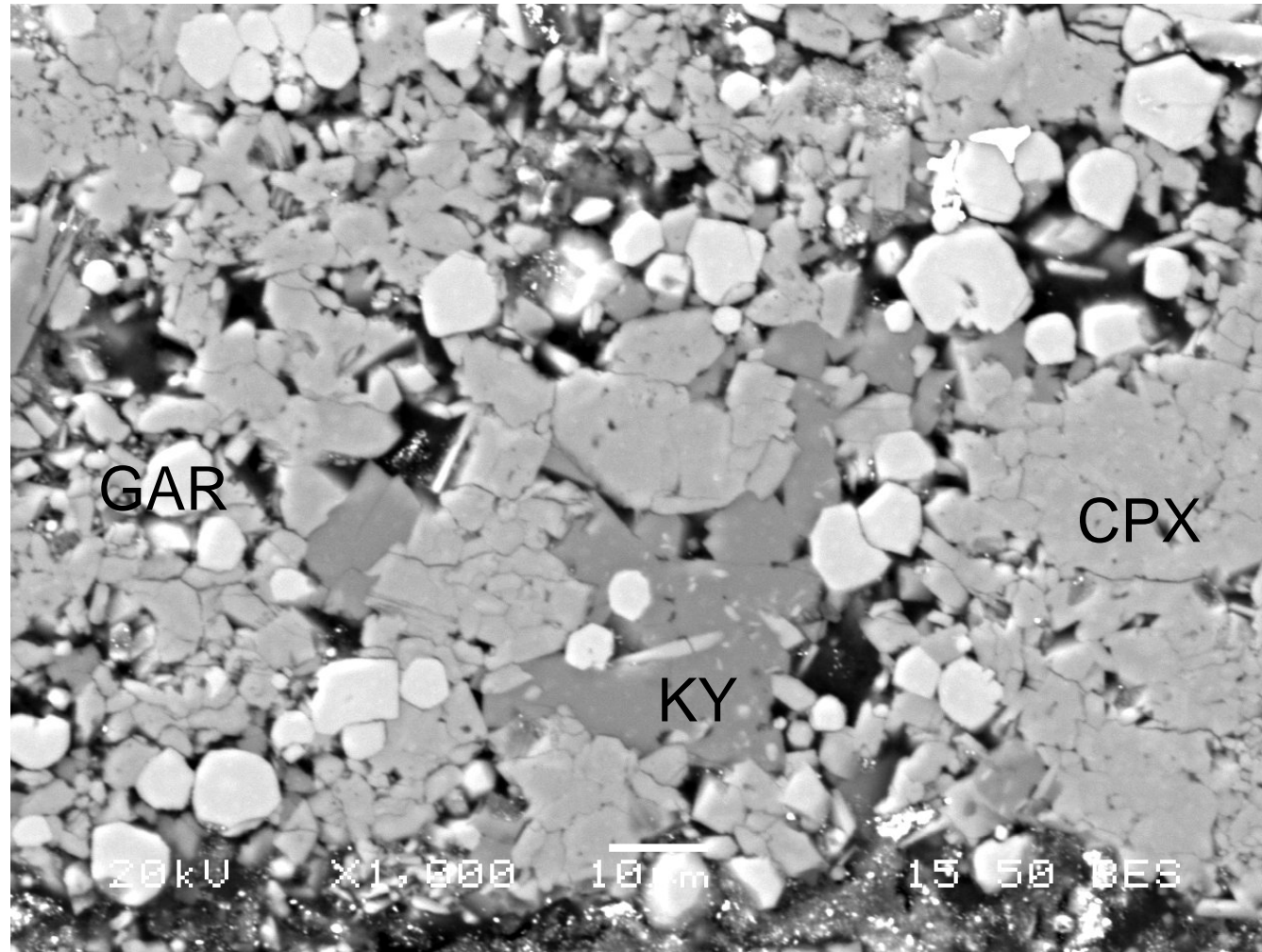


Metapelites and metagreywackes CKFMASH @ 0.8 GPa, 730°C, NNO



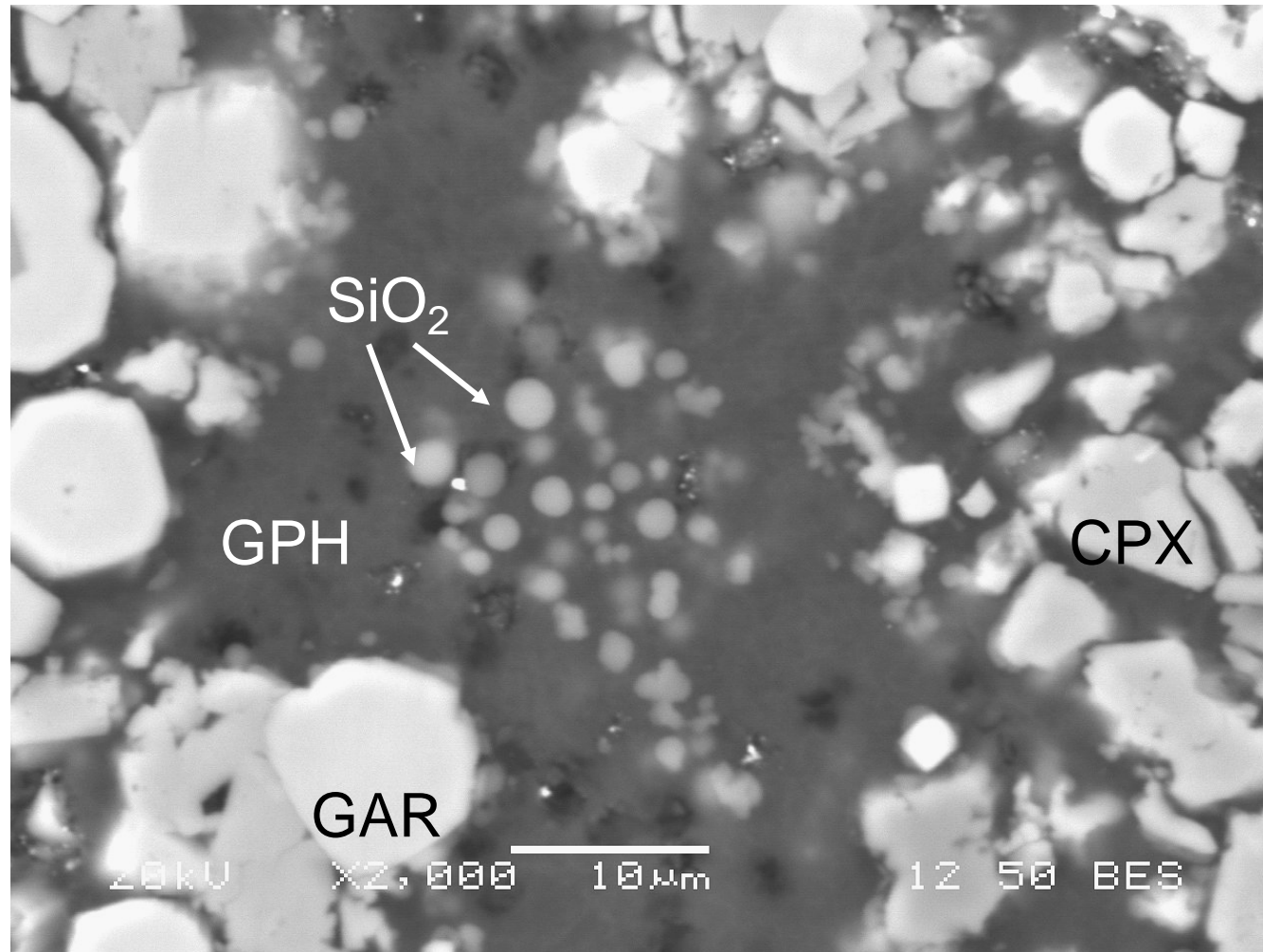
Metabasalts

NCFMASCOH @ 2.7 GPa, 730°C, NNO

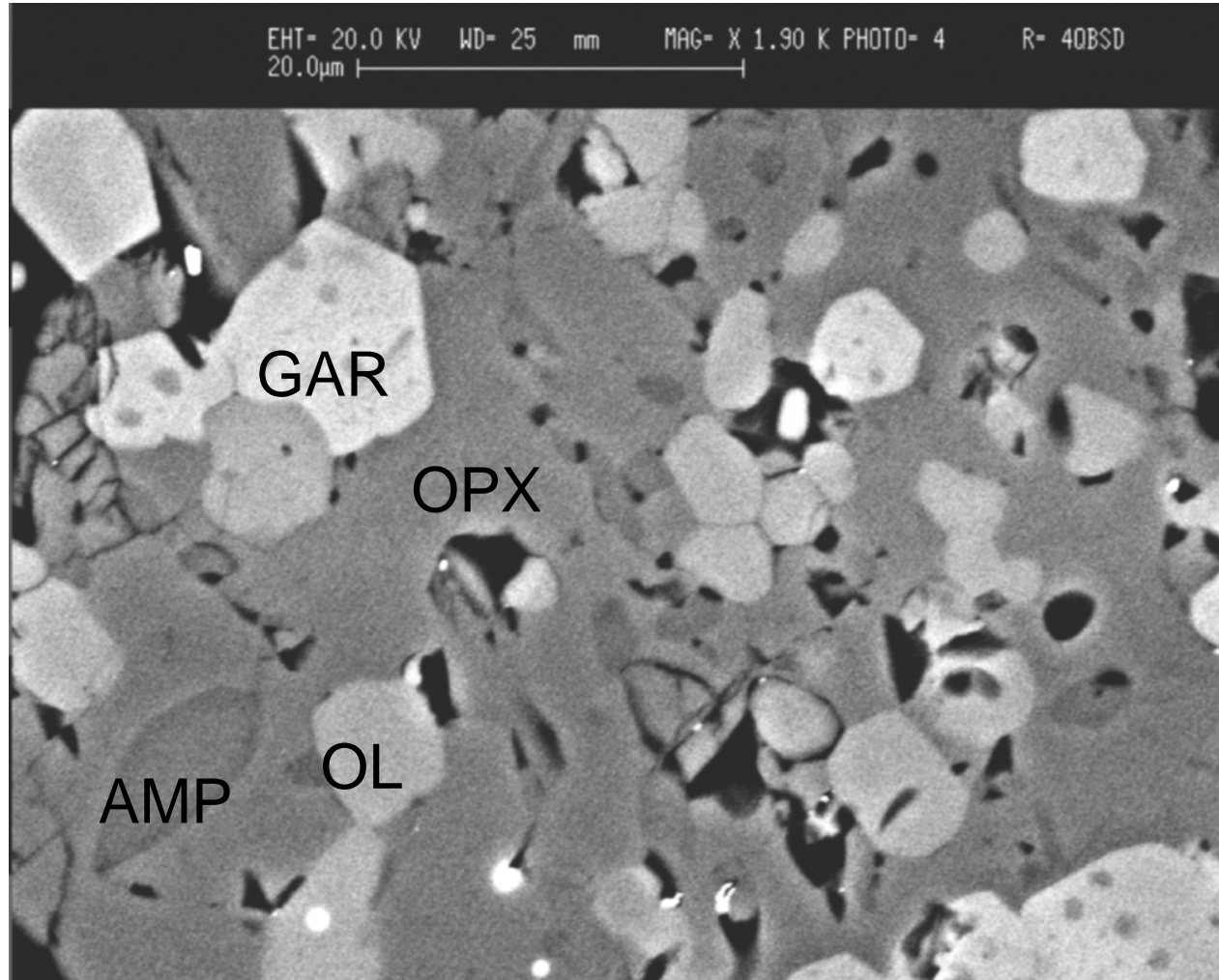


Metabasalts

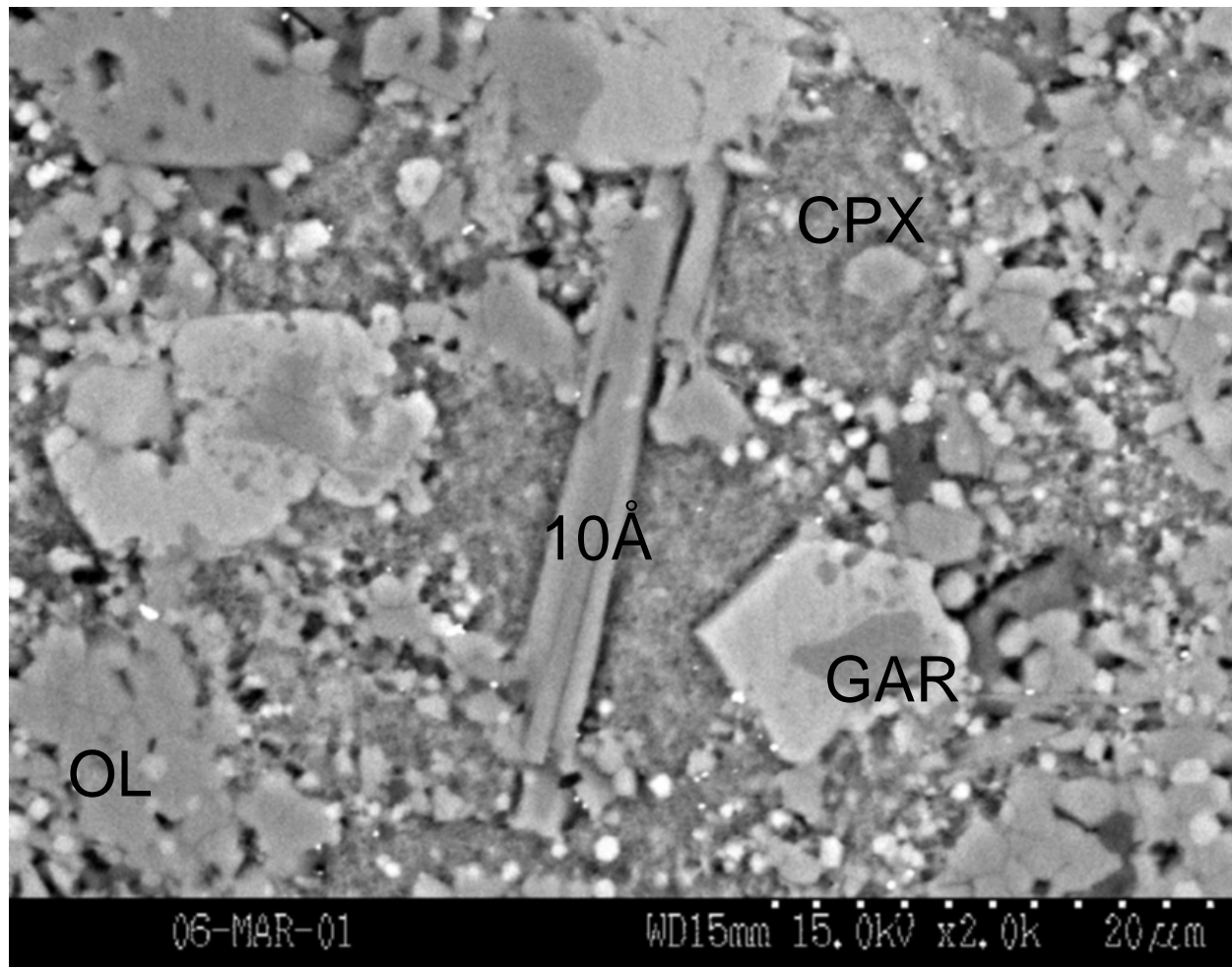
NCFMASCOH @ 2.7 GPa, 680°C, NNO



Hydrous peridotite NCFMASH @ 2.0 GPa, 800°C, GCOH



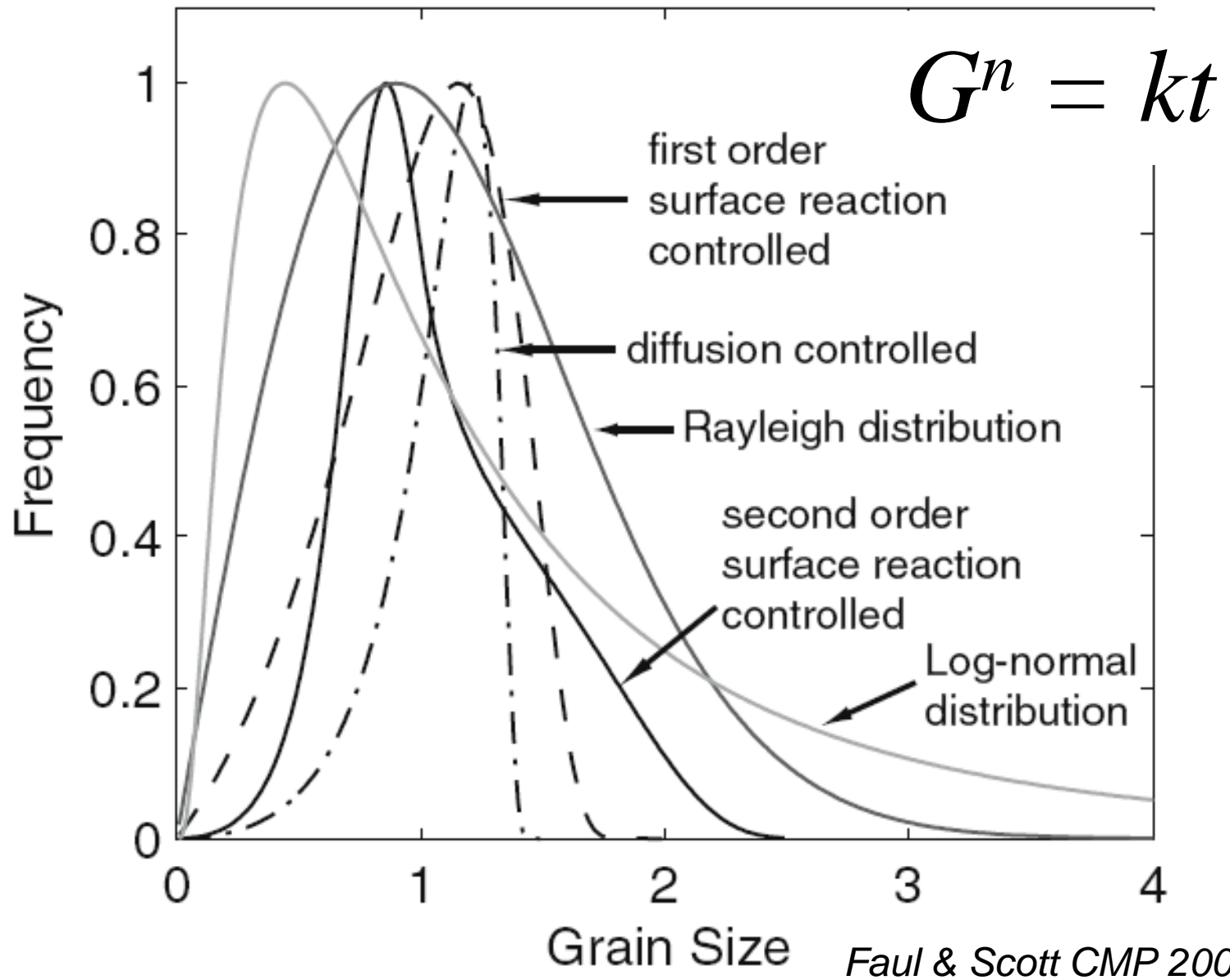
Hydrous peridotite NCFMASH @ 2.0 GPa, 800°C, GCOH



GRAIN SIZE

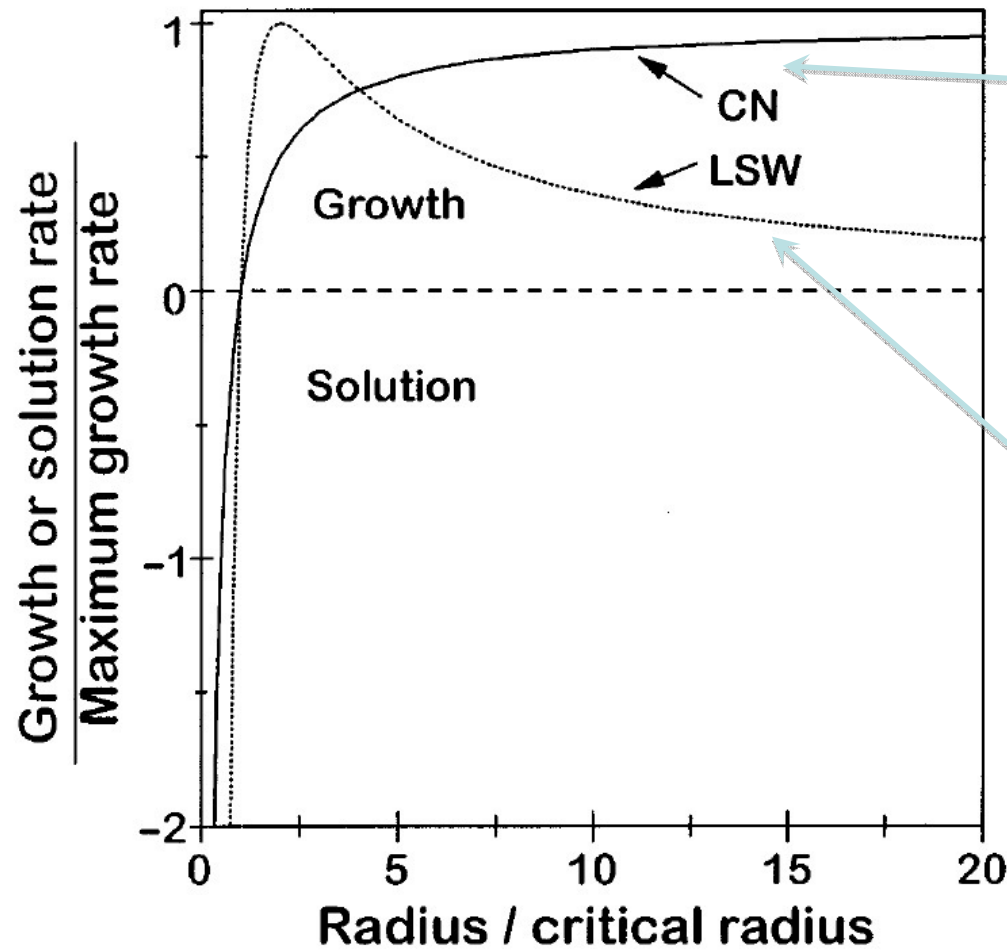
- Grain size, Grain size distribution, and Grain size heterogeneities affect viscosity, permeability, chemical diffusion, seismic attenuation, and other transport properties
- Texture is often characterized by:
 - matrix (e.g. ol, px in ultramafics)
 - “dispersed particles” (spinel, other aluminum phases)
 - porphyroblasts or megacrysts (e.g. pyroxenes): “abnormal grains”
- The role of minor phases in textural evolution



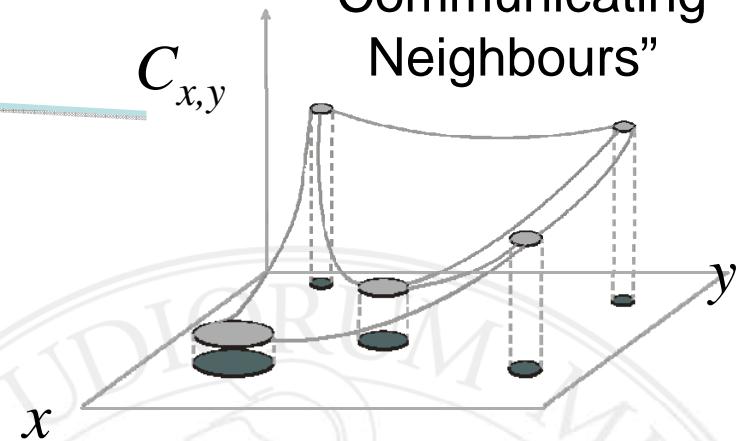


coarsening of dispersed particles

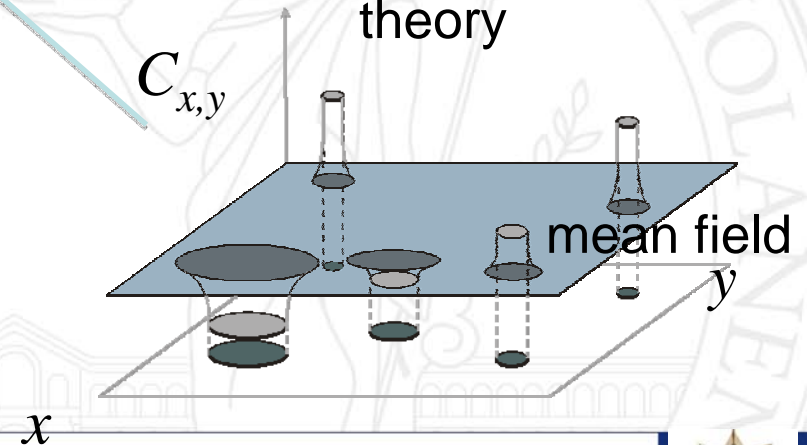
“Ostwald ripening”



DeHoff (1991)
“Communicating
Neighbours”

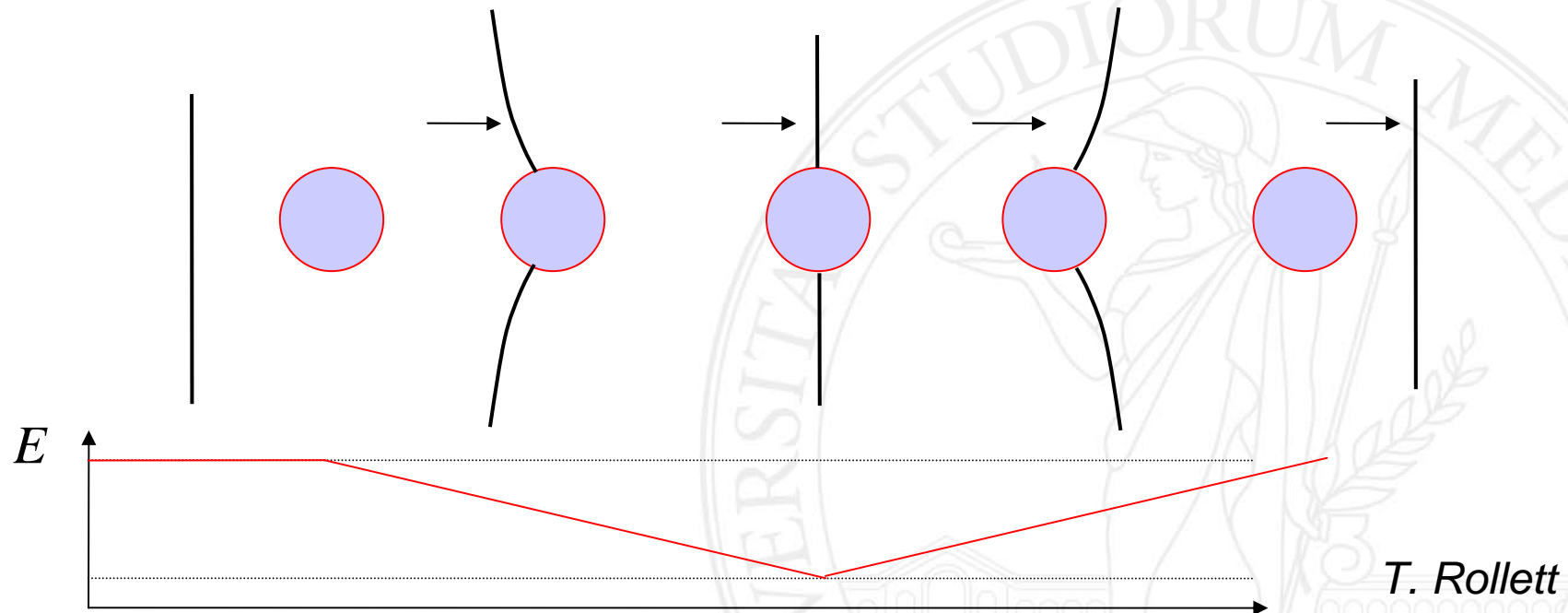


Lifshitz-Slyozov-Wagner
theory



Zener pinning (stagnation of grain growth)

- Why do particles have a pinning effect?
- Answer: once a boundary has intersected with a particle, a certain amount of boundary area is removed from the system. In order for the boundary to move off the particle, the “missing area” must be re-created. This restoration of boundary area requires an energy increase. Through the principle of virtual work, this requires a force.



matrix growth with pinning particles

Manohar et al. ISIJ Int. (1998)

Zener-Smith equation

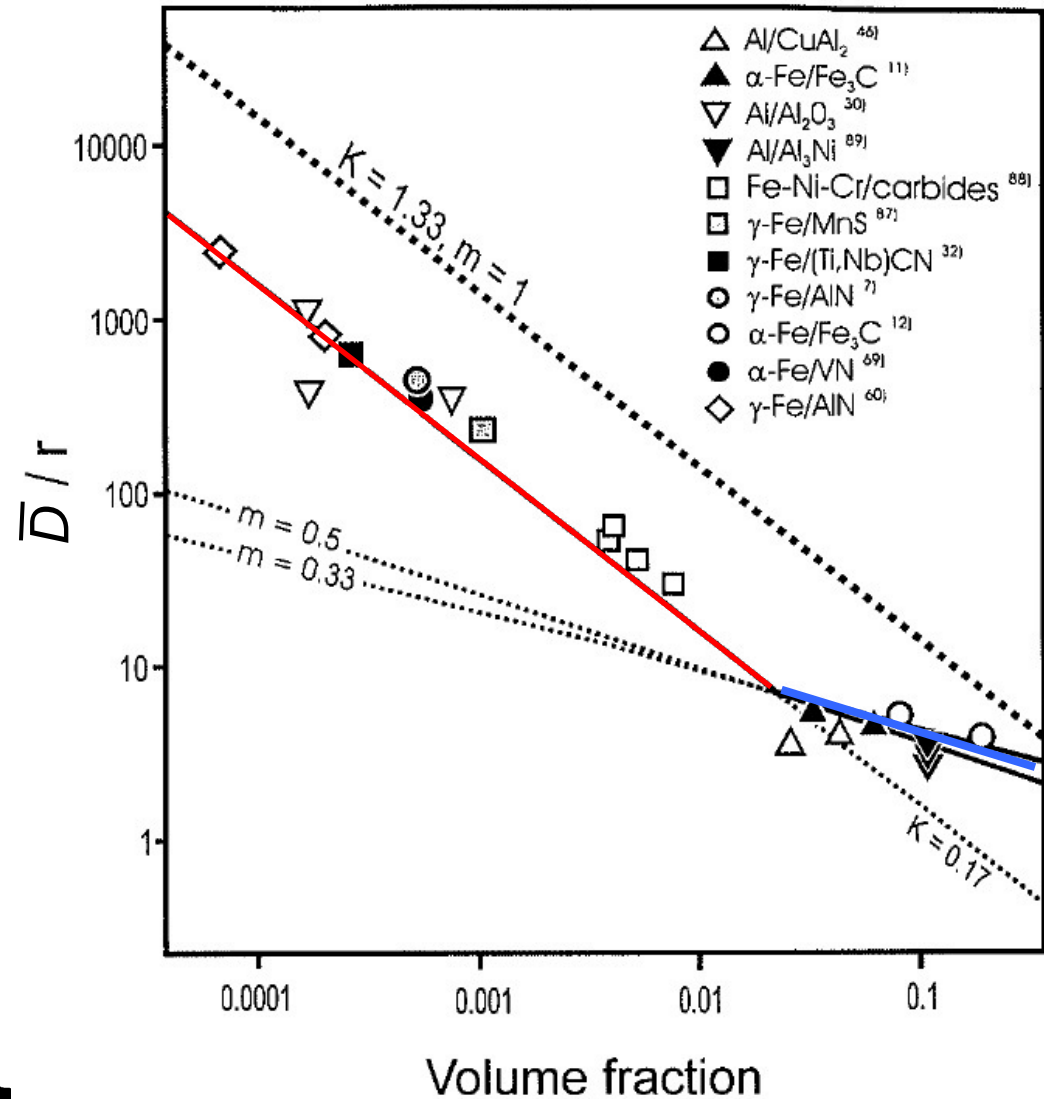
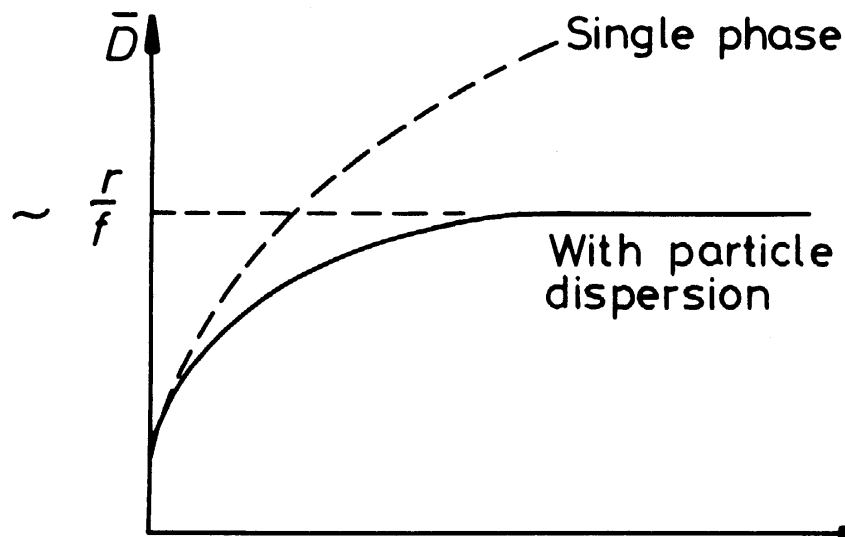
$$\bar{D} = k_z r / f^m$$

D = matrix size

r = particle size

f = volume fraction of particles

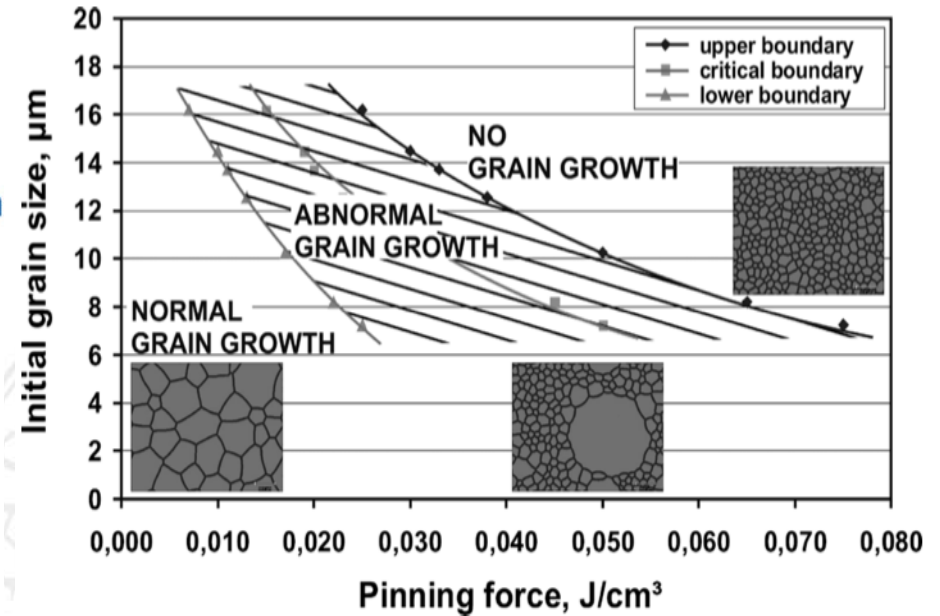
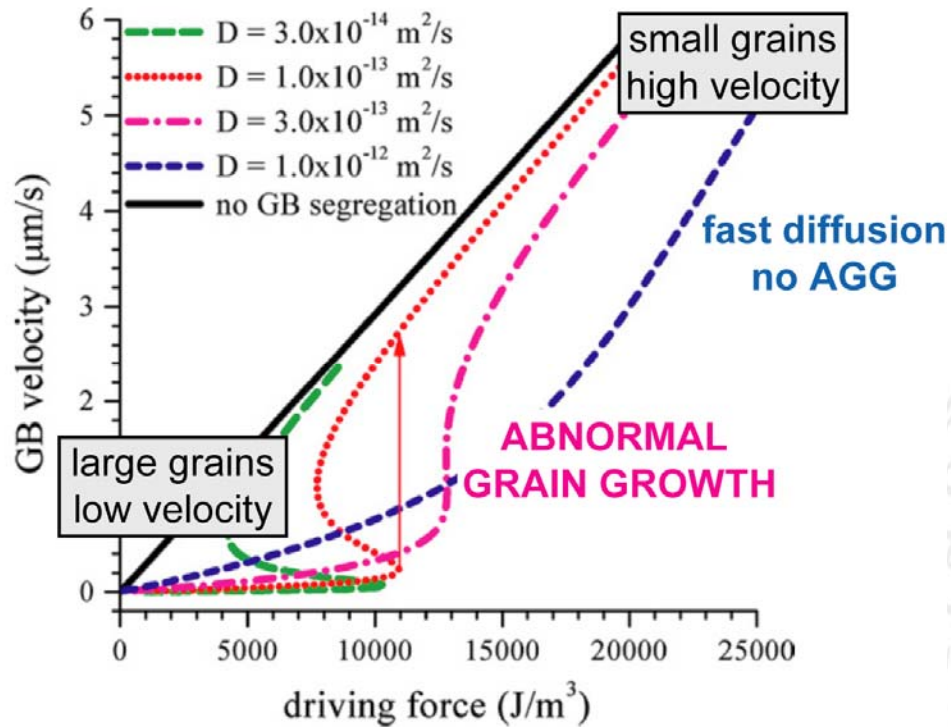
$k_z = 4/3$; $m = 1$, in ZS eq.



abnormal grain growth (AGG)

- solute drag effect

- particle pinning effect



Kim & Park, *Acta Materialia* (2008)

Apel et al. *ISIJ* 2009



experimental procedures

- spinel/garnet as dispersed phases
- starting materials:
 - a - gel model lherzolite - 40%olivine + 0.3% sp seeds
→ more spinel, unaltered phase relationships (model ol-websterite)
 - b – gel model lherzolite
- piston cylinder, pt-graphite capsule, salt-pyrex assemblies
- time series: 0.3, 2.8, 27.8, 88, 220, 523 hr (**10^3 , 10^4 , 10^5 , $10^{5.5}$, $10^{5.9}$, 10^6 s**)
- **1.0 GPa 1100 °C (spinel-bearing), 3.5 GPa 1200 °C (garnet bearing)**
- analytical: TEM, XRPD (ESRF Grenoble), SEM, EPMA on etched samples to enhance grain boundaries (Ohuchi 2006)
- image processing: watershed on Euclidean distance transform of binarized BSE images. Phase id. adding X-ray maps. Matlab®
- Crystal Size Distribution: Schwartz-Saltikov stereological correction and bin-size selection minimizing the difference between the 2nd and 3rd moments of population density, avoiding empty bins. Matlab®

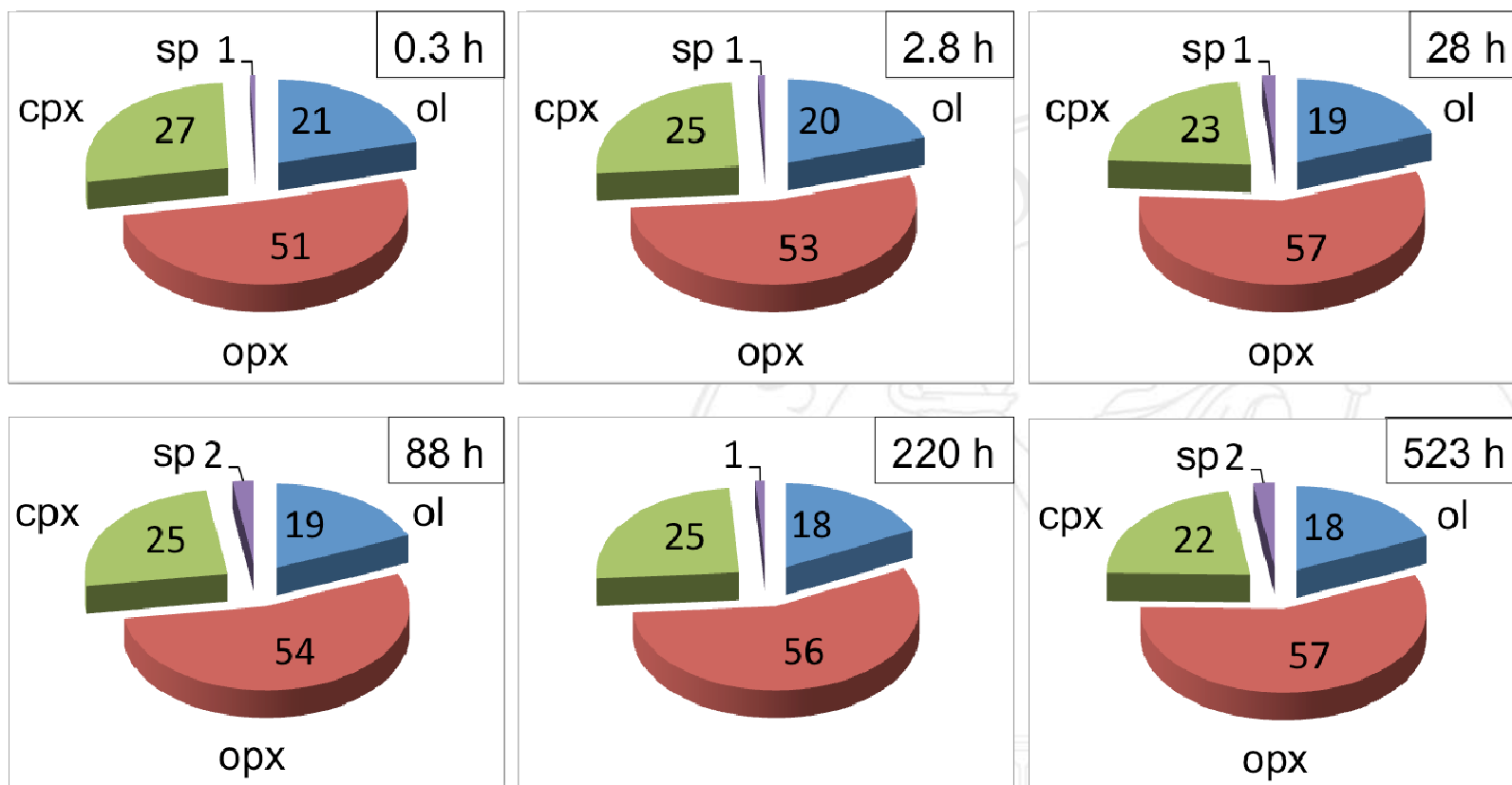


PHASE PROPORTIONS BY RIETVELD ON XRPD

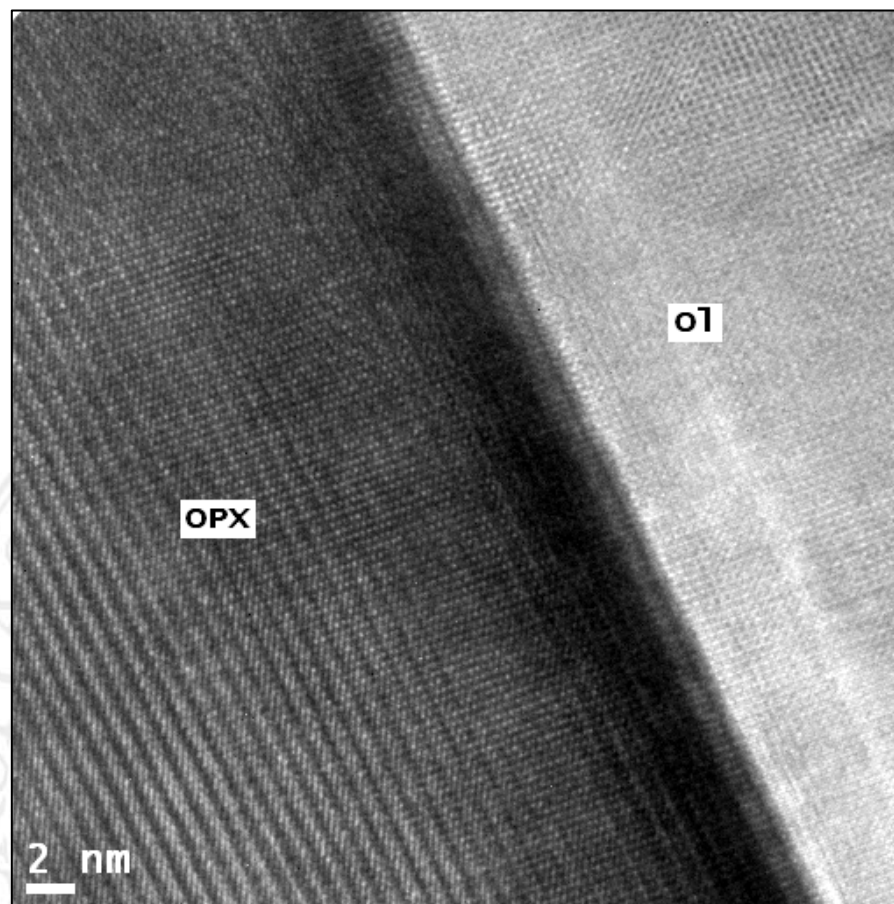
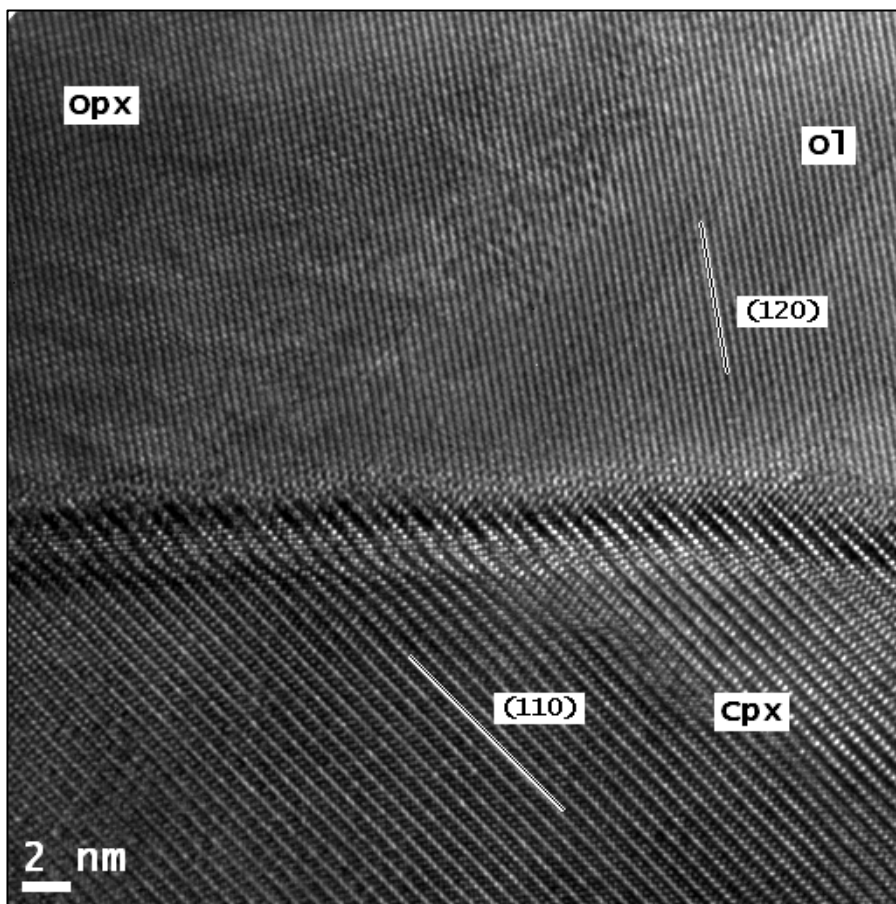
INDEPENDENT ESTIMATE OF CONSTANT PHASE
ABUNDANCES WITH TIME

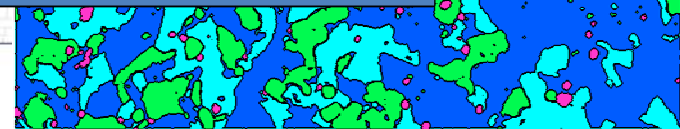
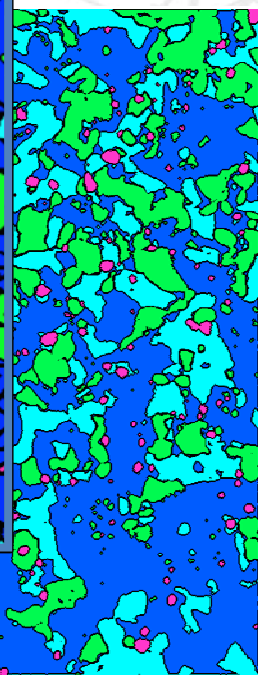
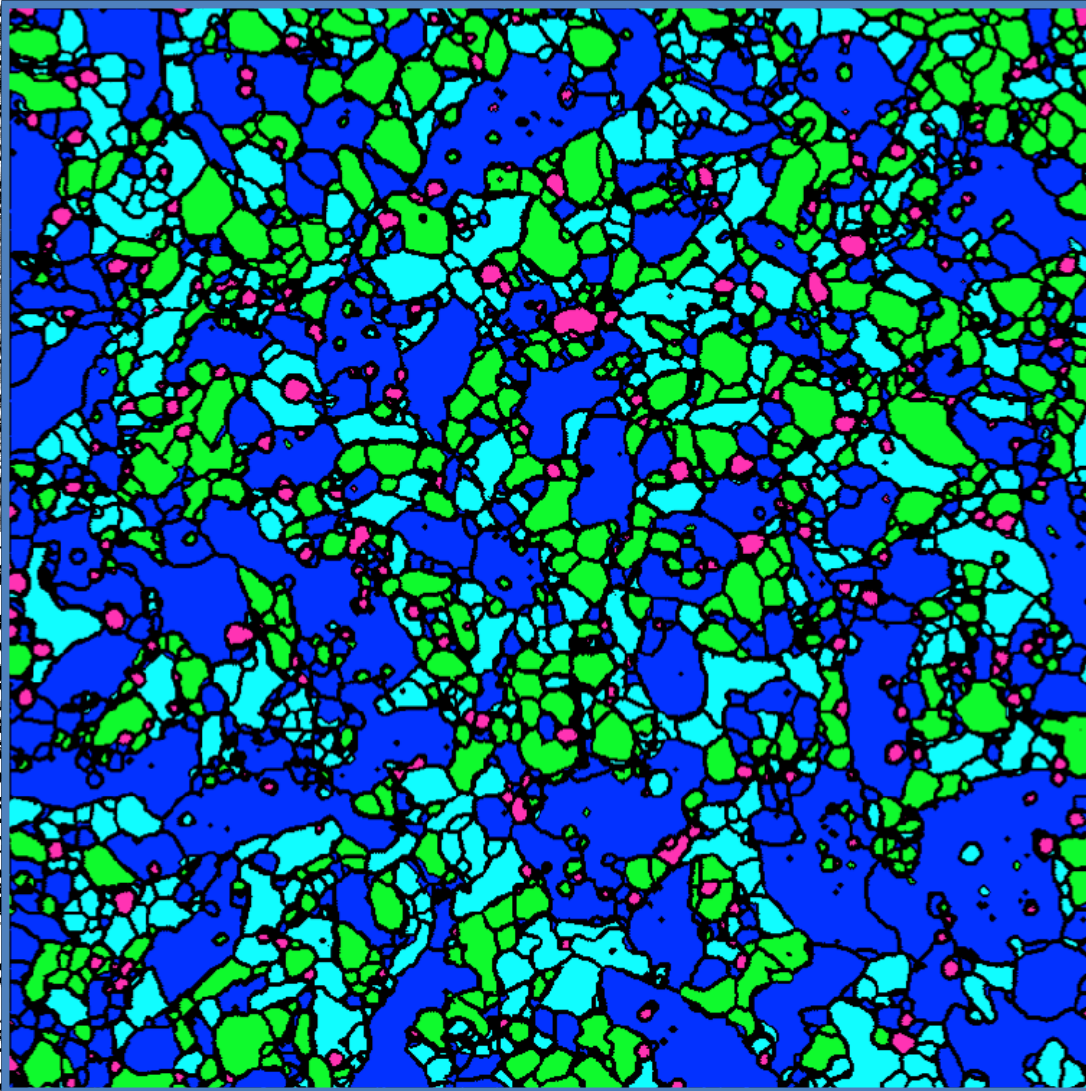
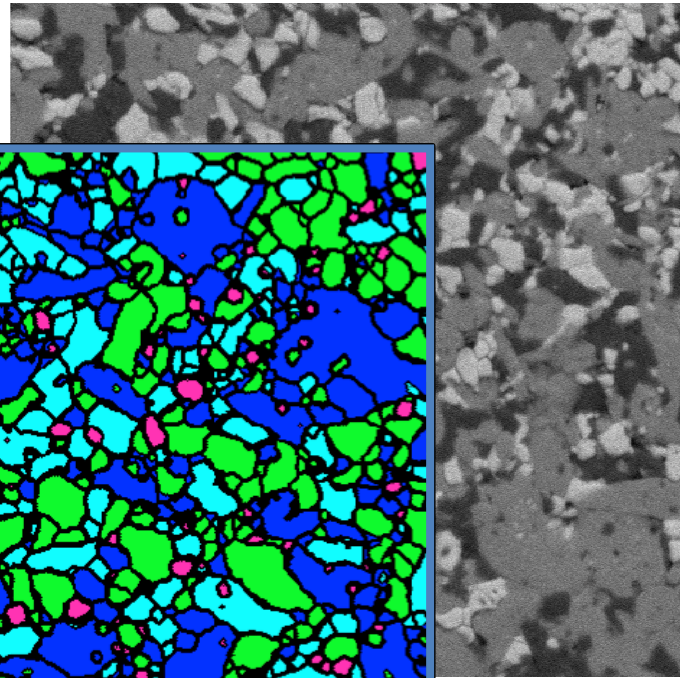
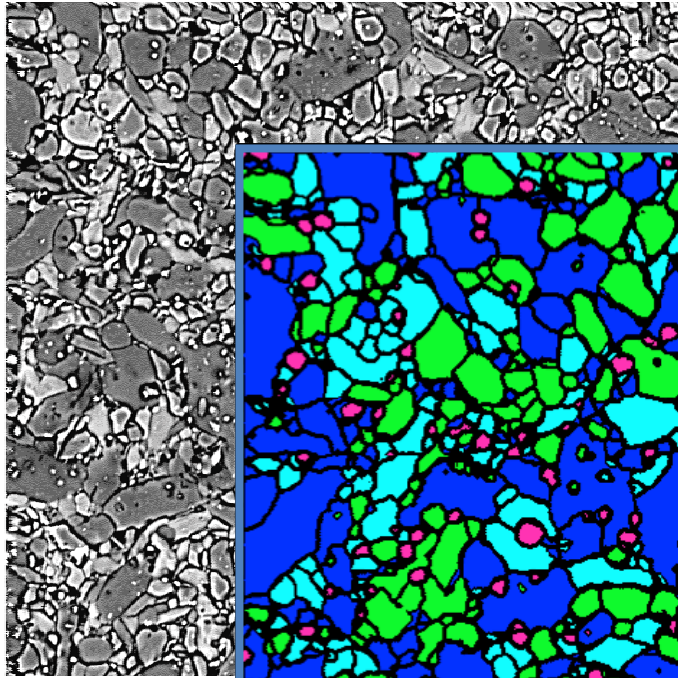


GRAIN BOUNDARY REARRANGEMENT ONLY



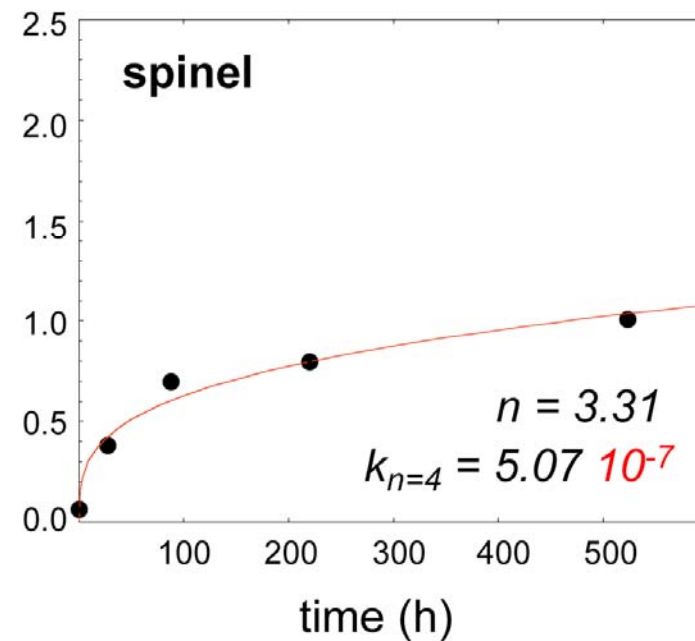
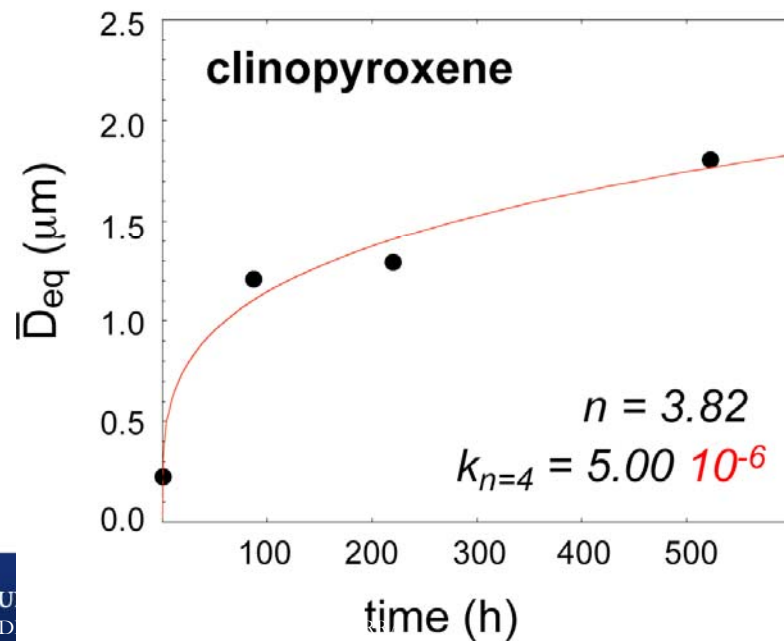
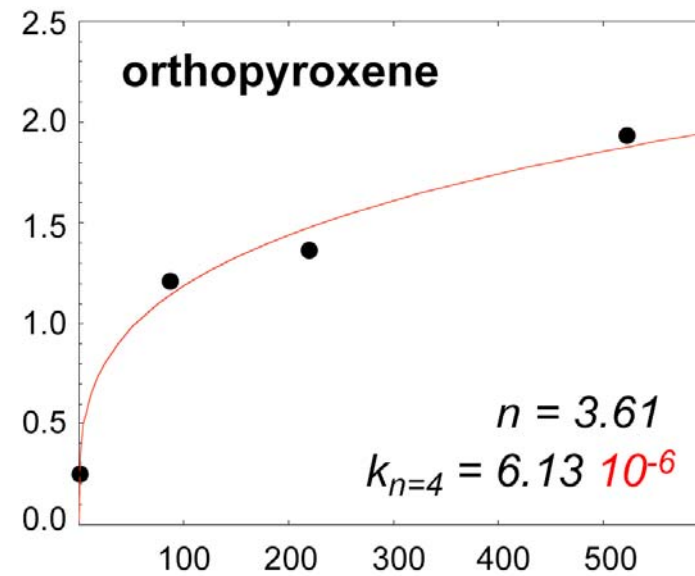
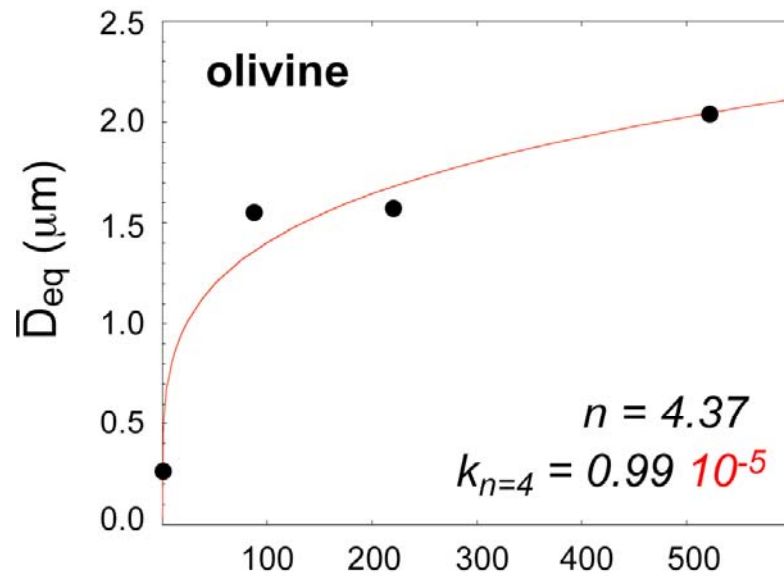
TEM: GRAIN BOUNDARY PROPERTIES



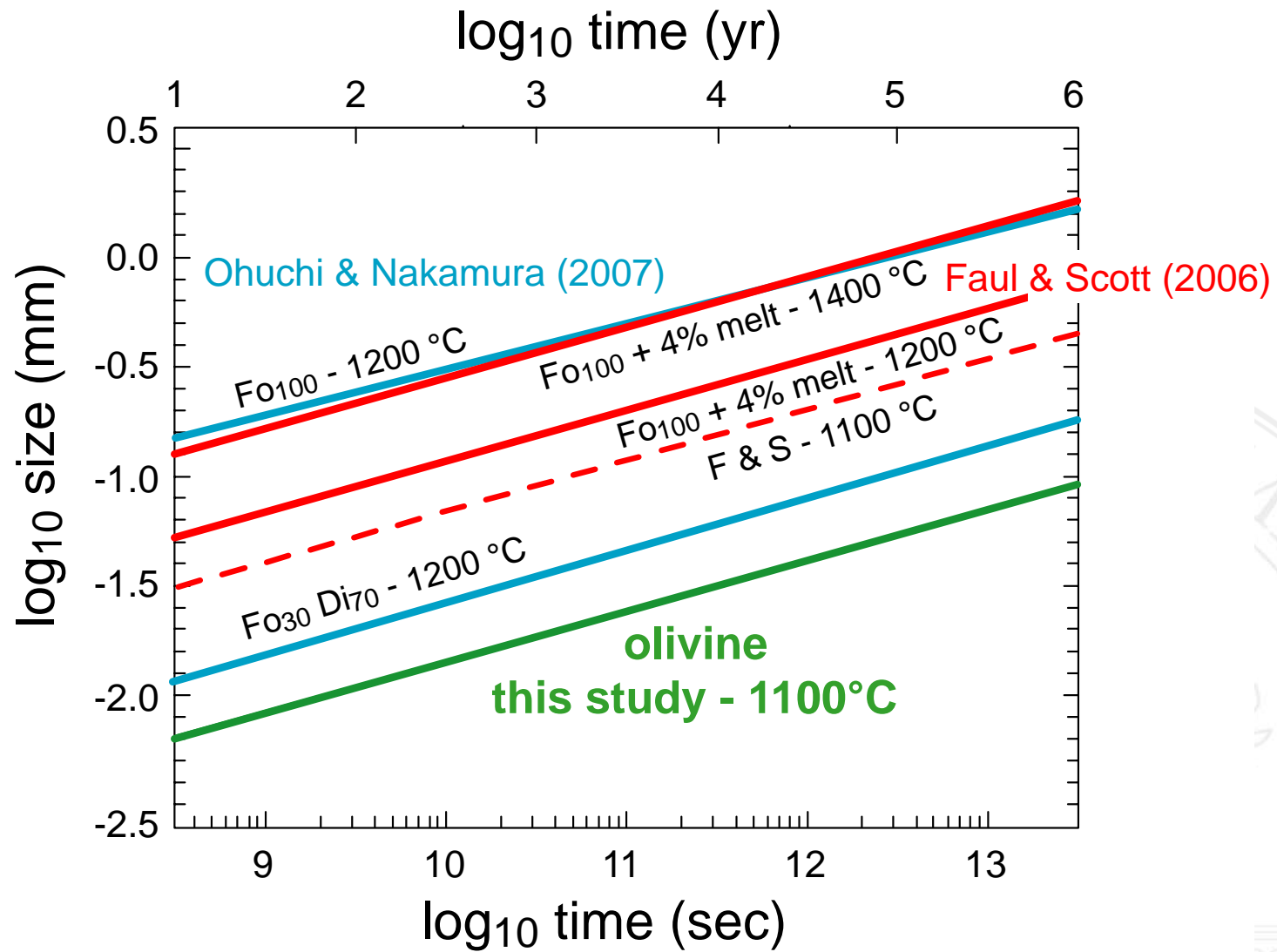


UNIVERSIDAD DE PINAR DEL RIO

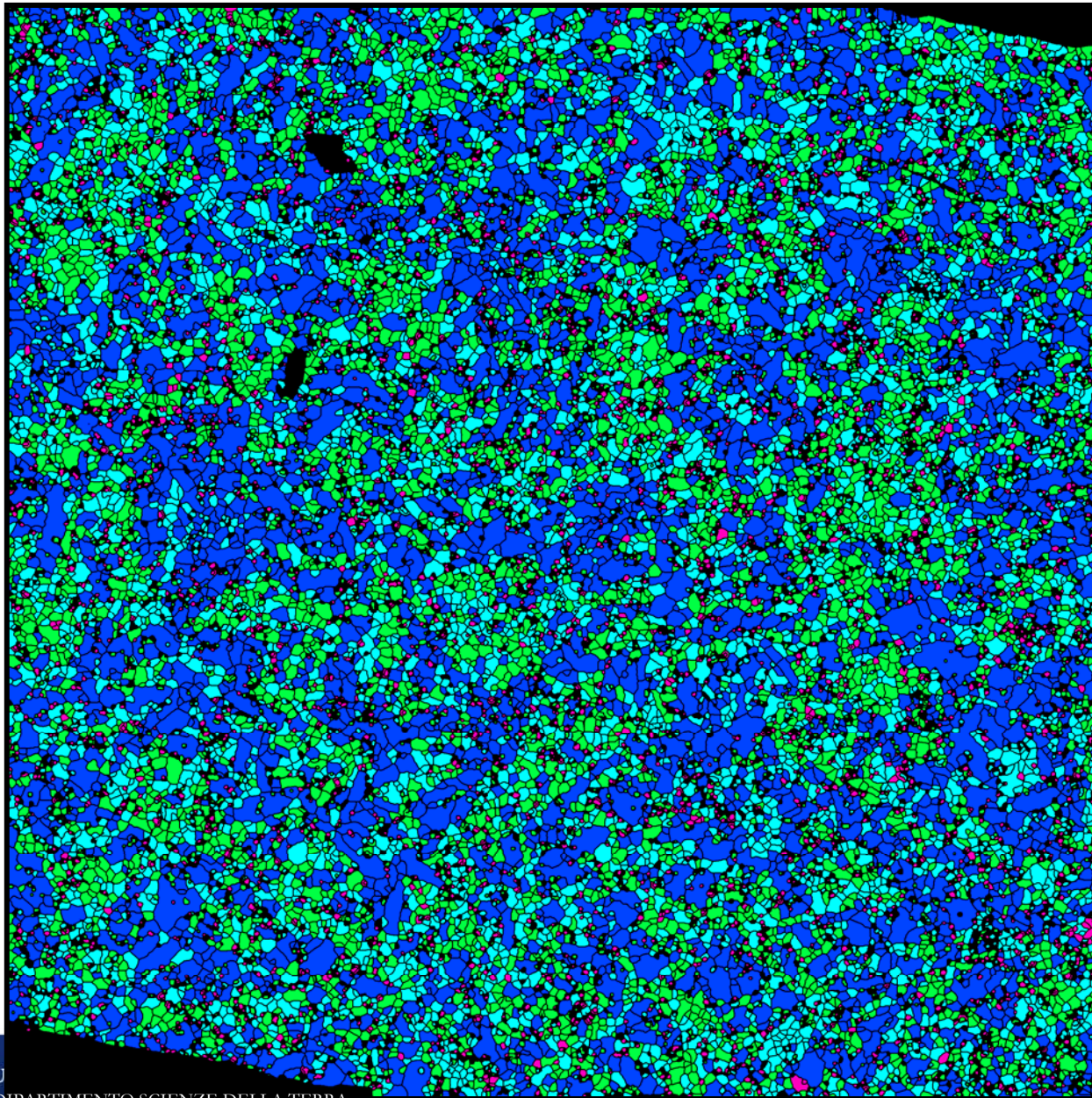
MEAN GRAIN SIZE — $D^n = kt$



OLIVINE MEAN GRAIN SIZE — $D^n = kt$



spinel – websterite @ 1.0 GPa 1100 °C

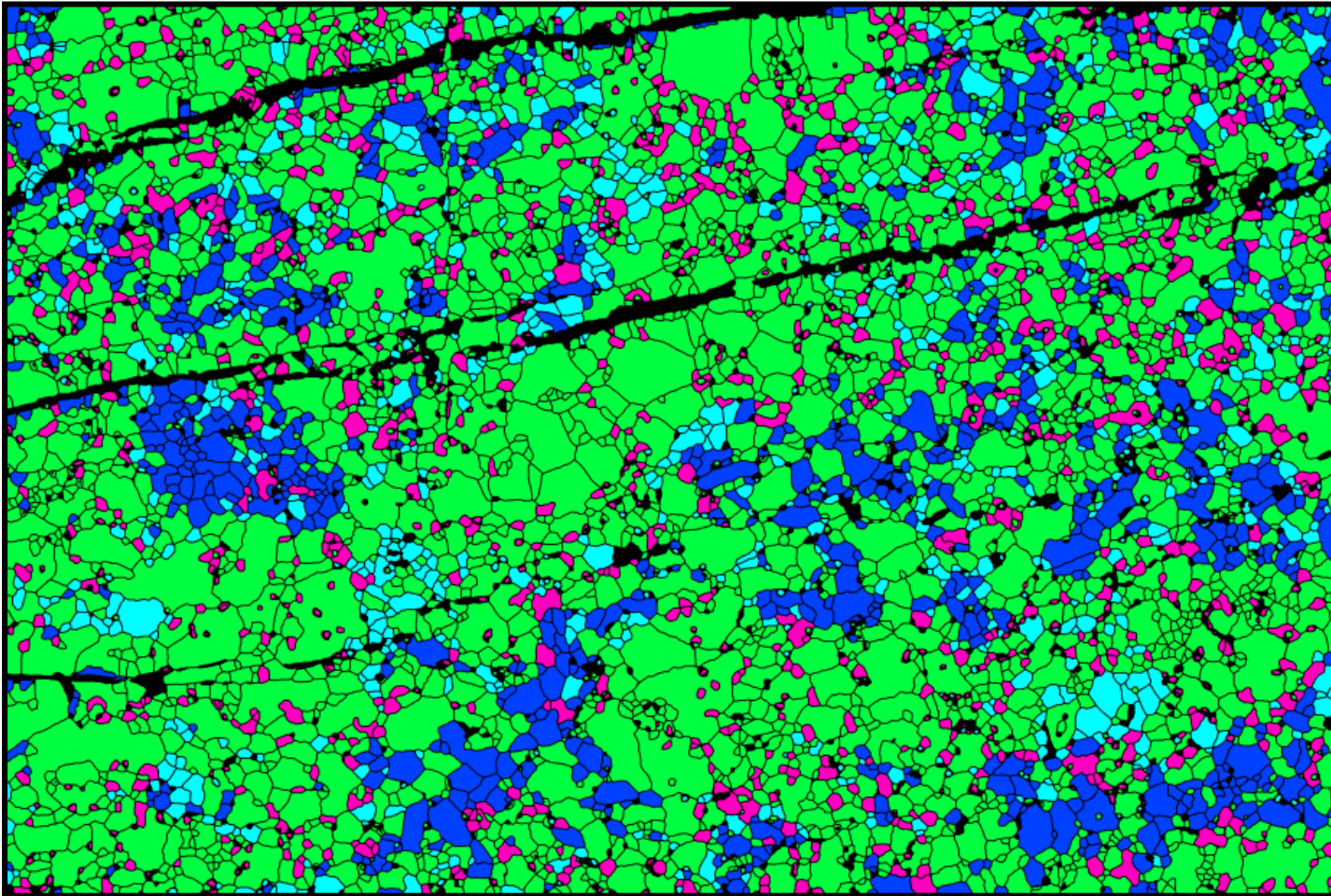


523 h

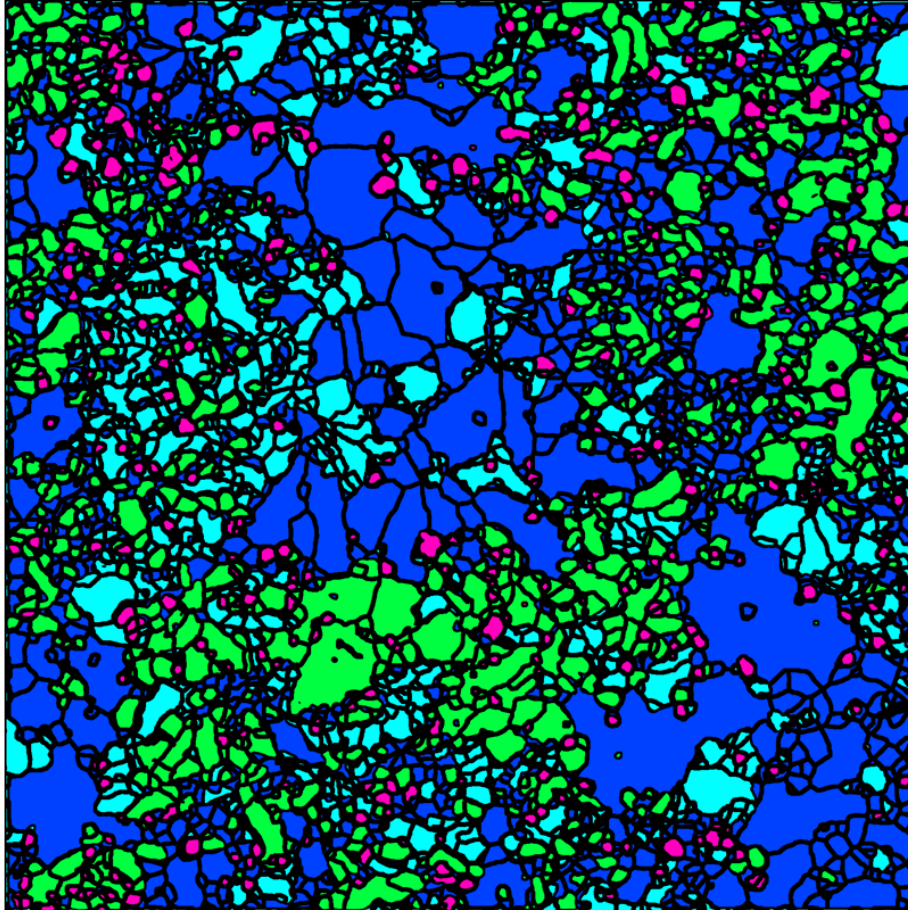


garnet – lherzolite @ 3.5 1200 °C

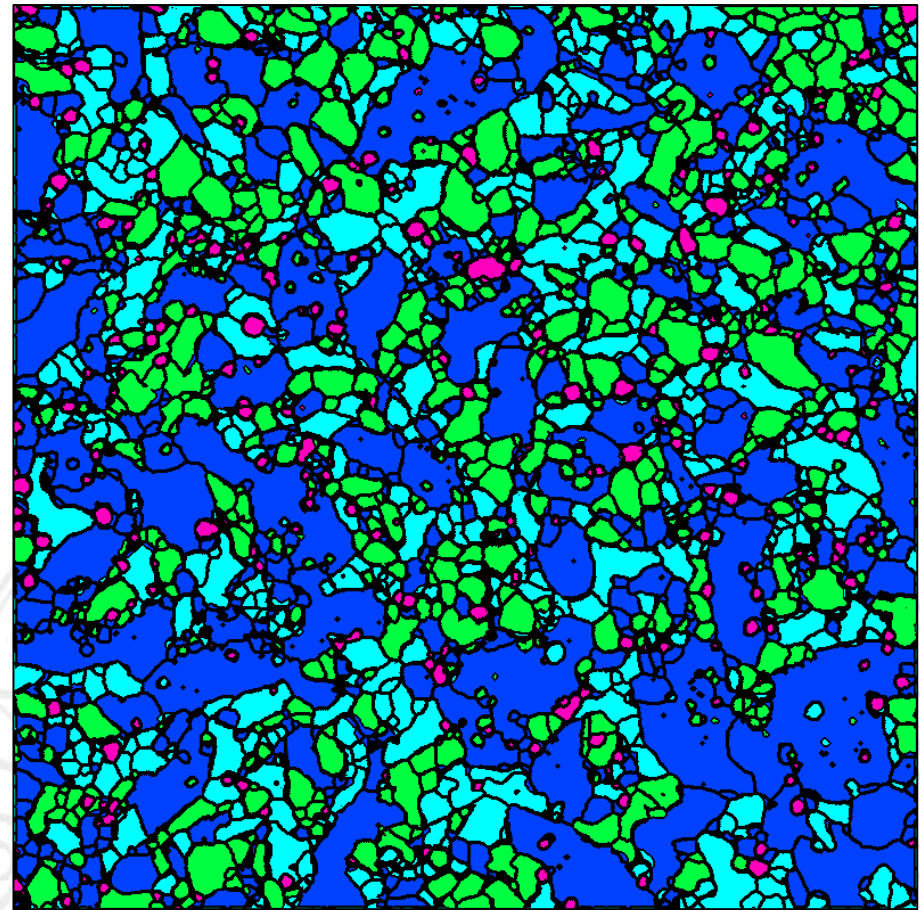
126 h



ABNORMAL GRAIN GROWTH IN ORTHOPYROXENE

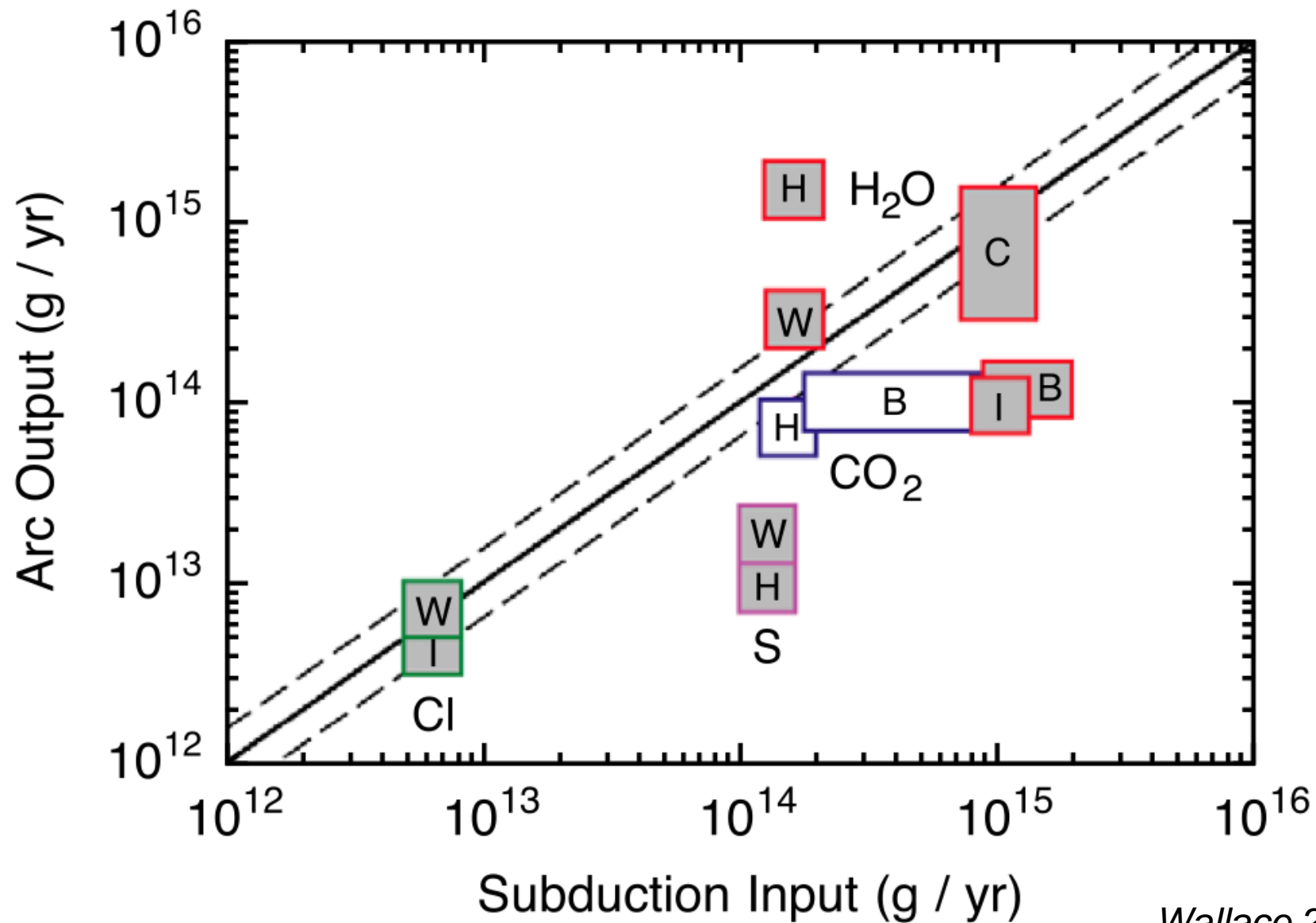


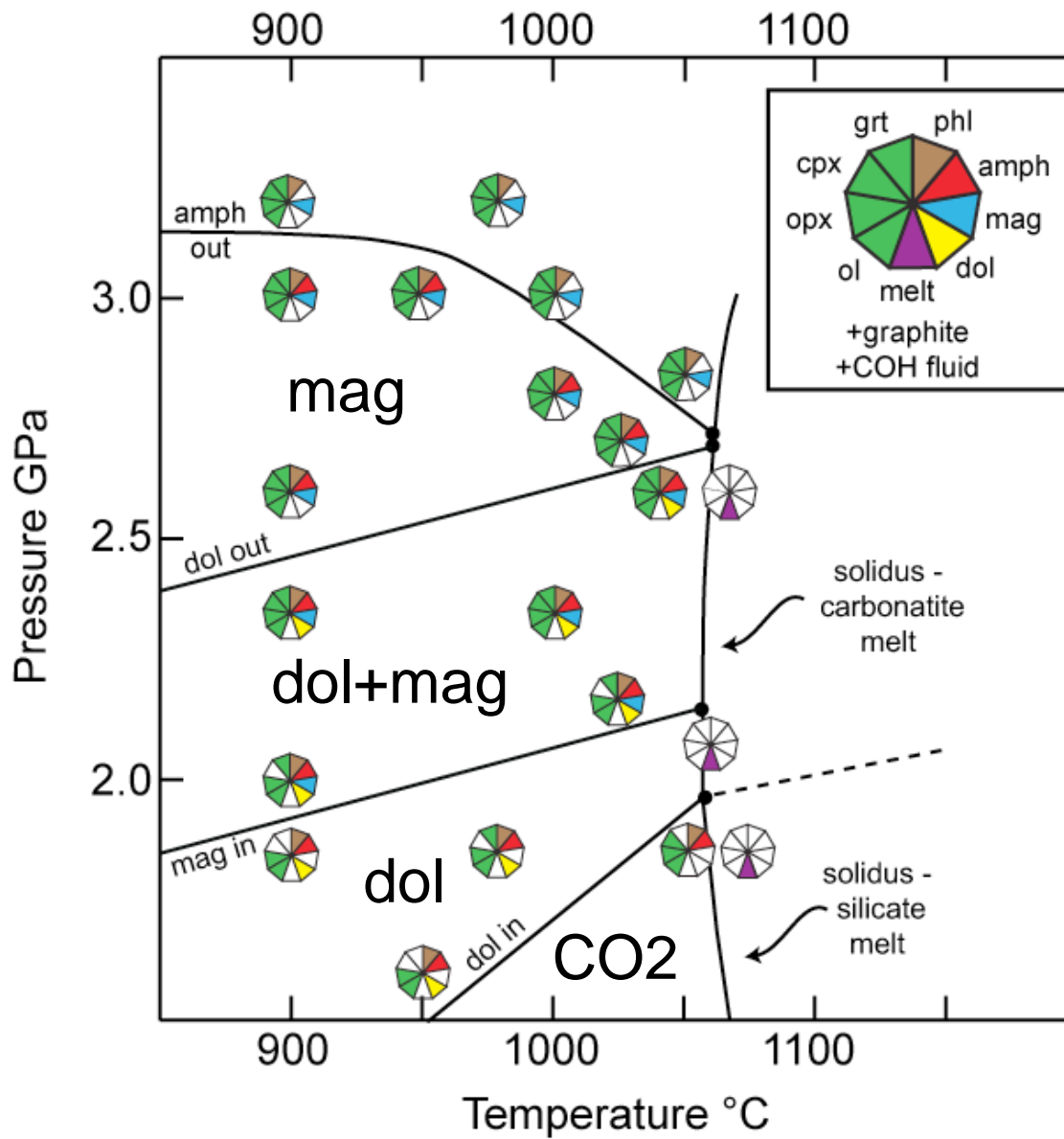
88 h



523 h



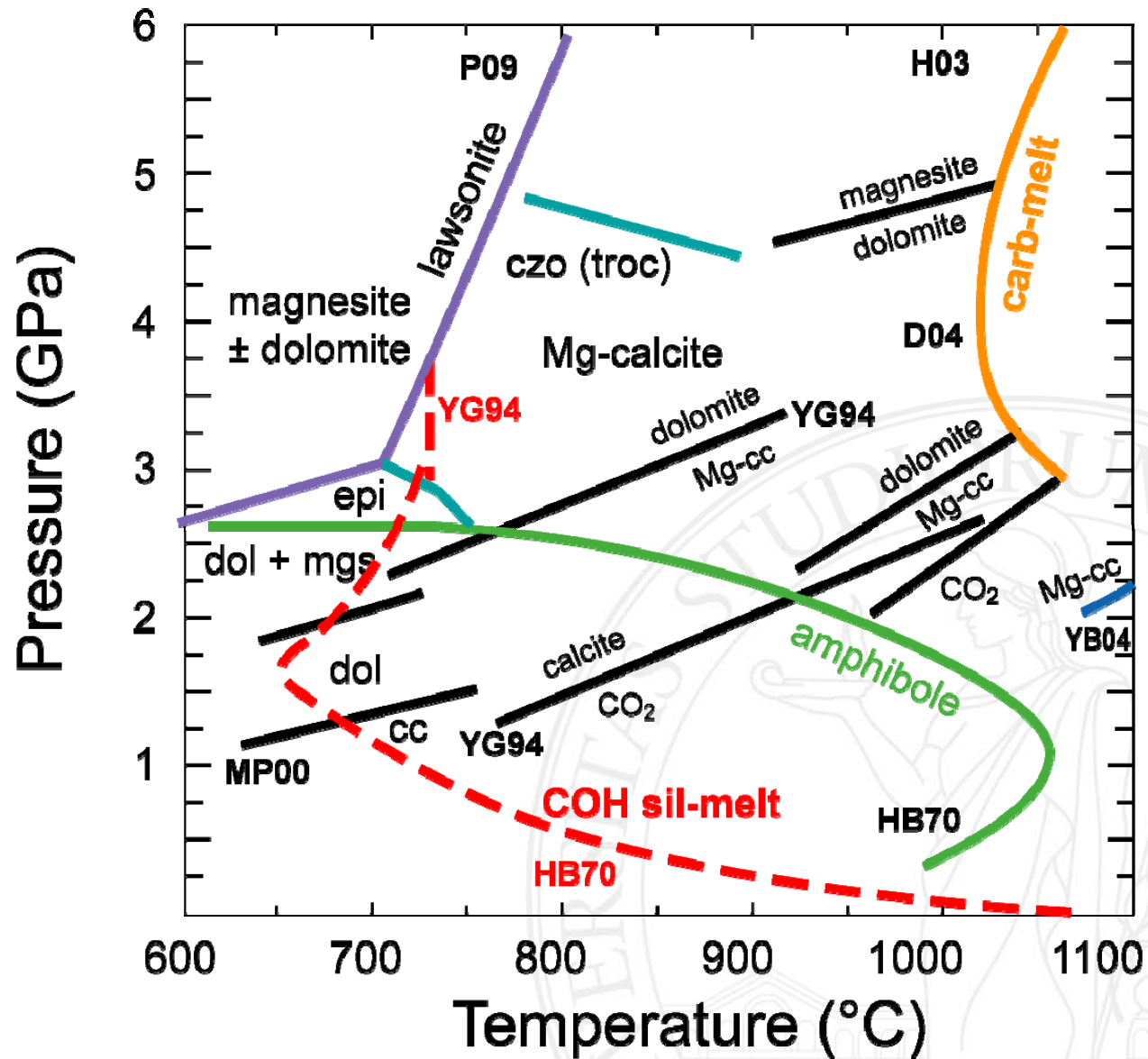




Tumiati et al. J. Petrol. in press



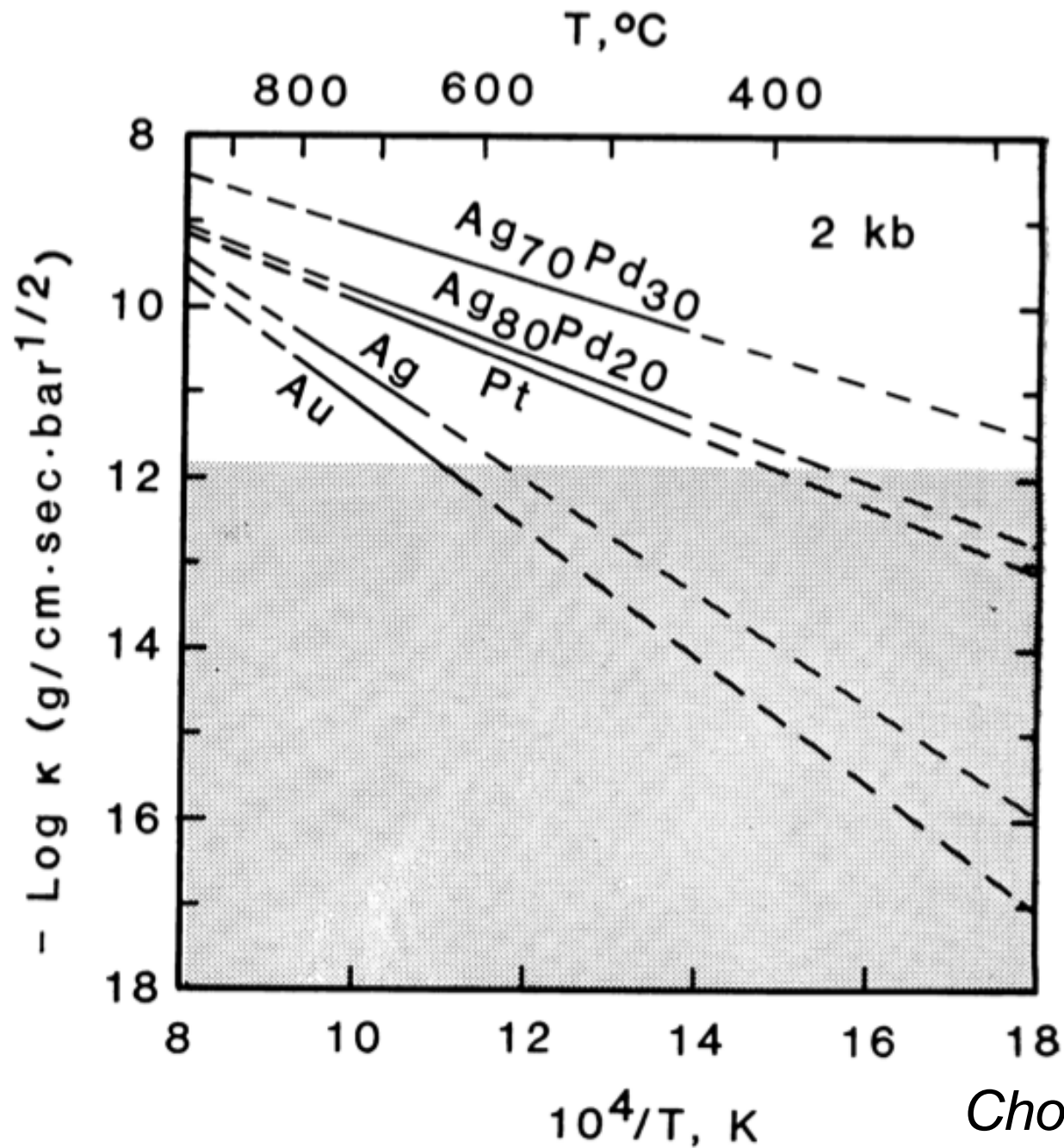
Phase relationships in mafic eclogites



Viable mechanisms for carbon transfer in orogenic systems

- ✗ Decarbonation via dolomite/magnesite breakdown is impossible at high pressure -> stable to more than 1000 °C at 3 GPa
- ✓ Carbonate partial dissolution in hydrous melts derived from wet melting is possible; to be explored, but assumes enough free H₂O fluid to promote reasonable melt quantities at wet solidus
- ✓ Carbonate partial dissolution in hydrous fluids is possible, but carbonate solubilities are known to be low; however the role of μO_2 - μH_2 to be explored
- ✓ A role for methane? entirely unexplored...



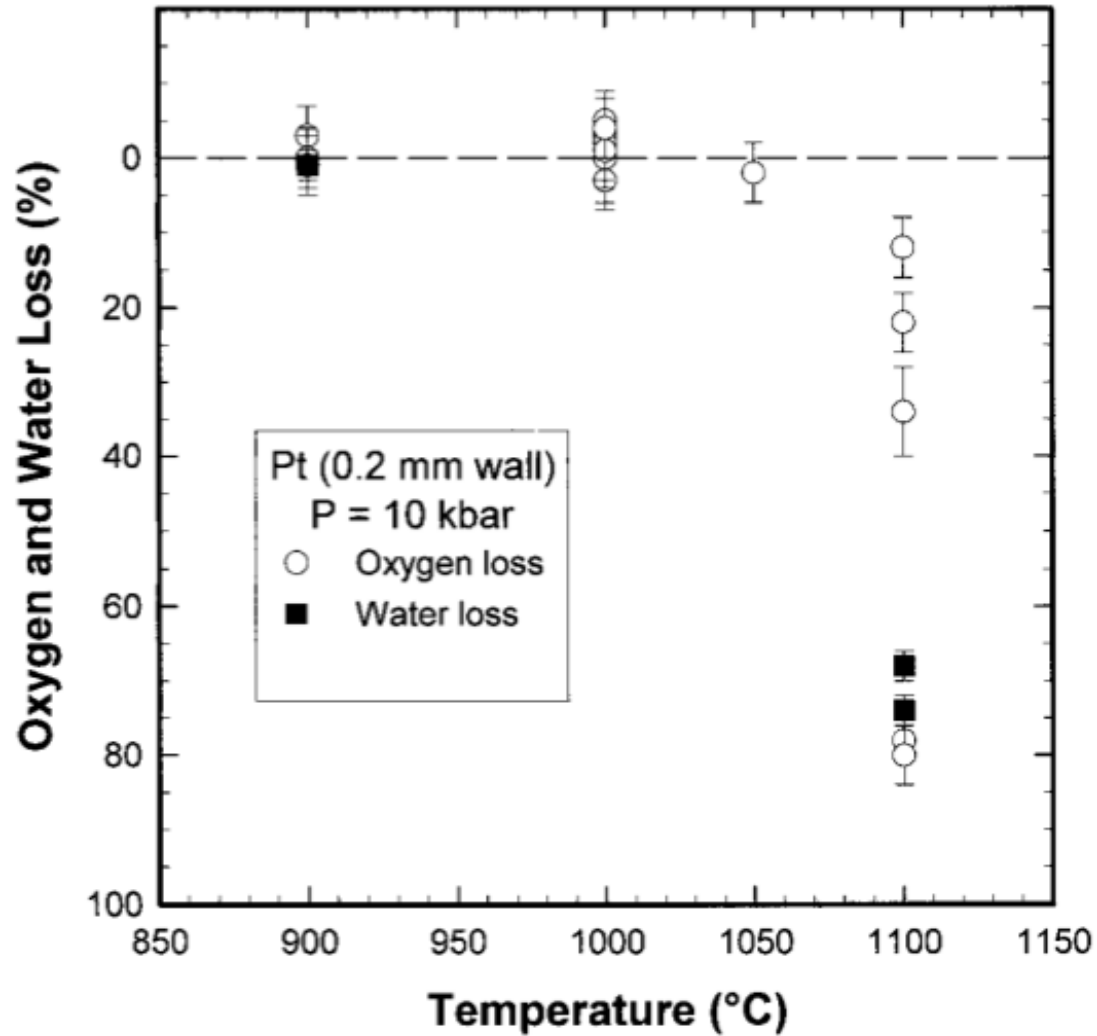


Chou, AJS, 1986

Fig. 3. Summary of the permeability constants obtained in this study. Eq (4) is plotted, and a and b are given in table 3. The dashed lines are extrapolations. The shaded area indicates where the metals cannot be used as an effective hydrogen membrane. For detail, see text.



oxygen loss - 1100 °C



carbon “infiltration” in Pt capsules at high T

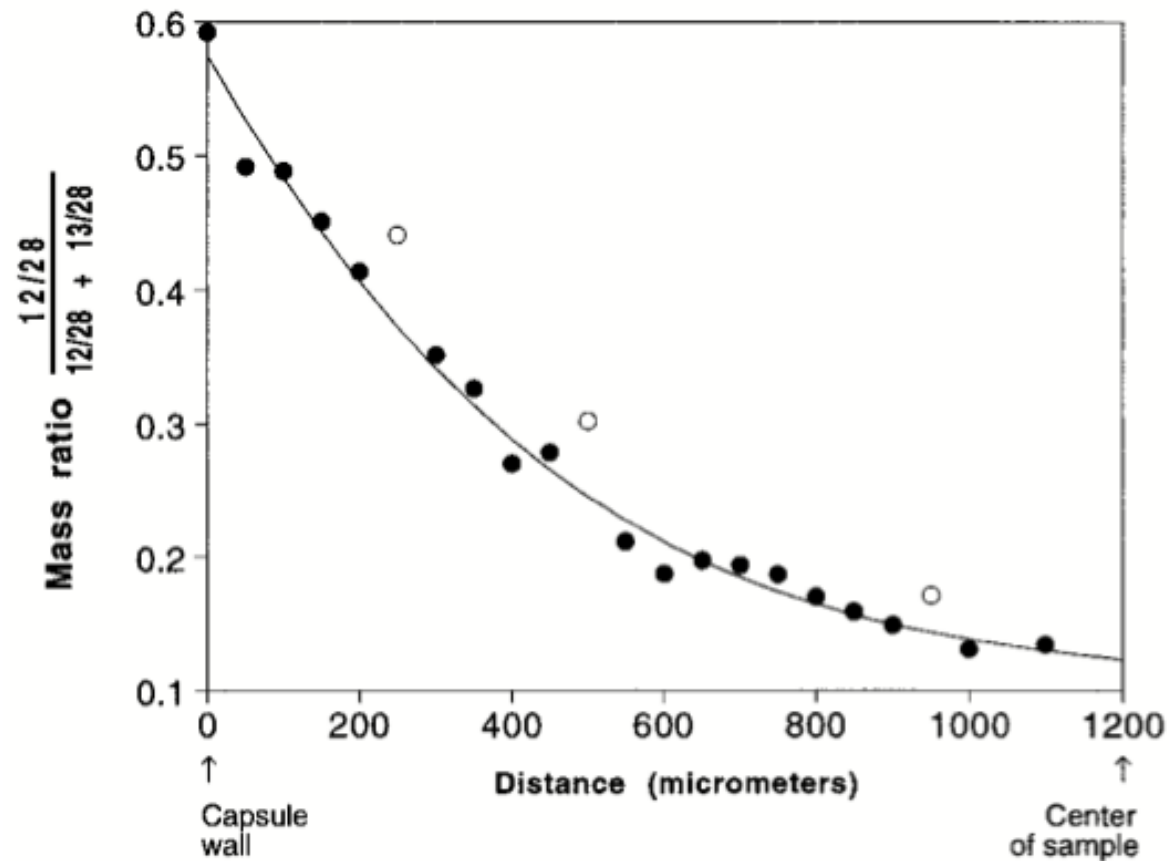
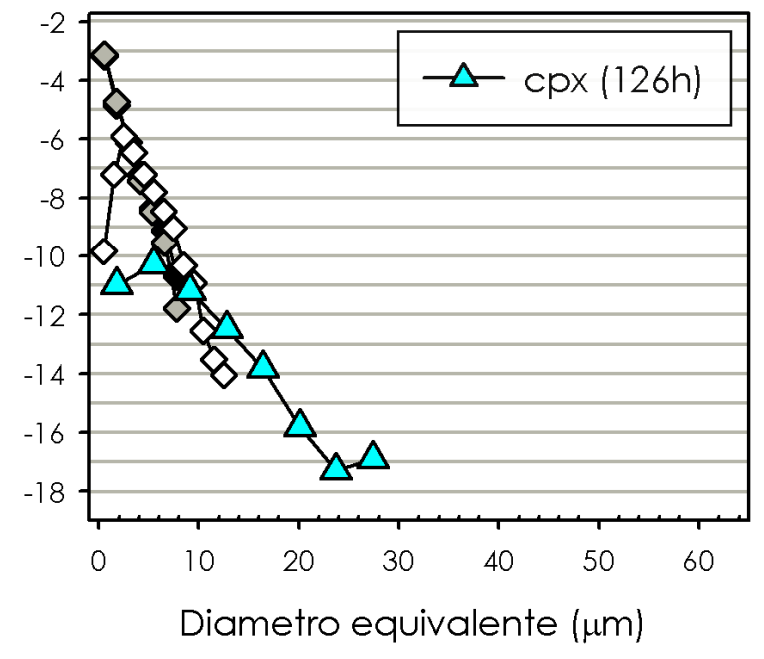
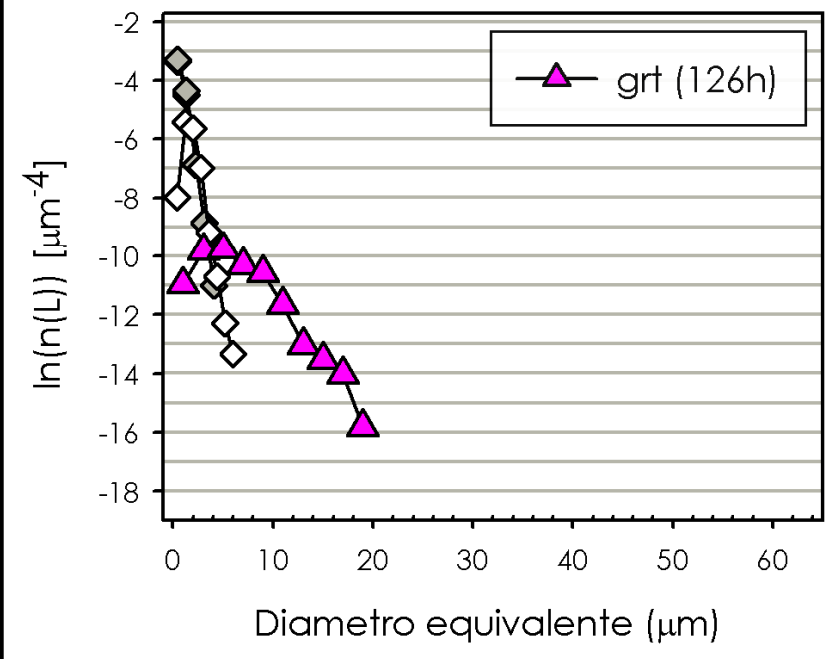
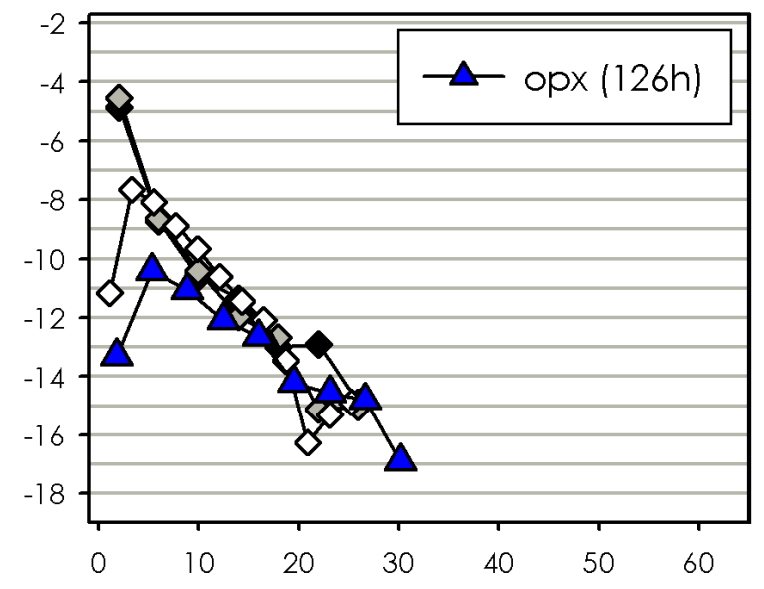
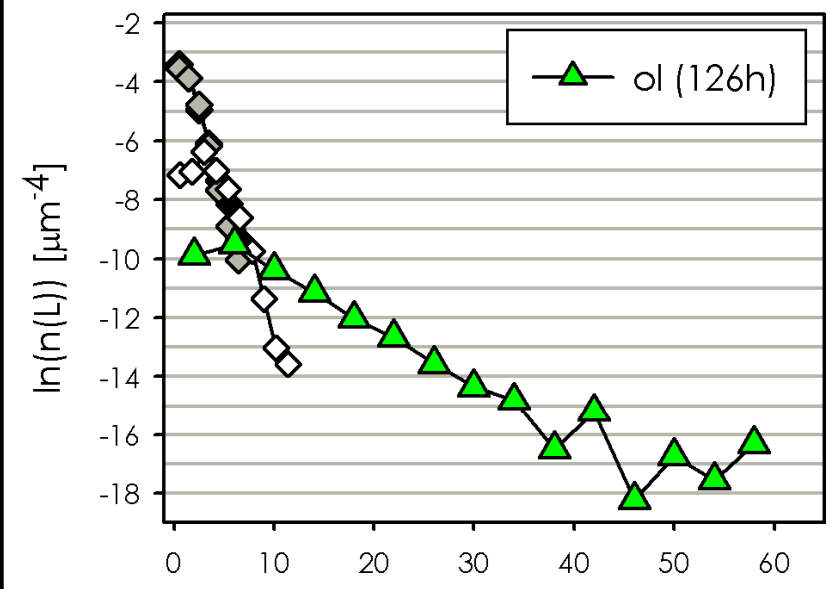


FIGURE 5. The SIMS data showing ^{12}C infiltration along the same profile represented in Figure 4. Masses 12 and 13 are normalized to mass 28 (Si) in the Jd glass. It should be noted that

Brooker et al. Am Min 1998

Laboratorio di Petrologia Sperimentale





CRYSTAL SIZE DISTRIBUTION

