ICARUS SUPERMAT

International Spring School on Forefront Alloys and Advanced Materials for Extreme Conditions

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Sardinia, Italy

Benefit of extreme Pressure in Materials Science

P<5GPa

Dr. Alain LARGETEAU, HDR
Research Engineer at University of Bordeaux
HEAD, Materials Synthesis Department
Resources Center in "Crystal Growth, High pressure, Sintering, Thin Films
ICMCB-CNRS (UPR9048)
National Center for Scientific Research (CNRS)
Pessac-33608
Bordeaux, France
email: alain.argeteau@u-Bordeaux.fr
phone: +33- (0)5 4000 8951

icmcb institut de chimie de la matière condensée de bordeaux

cnrs université de BORDEAUX

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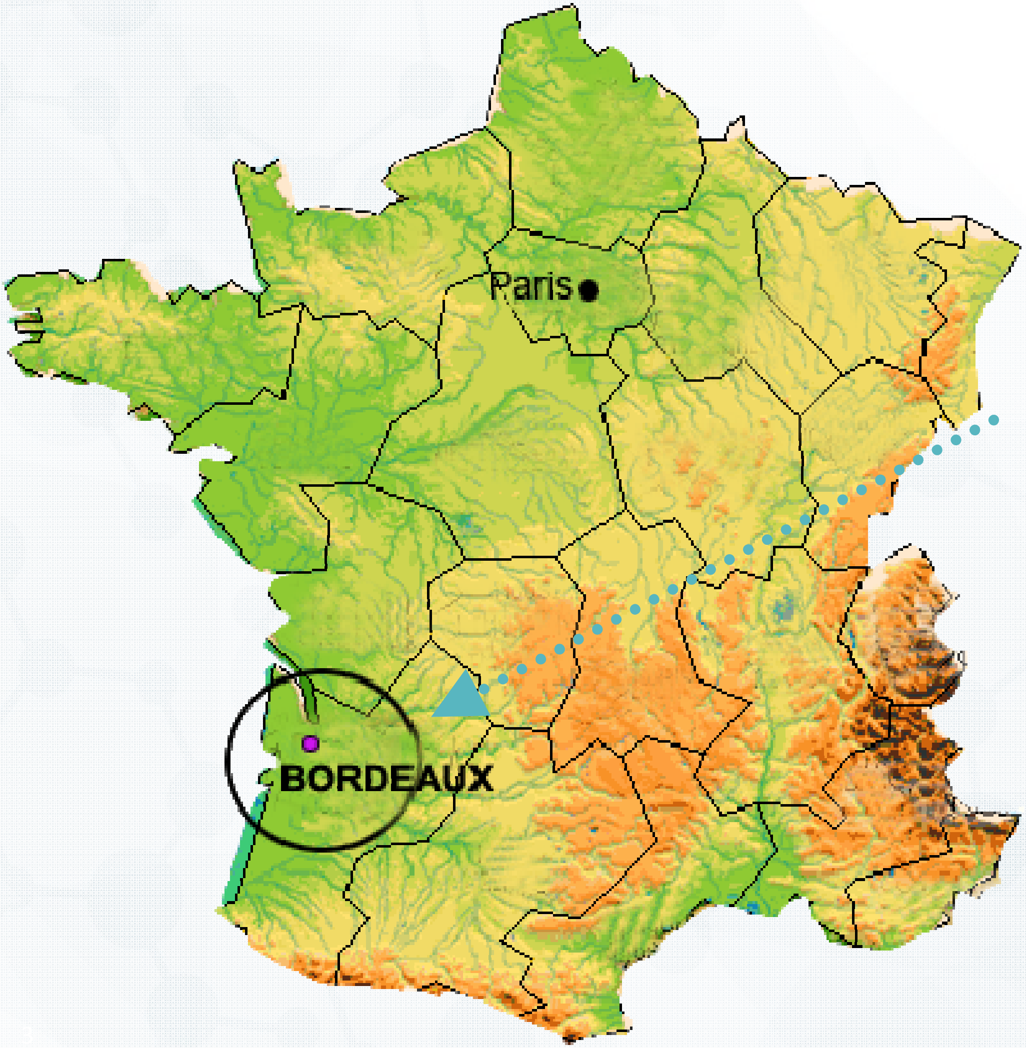
ICMCB = Institute of Condensed Matter Chemistry of Bordeaux
FRANCE



SOLID STATE CHEMISTRY
MATERIALS SCIENCE
MOLECULAR SCIENCES

Institute of Condensed Matter Chemistry of Bordeaux

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Dr Mario MAGLIONE

Director ICMCB

Administrative Management

European initiatives

CR

High Pressure:
Solid phase,
Liquid phase,
Gas phase
in
Material science,
Material chemistry,
Biomaterials
Material: Inorganic, Organic, Composite

Resources Centre = CR

Crystal growth, High pressure, Sintering, Thin films and Interfaces

Research groups

- Gr1 Oxides and architectures electro ceramics for energy and electronics
- Gr2: Materials and batteries
- Gr3 Chemistry and photonics of oxide and fluorine materials
- Gr4 Metallurgy and functional materials
- Gr5 Chemistry of nanomaterials
- Gr6 Molecules and commutable materials
- Gr7 Supercritical fluids

Shared facilities

Characterisation and specific shared facilities
- X-ray
- Chemical Analysis
- Magnetic measurement
- Electric measurement
- Thermal measurement
- Optical measurement
- NMR
- Mössbauer spectroscopy
- Granulometer

Common shared facilities divided Bordeaux 1 University
- Microanalysis (CECAMA)
- Electronic Microscopy
- Tomography

General services
- Cryogenics
- Mecanics
- Computing
- Library
- Electronics
- Infrastructure
- Hygiene and Security
- Photo
- Others

STAFF ICMCB 230

PERMANENT 119

CNRS	35	RESEARCH DIRECTORS ASSISTANT RESEARCHERS
UNIVERSITY	33	FULL PROFESSORS ASSISTANT PROFESSORS
CNRS + UNIVERSITY	51	PROFESSIONAL ENGINEERS TECHNICIANS AND ADMINISTRATIVE

NON PERMANENT 111

57 Ph.D STUDENTS
19 MASTER LICENCE OTHERS STUDENTS
16 POST-DOCS
2 FOREIGN VISITING SCIENTISTS
17 TECHNICAL STAFF

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Pressure ?

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10^{-7}

10^{-6}

Vacuum accessible with mechanical Pumps

10^{-5}

10^{-4}

Sound wave causing/at the verge of pain: 120dB

10^{-3}

10^{-2}

Summit of Everest

Universe 90% $\Rightarrow$ P > 10 GPa

10^{-1}

1

Atmospheric pressure at sea level (0.1 MPa)

10

Pressure inside tire

10^{2}

Vapor pressure in a nuclear power plant

10^{3}

Deep marine: Marine Trench (110 MPa)

10^{4}

Accessible pressure domain: 0.1 MPa to 500 GPa

10^{5}

1 bar = 1 kg/cm^{2}

1 bar = 100 000 Pa = 0,1 MPa

10^{6}

Center of the earth (360 Gpa)

10^{7}

Center of Saturn

Pressure (bar)

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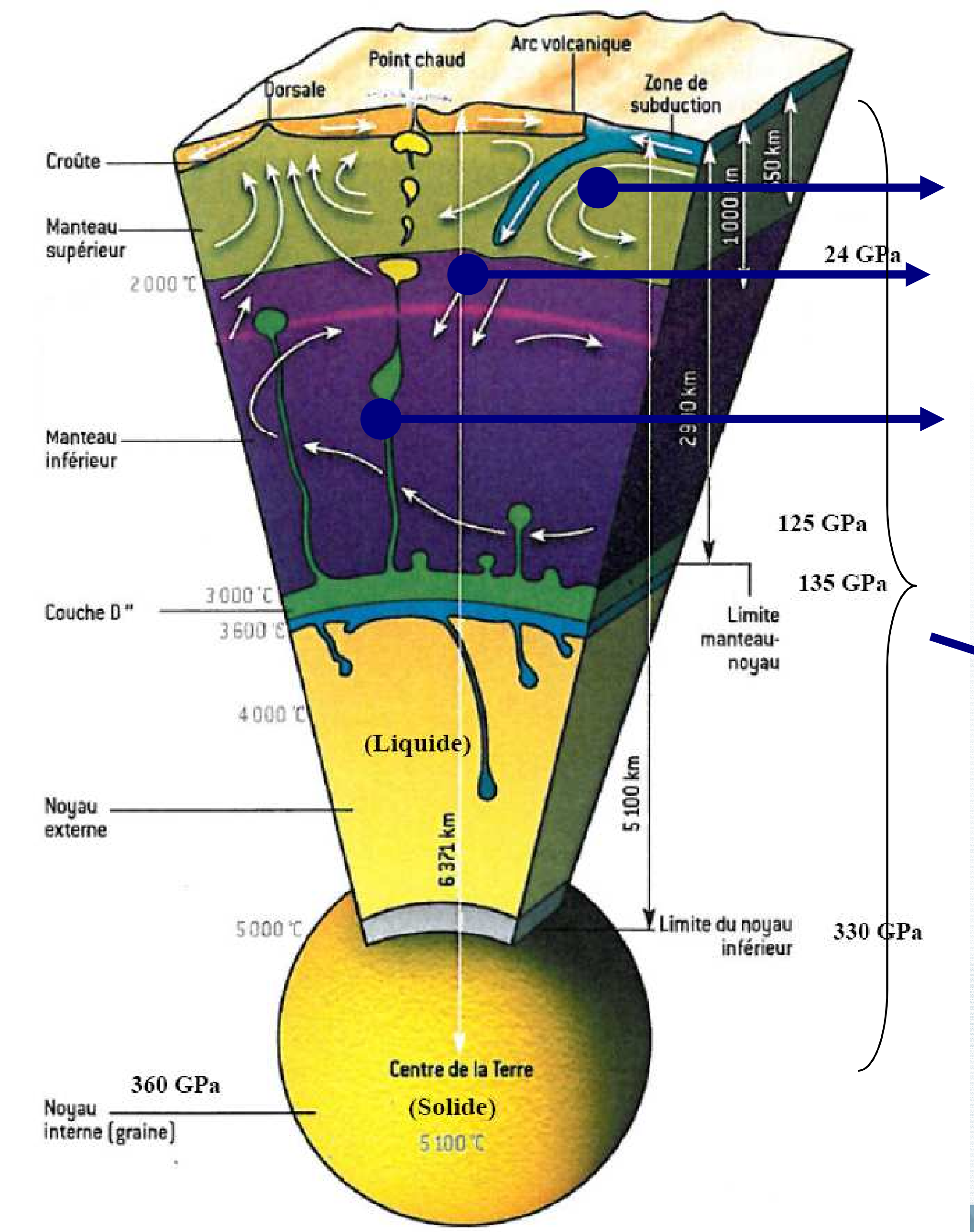
Pressure within earth



Bacteria "extremophiles"

Hydrothermal synthesis

Diamond synthesis

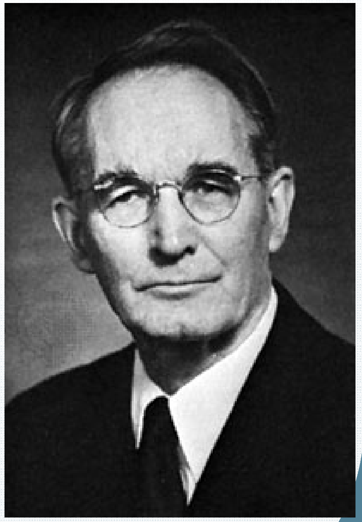
Behavior of the constituent materials

Mastery of "Pressure" and "Temperature" parameters: Important temporal shifts

Devices under pressure: knowledge of metal alloys and ultra-hard materials

Specific industrial needs: manufacturing cannons, ammonia synthesis, hydrometallurgical processes of Al from bauxite, etc. ..

P.W. Bridgman: Nobel Prize in Physics 1946



⇒ Developing and devising equipment

⇒ $P \approx$ 100 kbar (10 GPa)

⇒ Study of the mechanical and thermodynamic properties of the material at high pressure

Devices

Pressure = Force (F) / area (S) ⇒ P ↑ if F ↑ (Hydraulic Press)
or S ↓ (diamond anvils)

Vessel (HP bomb, HP chamber, Autoclave)

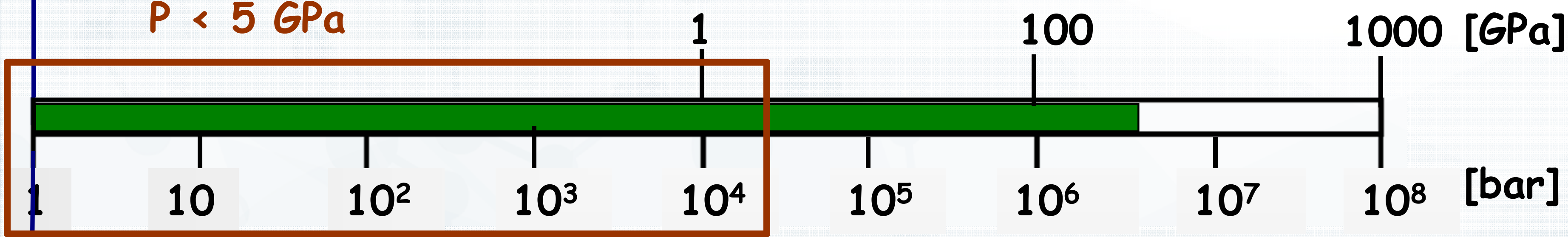
Piston / cylinder

No transparent to radiations

2 opposite anvils "Belt"

Shock waves (dynamic)

P < 5 GPa



transparent to radiations

2 opposite diamond anvils

Multi anvil

Vessel with optical windows (ambient T)

Applications

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P < 5 GPa

[bar]	1	10	10^2	10^3	10^4	10^5	10^6	10^7	10^8
[MPa]	0.1		10		1000		10^5		10^7
[GPa]					1		100		1000

Synthesis of high density polyethylene (PEhd): 1953

Hydrothermal crystal growth of quartz : 1953

Diamond synthesis: 1953 ASEA ↔ 1954 GE
(Thermodynamically stable domain)

Densification under pressure (CIP): 1956

Cutting by water jet: 1979

Food treatment (Pascalisation): 1990

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Principal effects of Pressure

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Le Chatelier's Principle

Any phenomenon accompanied by a **volume decrease** is enhanced by an **increase in pressure**

→ Opposes the effect related to the increase of T (expansion)

→ Favorize the change of states : gas → liquid → solid

→ Favorize structure with denser phase:

* Direct conversion of $C_{graphite} \rightarrow C_{diamond}$ (P > 12 GPa / T ≈ 2000°C)
* Indirect conversion of $C_{graphite} \rightarrow C_{diamond}$ (P ≈ 6 GPa / T ≈ 1500°C) by dissolution/precipitation in liquid metal
* Extremely dense ceramics (porosity ≈ 0) → Optoceramic

→ Elevates the melting point (P induces condensation) : P increases the domain of stability → stabilize precursors for the reactivity.

→ Increases reactivity in addition of T

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Principal effects of Pressure

1/ Energy generated by Pressure

(a) According to the pressurized medium

Energy implementation in the medium:
- Gas: high due to its high compressibility
- solid: weak and dependent of the bulk modulus

Comparison: Energy induced by compression according to the nature of the medium / Energy of a chemical reaction

Pressure (bar)	Medium	Energy cal/mol
1000	gas	3000
1000	solid	1
10 000	solid	5
100 000	iron	20
100 000	H_2O	1000
1	chemical reaction	20 000

(table from [Wentorf, Chem. Eng. (1961) 6:177])

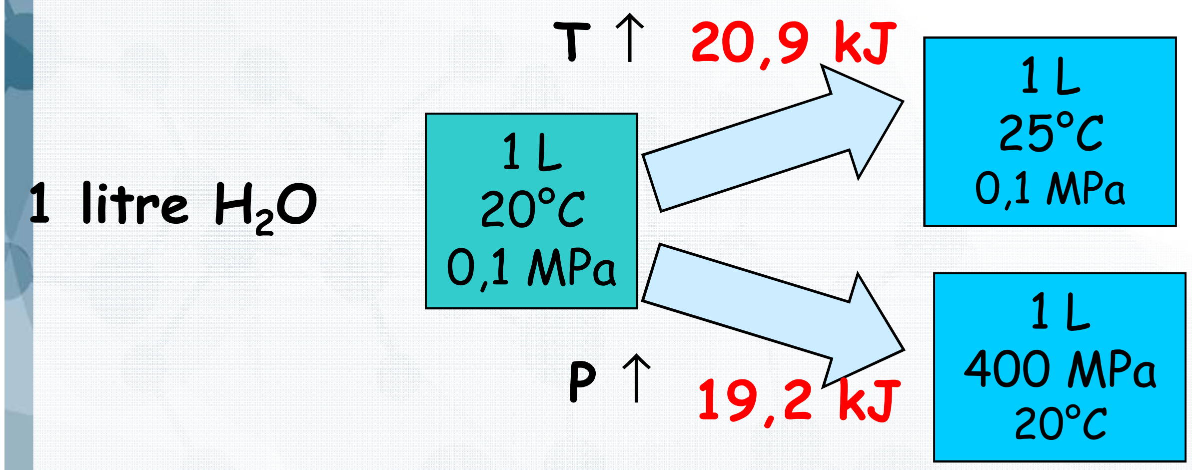
⇒ **Pressure: low energy / chemical reaction**

Interests : Need contribution of T for the synthesis of materials under high pressure.

Principal effects of Pressure

1/ Energy generated by Pressure

(b) Comparison with temperature (liquid medium)



The energy involved in 5 units of temperature is close to that corresponding to the compression from 1 to 4 000 bar

[Mertens, In New Methods of Preservation. (1995) 135]

⇒ Pressure: low energy / temperature

Interests: Alteration only weak bonds (and those leading to $\Delta V < 0$) (Ex: Biological Applications)

Principal effects of Pressure

2/ Densification effect

(a) For chemical reaction

By defining chemical reaction of two precursors: $A + B \rightarrow C$

With : V/Z = Volume Form V_A/Z_A V_B/Z_B V_C/Z_C

and $\Delta \mathbf{V} = V_C/Z_C - (V_A/Z_A + V_B/Z_B)$

if: $\Delta \mathbf{V} < 0$: reaction is activated by pressure

$\Delta \mathbf{V} > 0$: reaction will be hindered by pressure

⇒ Pressure: Initiate chemical reaction in one way

Interests: Promotes the denser phase during a reaction at the expense of others

Principal effects of Pressure

2/ Densification effect

(b) For stability of chemical bond (liquid medium)

By defining ΔV of dissociation = $(V_{A_{atom}} + V_{B_{atom}}) - V_{(A\text{-}B)_{bond}}$

With dissociated atoms $A_{atom} + B_{atom}$ and the bonding $(A\text{-}B)_{bond}$

Type of bonding	ΔV of dissociation (ml/mol)	Action of the pressure on the bonding
Covalent	+10	Strengthening
Ionic	-10 (each ion involved)	Destabilisation
Hydrogen	+3 à -1	Strengthening (ΔV > 0) or reduced destabilizing effect (ΔV < 0)
Hydrophobic	-10 à -20	Destabilization

(Table modified according to *[Federighi et al., Microbio-Alim-Nutr. (1995) 13: 115 et 225]*)

No alteration of strong chemical bonds (covalent)

⇒ Pressure: impact only weak bonds ($\Delta V<0$)

Interests: Conservation of molecular structure when it consists solely covalent bonds (Ex: Save original properties in Food)

Principal effects of Pressure

3/ Chemical reactivity

- In fluid phase (gas or liquid)

Increasing concentration of species ⇒ decreasing mean free path

Application: Hydro(solvo)thermal reactions - solid/liquid interface (*Heterogenous system)*

For a given T: P allows dissolution of material, although it is relatively insoluble under ordinary pressure

- In solid phase

Decreasing mean free path + Energy ⇒ increasing the reaction kinetic

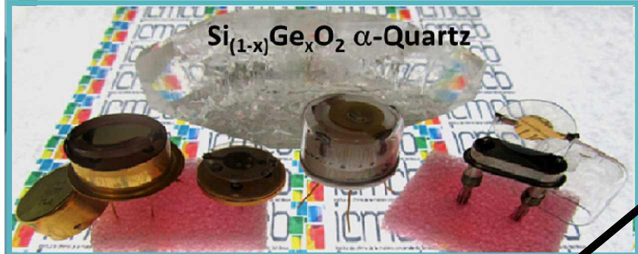
⇒ **Pressure: Increasing reactivity in addition T**

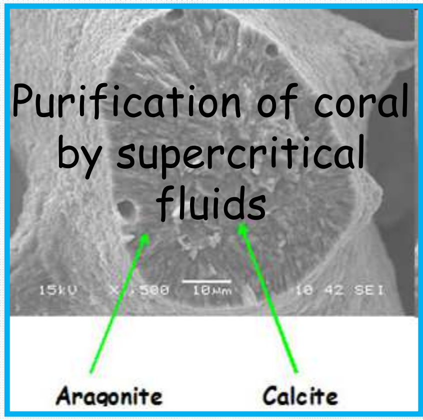
Interests: Increase the kinetics of chemical syntheses (Ex: solvothermal crystal growth, ...)

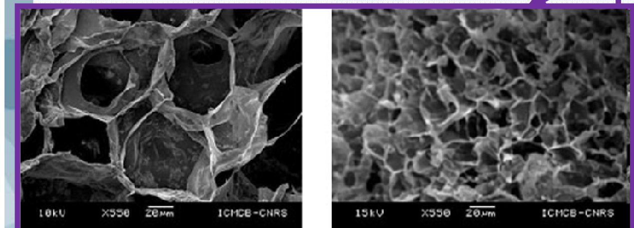
Crystal growth

Single Crystal

SiO_2 α-quartz, $Si_{1-x}Ge_xO_2$ α-quartz, ZnO, $CaCO_3$





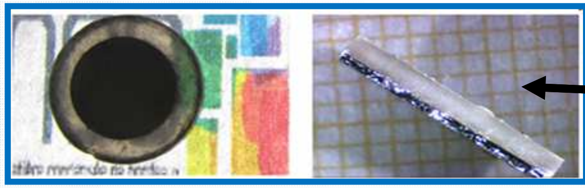


Porous biomaterials densified without heating to preserve biocompatibility

High Pressure

Bioscience

- Multilayers material packaging adapted for High Hydrostatic Pressure processing (HHP / HPP)
- Purification of natural material: **Material for medicine: coral,..**



Material science

Cold isostatic pressure (CIP) of powder

Biomaterials

Porous structure/polymer's impregnation to improve osteoinduction

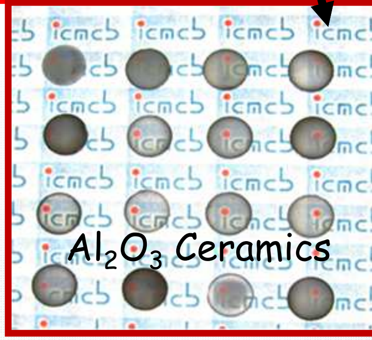
Material chemistry

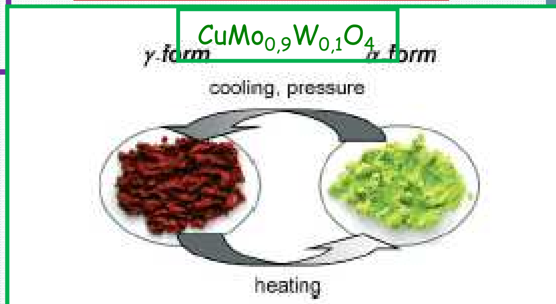
- Relations structure/properties in correlation with oxidation states of transition elements (Fe, Ir, ..)
- **Piezochrome behavior**

Sintering/bonding

Material Science

- **Densification**
  - **optoceramic**
  - refractory/hard material
  - biocompatible
- **Bonding**
  - composition gradient
  - **multimaterial**





Transitions γ→α and α→γ with T and α→γ with P or T

P<5 GPa at ICMCB

Vessel non «borgne» (cylinder with two opening in the same axis)

Solid phase

Sliding pistons in matrix

SPS
PC

Opposite anvils with cylinder

Belt

Opposite anvils without cylinder

Vessel «borgne» (cylinder with one opening)

Liquid phase

CIP

Hydro(solvo)thermal phase

Phase diagram (critical point: Pc - Tc)

Aqueous (Hydrothermal) / Non aqueous (Solvothermal)

H_2O: Tc=374°C - Pc=22MPa / CO_2: Tc=31°C - Pc=7MPa / NH_3: Tc=132°C - Pc=11MPa

T<Tc + P<Pc
subcritical

T>Tc + P>Pc
supercritical

Hydro(solvo)thermal

Extraction - Purification

Gas phase

HIP reactive
HIP non reactive
(Scelled tube)

Densification/Sintering/ Bonding activated by pulsed current (SPS)

Dr. SINTER LAB SPS-515S
2000°C / vacuum, gas (N_2, Ar)

Graphite mold
100MPa / 2000°C

WC/Co mold
800MPa / 600°C

Composite mold
100MPa / 1300°C / **air**

HAp Ceramics

Oblong graphite mold

Oblong ceramics

without mold

Al_2O_3 Ceramics

$MgAl_2O_4$ Ceramics

Bonding / Sintering (Multimaterial)

Densification/Sintering/ Bonding activated by pulsed current (SPS)

SPS under high pressure : HP-SPS (pulsed current)

P<5GPa / T<1500°C
Vol≈2cm³ / air

Cutter for drilling in petroleum
WC-Co / PCD (diamond + Co)

Crystal growth under fluid pressure

Liquid phase : P + T
hydro(solvo)thermal

200MPa / 0.1l

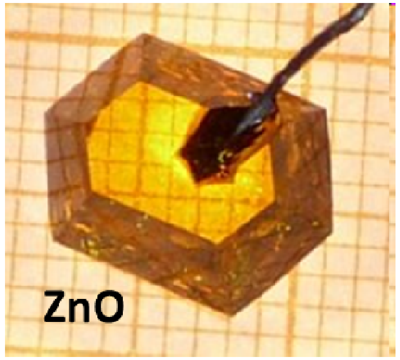
20°C <T< 450°C

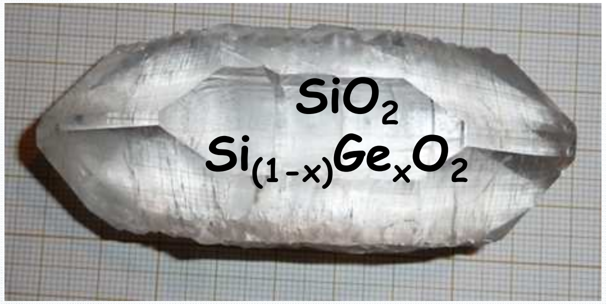
350MPa / 1.5l

20°C <T< 450°C

300MPa / 1.5l

20°C <T< 500°C





Densification/Sintering/Bonding under fluid pressure

HS
Hydro(solvo)thermal Sintering
Sub/Supercritical phase

P<350MPa / T<500°C
Vol≈2cm^3
H_2O or others aqueous liquids

CIP
(Cold Isostatic Pressure)
Liquid phase

P_{H20}<600MPa / T<80°C / Vol≈3l

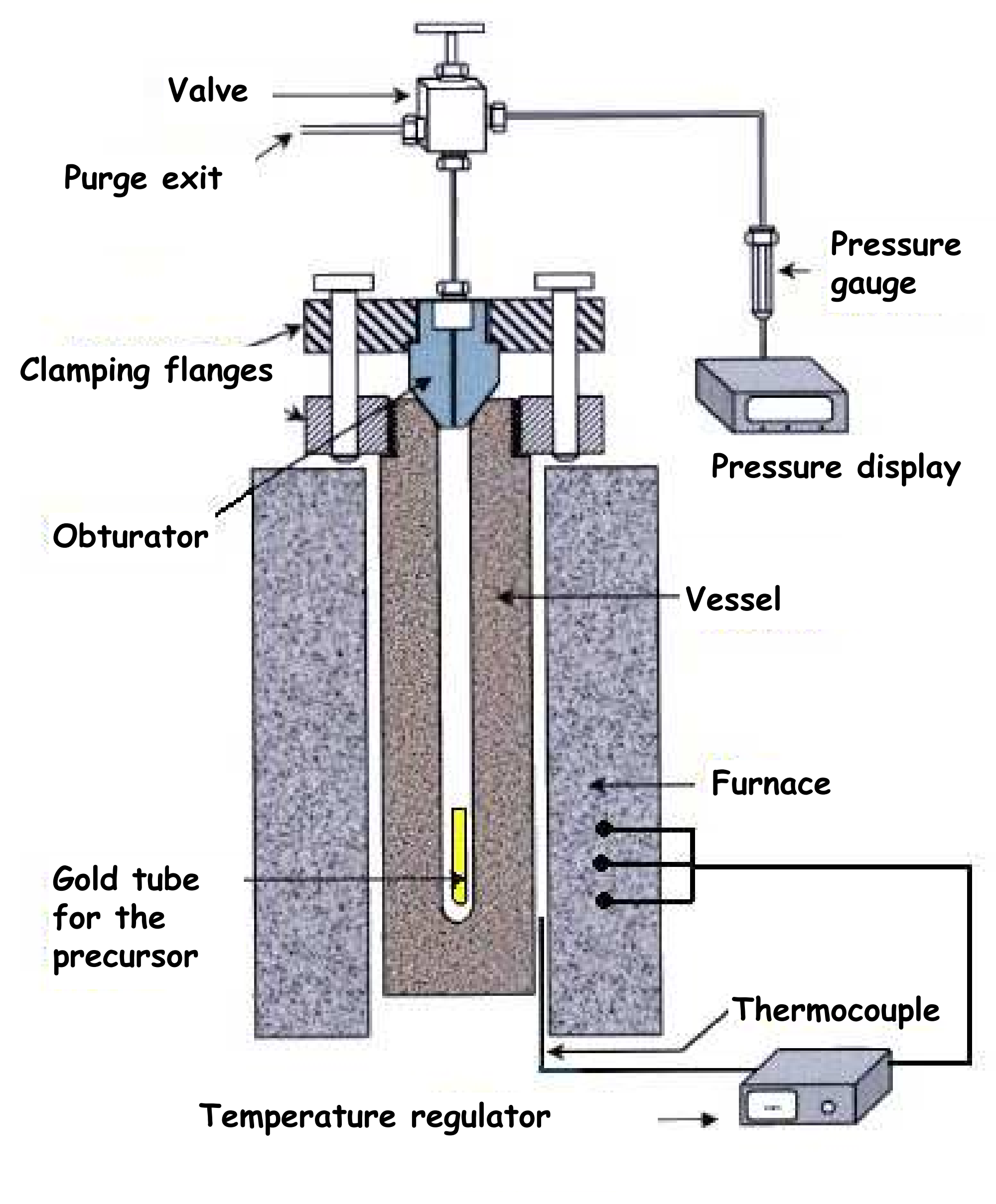
(with support of HPBioTECH)

HIP
(Hot Isostatic Pressure)
Gas phase

P_{gas} (O_2, N_2, Ar, CO_2)<200MPa
T<800°C / Vol≈30cm^3

Pressure: gas phase

P < 300MPa / 20°C < T < 600°C / 0.2 liter



Difficulty and dangerous (energy) due to the compressibility of fluid : gas >> liquid

Dangerosity due to the type of fluid: O_2 >> N_2, Ar, CO_2

Interest:

O_2: Oxide (powder), stabilization of unusual oxidation state of transition element (Fe, Ir, ..) for theoretical study

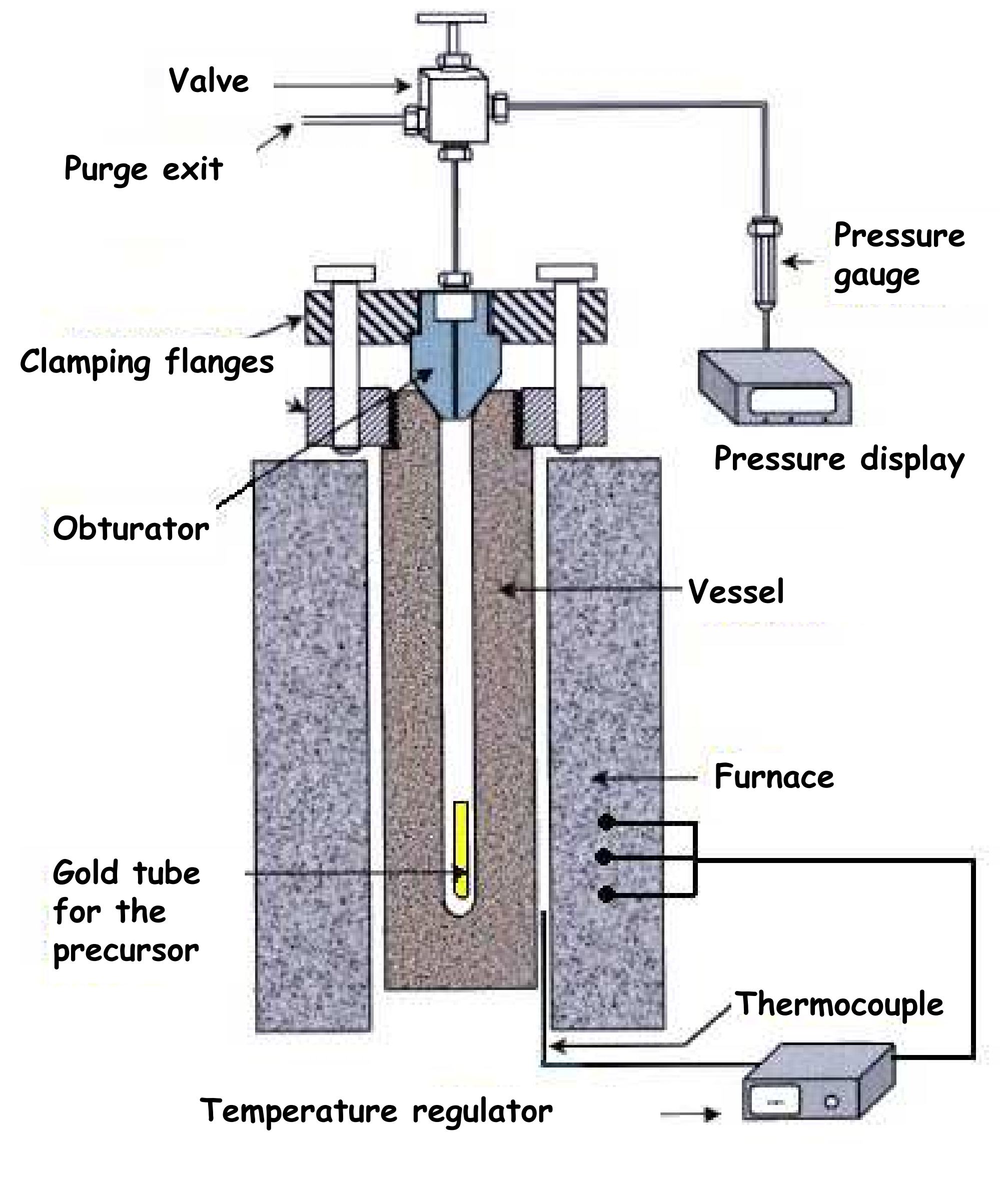
O_2: Oxide (ceramic) to correct the stoichiometric balance (impossible in single crystal)

N2, Ar: Hot Isostatic Pressure (**HIP**) to sinter powder in inert gas

O_2: Hot Isostatic Pressure (**HIP**) to sinter powder in reactive gas

Pressure: liquid phase

P < 300MPa / 20°C < T < 600°C / 0.2 liter



Difficulty and dangerous (caustic, toxic) due to the type of fluid: NaOH, KOH, NH_3, ..

Interest:

Liquid:

H_2O: Process for biological material
H_2O: Porous structure (T<0°C)
CIP: Cold Isostatic Pressure to densify powder (pre-sintering, ..)

Liquid/Temperature:

Hydrothermal: Oxide synthesis (powder, crystal, ceramic)
Solvothermal: Ammonothermal (NH3) for nitride synthesis (powder, crystal)
Extraction of organic compound: Supercritical fluid

Liquid phase at Tamb: CIP

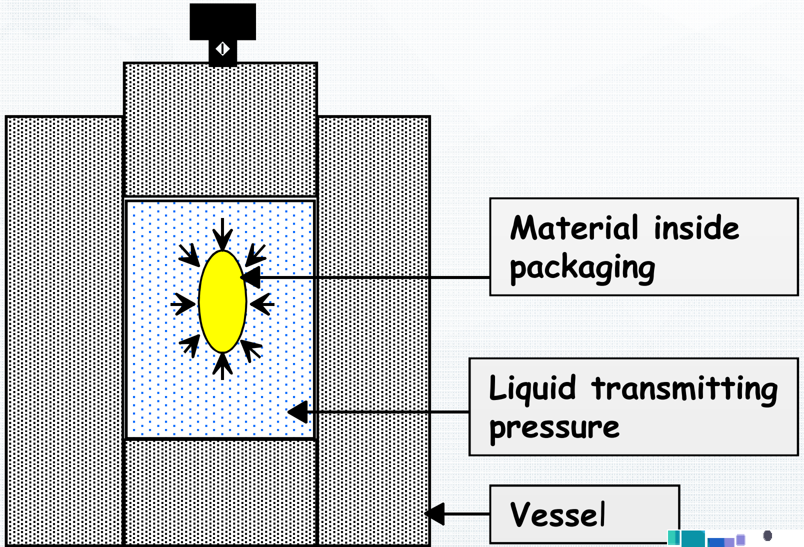
(with support of HPBioTECH

P < 600MPa / -20°C< T <80°C
5 liters

Interest :

- Increasing density of raw pre-ceramics before thermal treatment,
- Diffusion of polymer inside inorganic material structure such as biomaterial

Vessel: Ethylene glycol/water (freezing: -50°C)



H_2O at T>20°C

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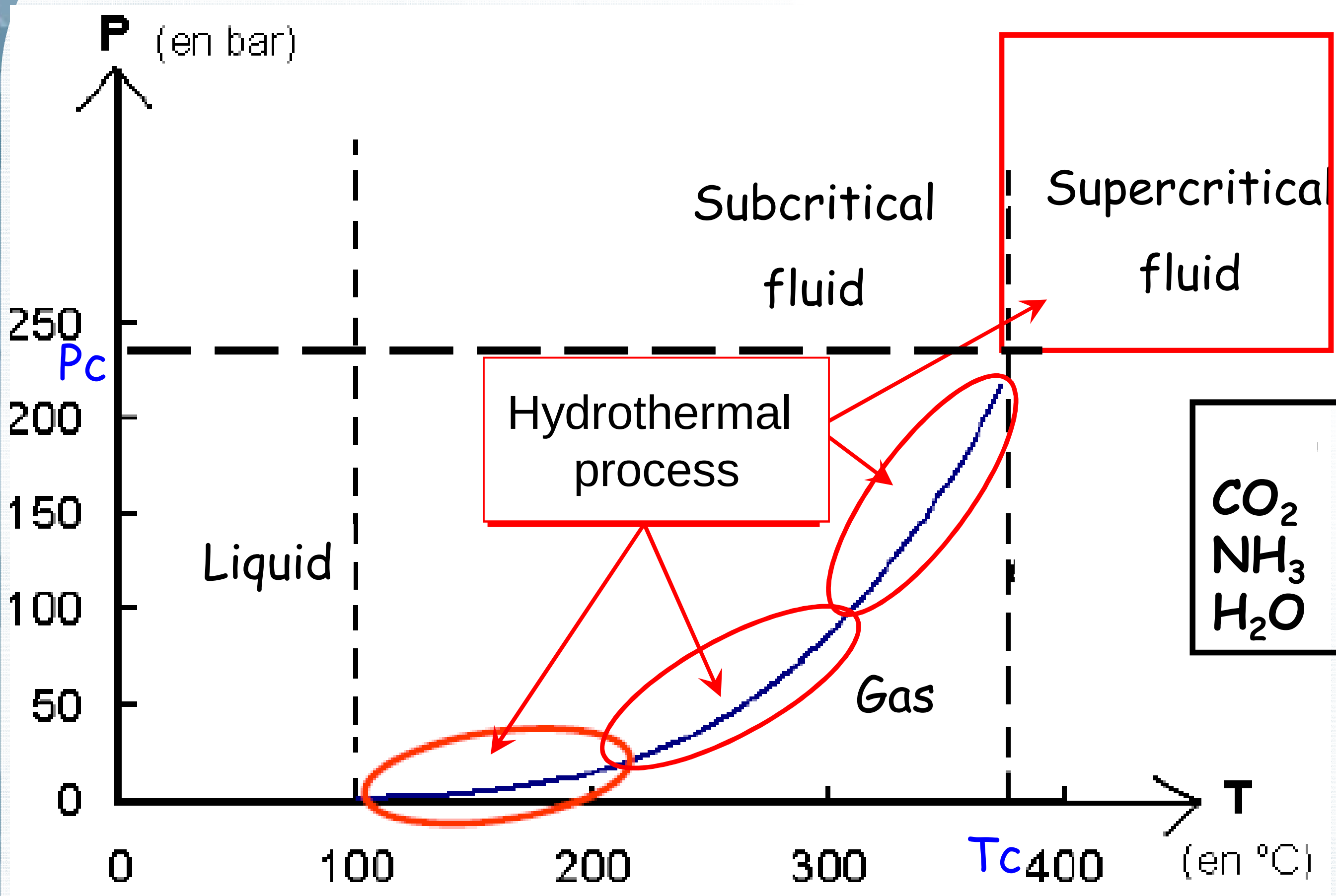
Hydrothermal/solvothermal synthesis



	Tc (°C)	Pc (MPa)
CO_2	31.2	7.38
NH_3	132.4	11.29
H_2O	374.1	22.1

Pc/Tc characterizing the medium are modified by presence of additives in H_2O

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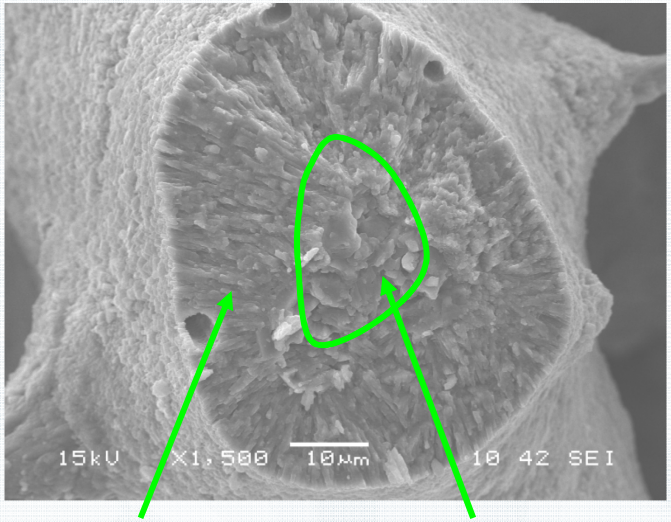
Purification of Coral by supercritical fluid

Elimination of coral's organic contents by ethanol under **supercritical conditions**
and
Conservation of properties (chemical, mechanical, structural) of coral (**Aragonite**)



Interest of P: preserve Aragonite structure at 240°C /300MPa / 1 h

At ambient Pressure:
Aragonite → Calcite T≈ 240°C

P < 400MPa / 20°C < T < 500°C / 1 liter

[FR 2863172 (2005-06-1) & WO 2005055885 (2005-06-23)]

Hydrothermal synthesis

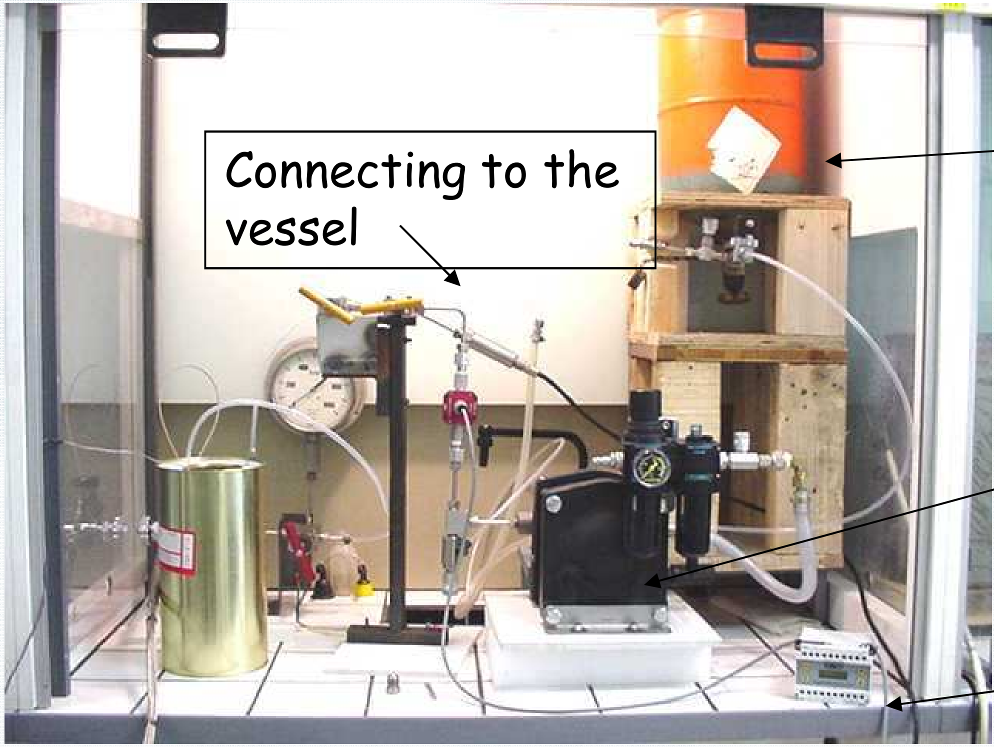
- **Liquid phase could be :**
  Aqueous solution : pure water and all solution based on water solution

P < 300MPa
20°C < T < 500°C
0.5 liter

- **Hydrothermal reaction to synthesize :**
  – Fine powder: micro/nanocrystallites of composition versus chemical nature of solvent
  – Single crystal : SiO_2, ZnO,$CaCO_3$

Solvothermal synthesis

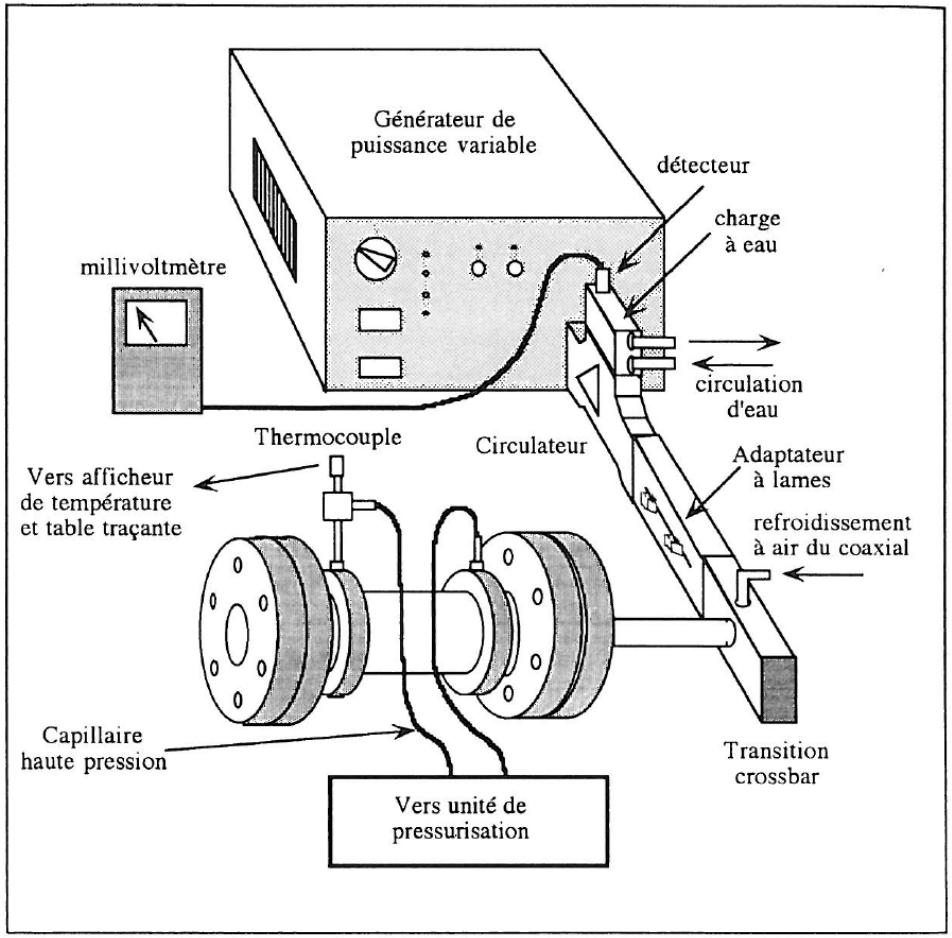
- **Liquid phase could be :**
  Non aqueous solution (solvothermal reaction): NH_3

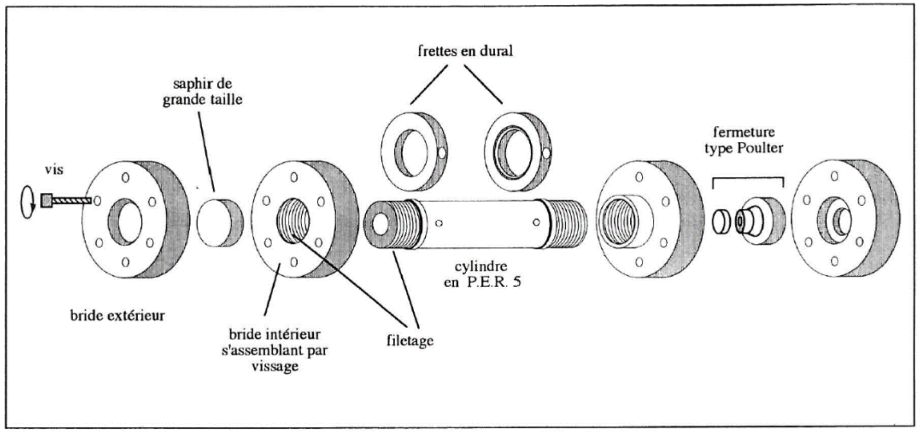


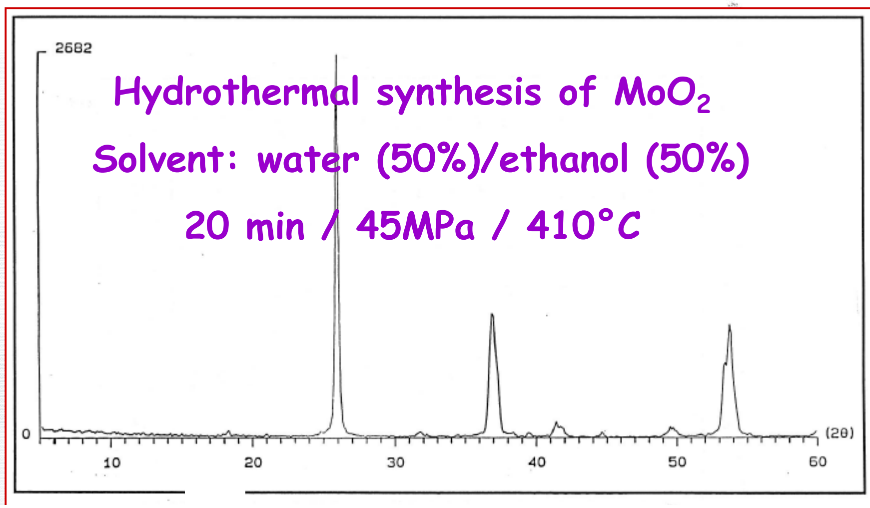
P < 300MPa
20°C < T < 500°C
0.5 liter

- **Solvothermal reaction to synthesize :**
  - Fine powder: micro/nanocrystallites of composition versus chemical nature of solvent
  - Large Single crystal : AlN, GaN

Hydrothermal synthesis activated by microwave: nano/micro particles







[Largeteau, High Pressure Research, (2001) 20:1-6, p.281-288]

Conclusions

Principal domains of high pressure applications at ICMCB

Media: solid, liquid and gas

- Promotes the densest form
- Increases reactivity

Medium : liquid

- Implement low energy
- Promotes the densest form

Materials Chemistry

- Reactive gas pressure (HP gas)
- Hydro(solvo)thermal reaction (Synthesis in sub/supercritical by radiation heating and microwave)
- Reactive sintering (SPS, microwave, hot pressing, hydrothermal)

Materials Science

- Hydro(solvo)thermal crystal growth
- Crystal growth by Template/SPS
- Hydro(solvo)thermal synthesis of nano and microcrystallites
- Densification by heat (SPS, microwave, hot pressing, solvothermal)
- Densification at cold (CIP)
- Assembling multimaterials (SPS)

Biocomposite

- HP liquid
- HP gas

Thank you!

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