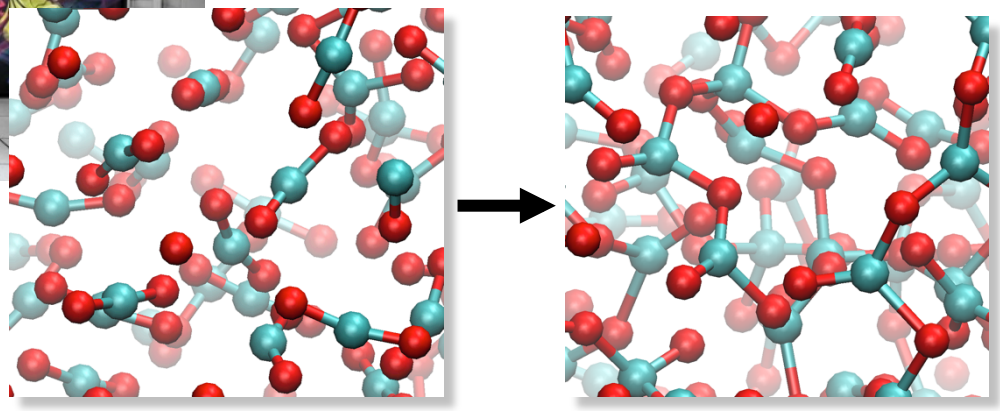
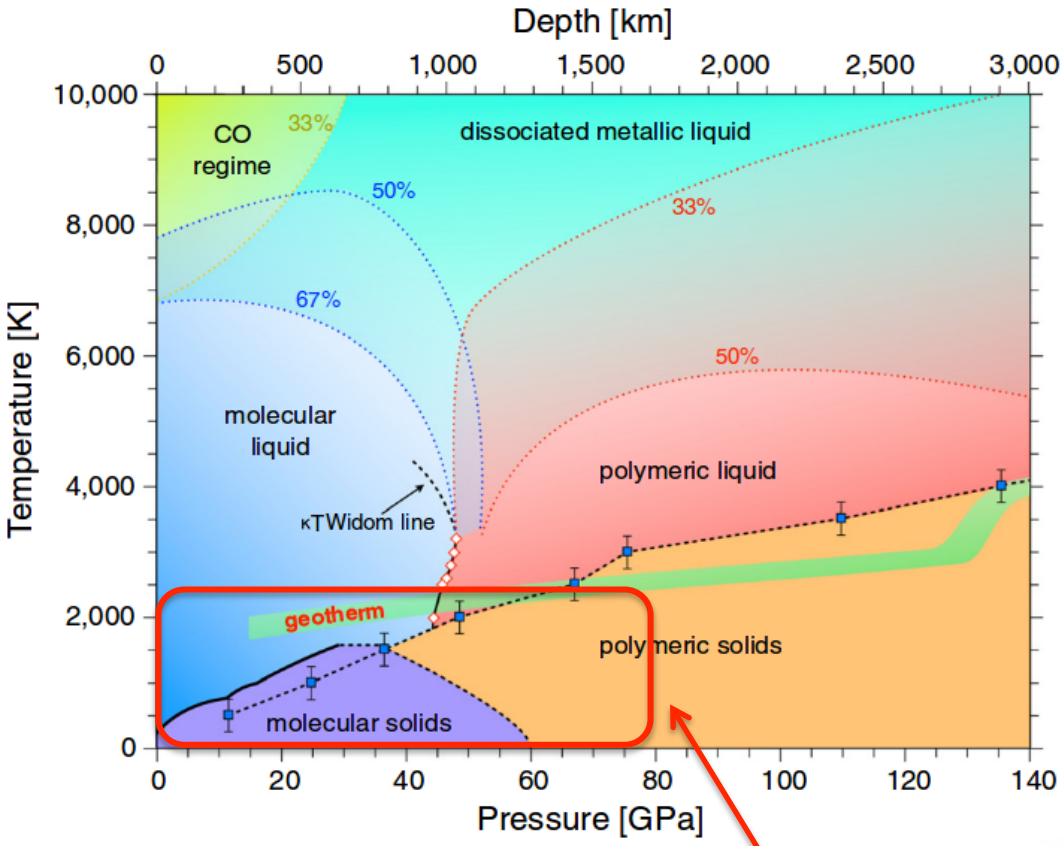
journée des « Grands Challenges » Joliot-Curie



Transformations of condensed carbon dioxide under extreme conditions

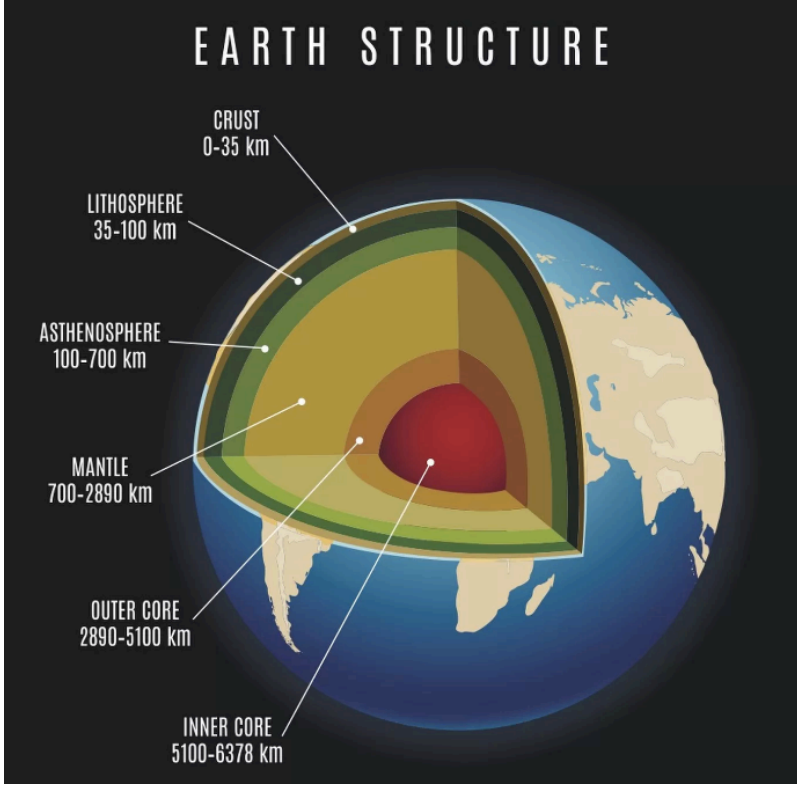
Mathieu Moog, Fabio Pietrucci, Marco Saitta

Sorbonne Université, IMPMC, Paris



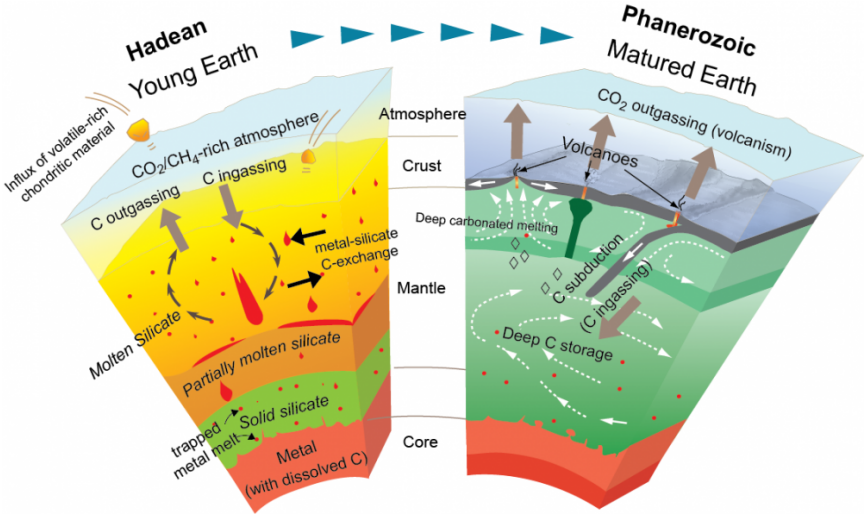
Boates et al, PNAS (2012)

exp. studies



understanding the carbon cycle in the mantle:

* dissociation of CO_2 => volcanism?
* polymeric liquid => metallisation ?

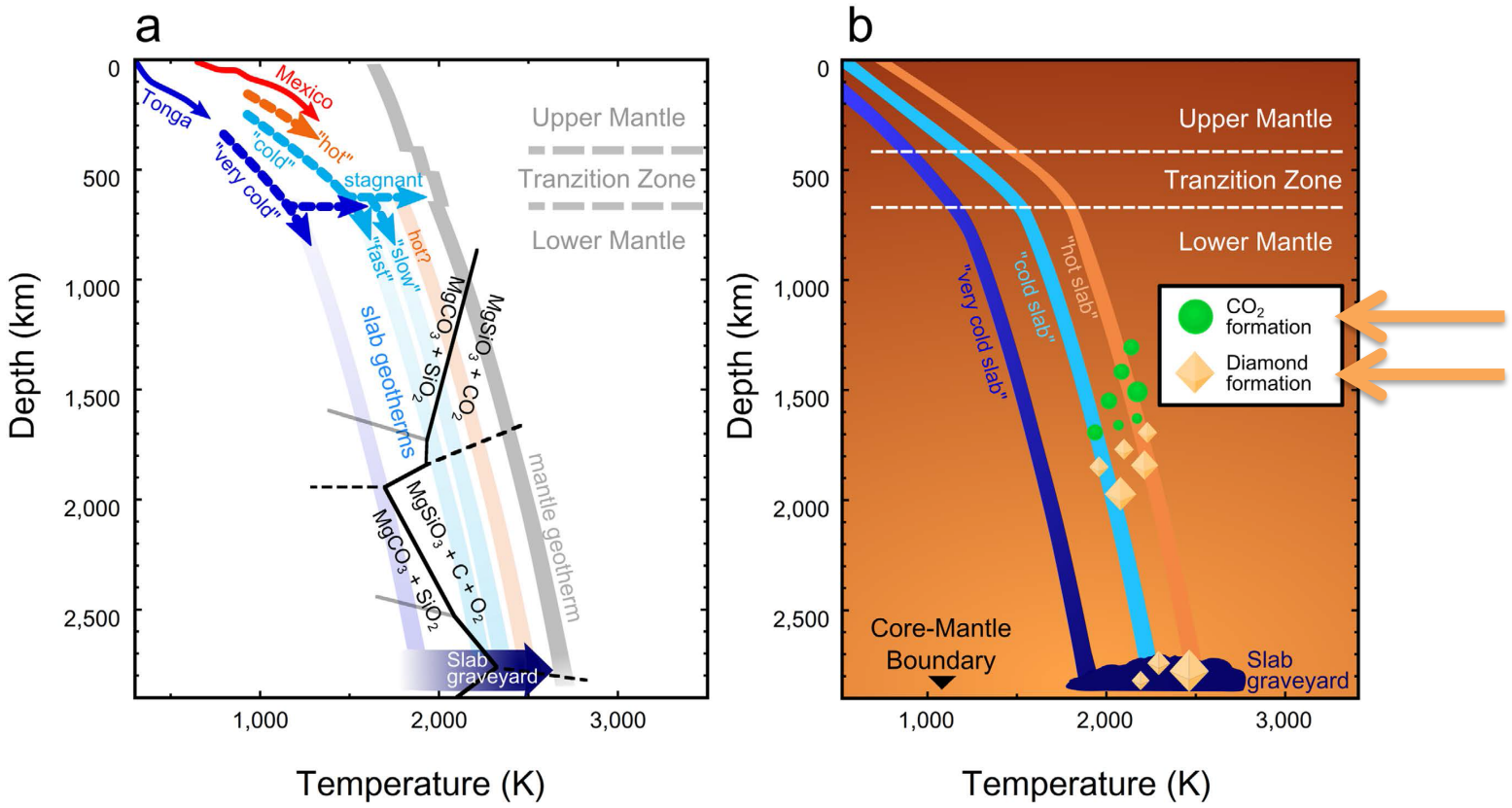


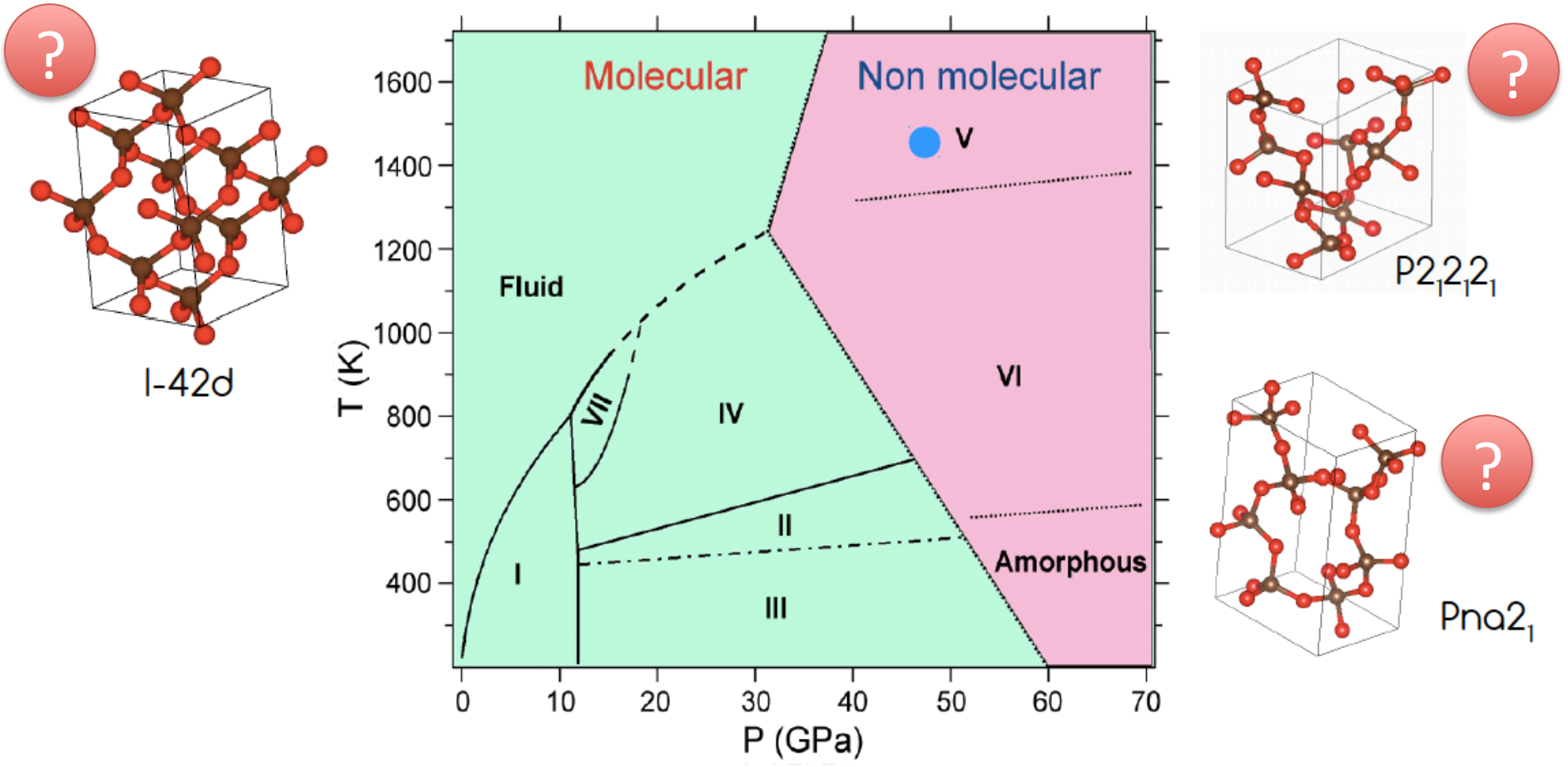
CO_2 high P,T phases form in the mantle by reaction of carbonates + silicates:

$SiO_2 + MgCO_3 \rightarrow MgSiO_3 + CO_2$ (Maeda et al, Sci. Rep. 2017)

$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$ (Li et al, Geophys. Res. Lett. 2018)

high P,T experiments: diamond anvil cells, synchrotron X-ray diffraction

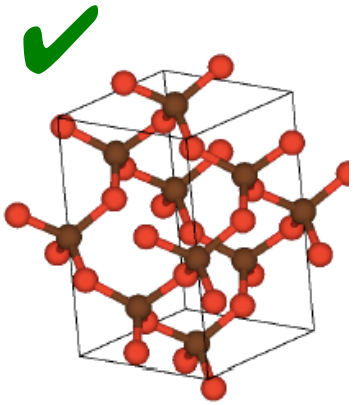




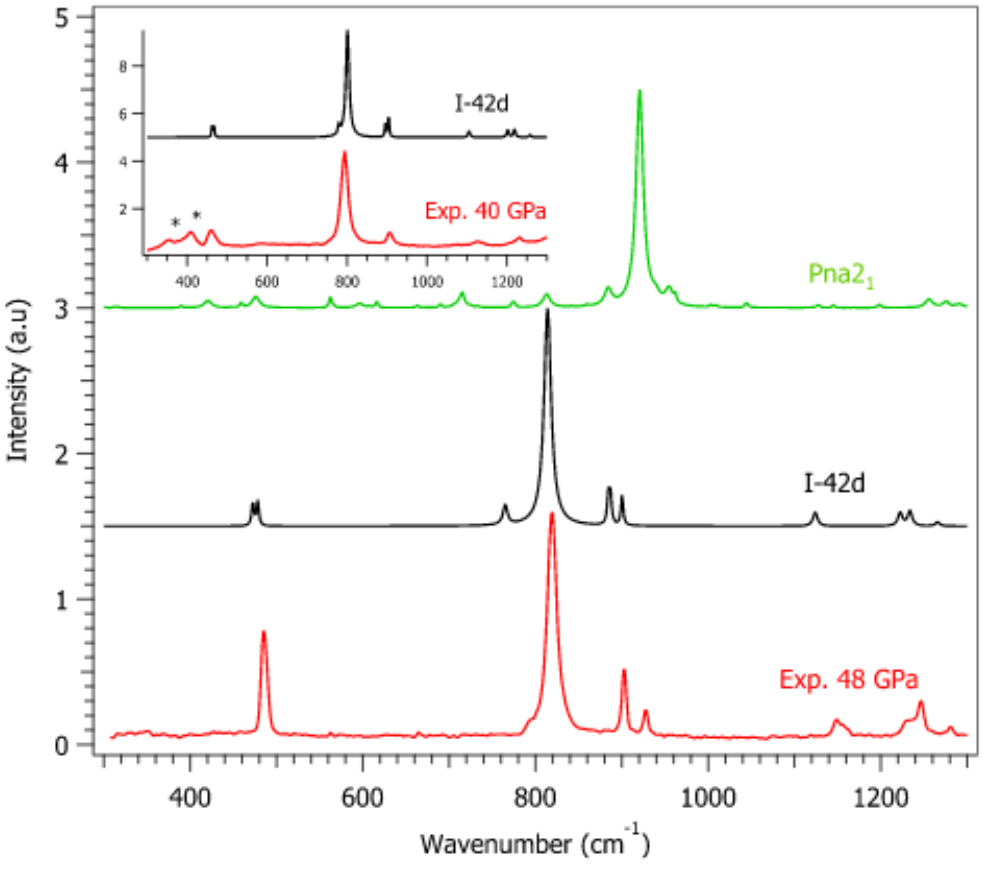
Yong et al, *PNAS* 113, 11110 (2016):
→ they proposed new structure
→ they claim recovery of phase V at ambient pressure

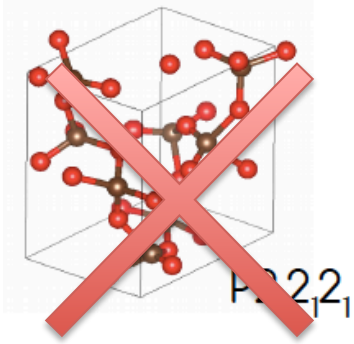
Disproved in : Datchi, Moog, Pietrucci, Saitta, *PNAS* 114, E656 (2017)

Raman spectra (density functional perturbation theory)

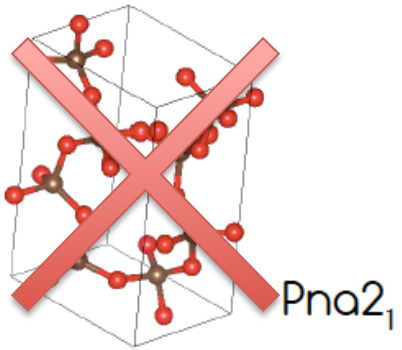


I-42d





$P2_12_12_1$



$Pna2_1$

Yong et al, *PNAS* 113, 11110 (2016):
→ they proposed new structure
→ they claim recovery of phase V at ambient pressure

Disproved in : Datchi, Moog, Pietrucci, Saitta, *PNAS* 114, E656 (2017)

objective of the project:

understand the structure, dynamics, and transformations of CO_2 fluid phases between 2000 – 3000K and 25 – 65 GPa

numerical approach:

ab initio molecular dynamics

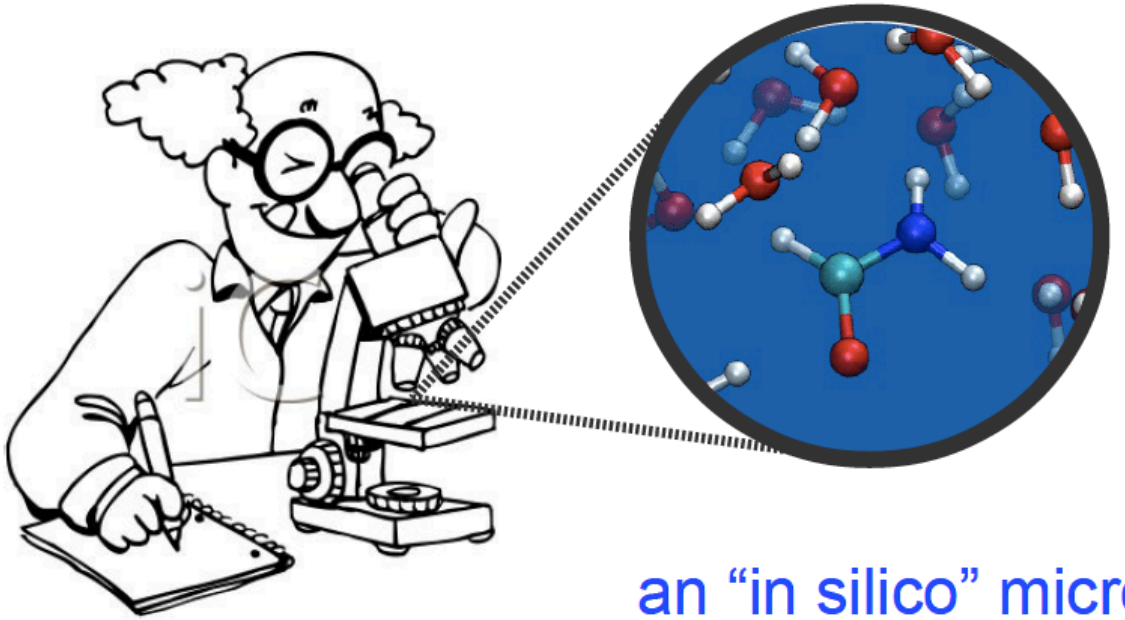
108 CO_2 molecules, long trajectories of 100 ps (total 5 ns)

necessary for complex topologies

necessary to sample slow dynamics

(previous state-of-the-art: 32 molecules, 10 ps)

why molecular dynamics simulations?



an “in silico” microscope,
a computer experiment

why “ab initio” (DFT) instead of classical?

electronic structure,
high accuracy and transferability,
bond breaking and formation ...

Born-Oppenheimer approximation:

nuclei evolve as classical particles, in a potential energy landscape given by the ground state electronic energy at fixed nuclei

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle\}$$

$$E_0 \Psi_0 = \mathcal{H}_e \Psi_0$$

rationale:

$$\frac{\omega_{el}}{\omega_{nuc}} \sim \sqrt{\frac{M}{m}} \sim 100$$

- adiabatic separation of time scales (fast electrons and slow nuclei)
- nuclear dynamics does not induce electronic transitions
- nuclei have small De Broglie wavelengths

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{M k_B T}}$$

hydrogen: handle with care...

algorithm is simple:

optimize electrons,
move nuclei (e.g., Verlet),
repeat

Born-Oppenheimer approximation:

nuclei evolve as classical particles, in a potential energy landscape given by the ground state electronic energy at fixed nuclei

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle\}$$

$$E_0 \Psi_0 = \mathcal{H}_e \Psi_0$$

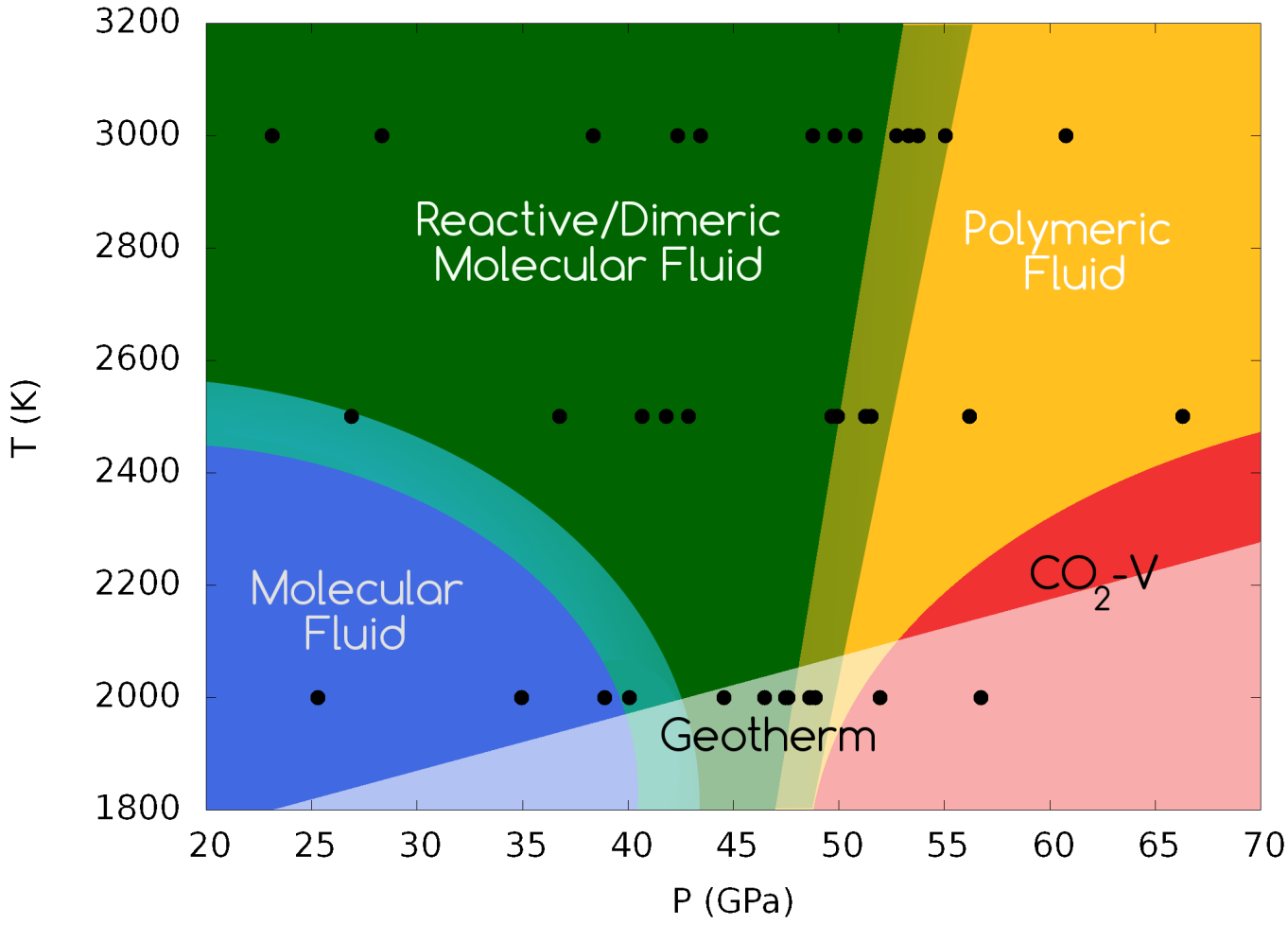
very expensive ⟶ grand challenge !

300 atoms, 100 ps ≈ 1 million CPU hours

Technical details:

- density functional theory, PBE exchange-correlation functional
- plane-wave expansion of Kohn-Sham orbitals up to 120 Ry
- Martins-Troullier pseudopotentials (+ GTH tests)
- CPMD code (developed at IBM-Zürich)

Structural and dynamical properties at different P,T conditions: a detailed map of CO2 forms

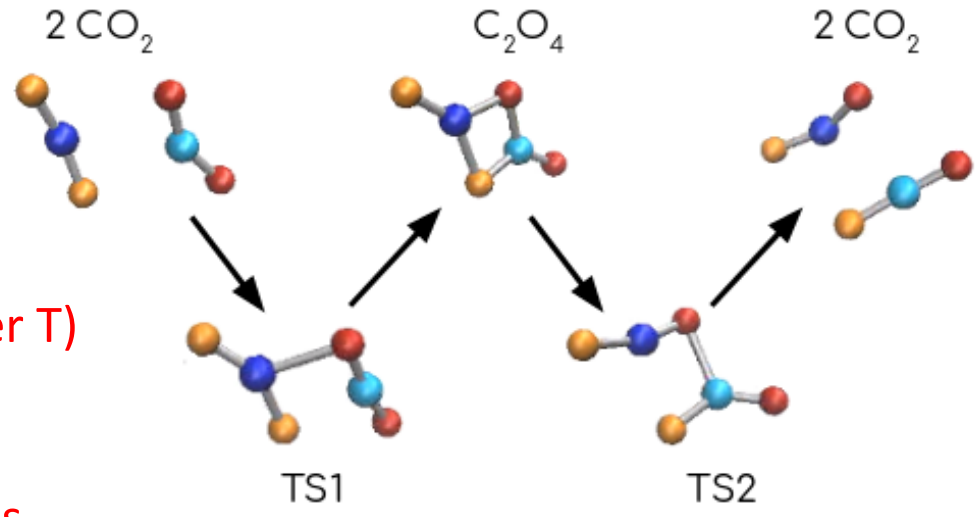


The important role of CO_2 dimerization processes

Previously reported at very high T = 5000 K (Tassone et al, *Chem Phys Chem* 2005)
or during decompression of amorphous form (Plasienka & Martonak, *Phys Rev B* 2014)

Our results:

- dimerization occurs in a wide PT region (25 – 50 GPa, 2000 – 3000 K)
- frequency of events: 0.2 – 20 ps^{-1} (growing with T and P)
- short lifetime: ≈0.15 ps
- also C_3O_9 rings above 40 GPa

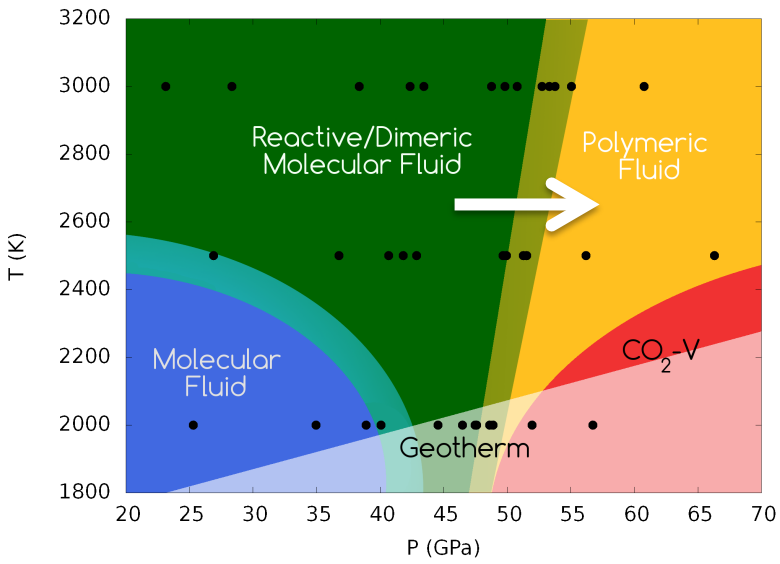


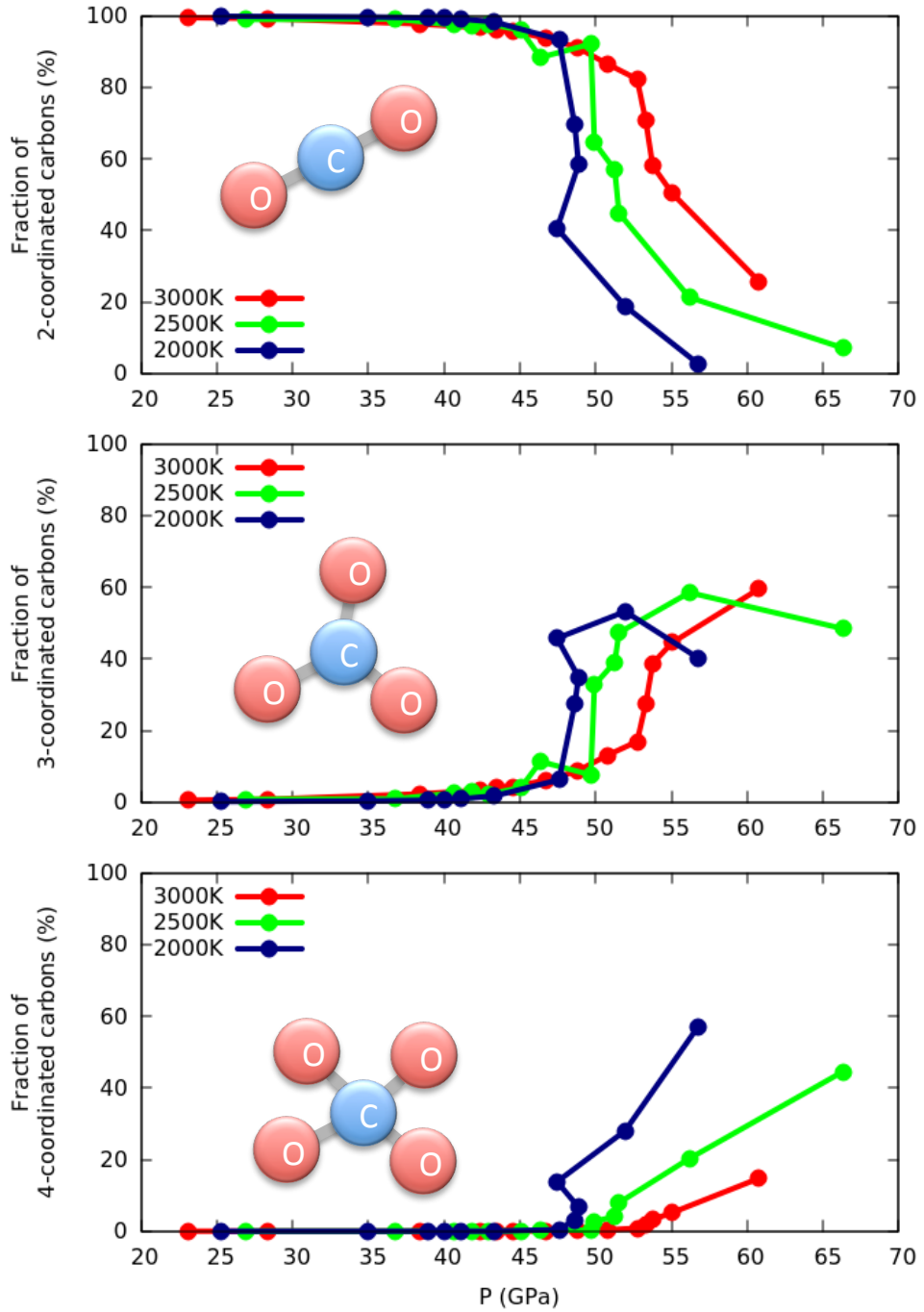
a distinct reactive fluid,
precursor to dissociation (at higher T)
or polymerization (at higher P)

reaction with carbonates / silicates
in Earth mantle?

C=O bond breaks, O exchange

transition from reactive molec. fluid to polymeric fluid

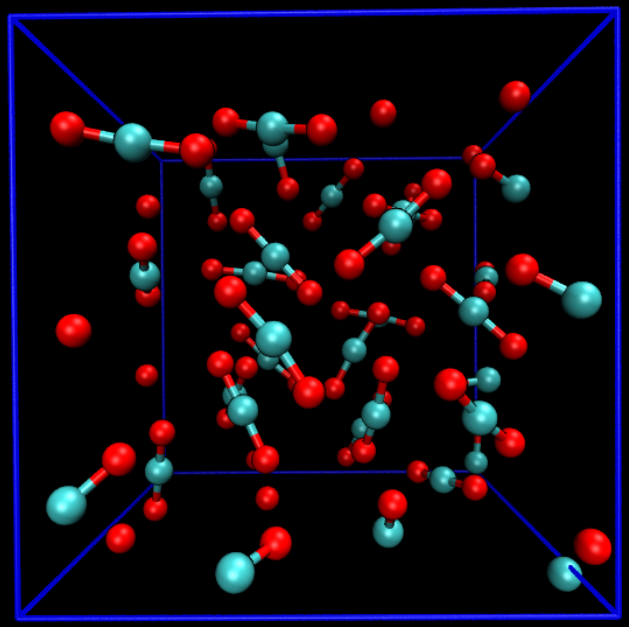


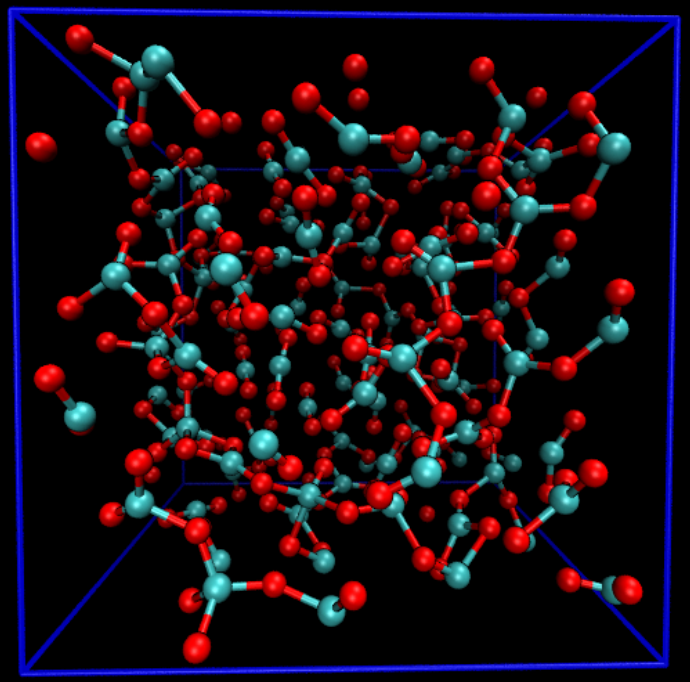


first, 3-coordinated carbon atoms increase: formation of chains

4-coordinated carbons increase more slowly with pressure

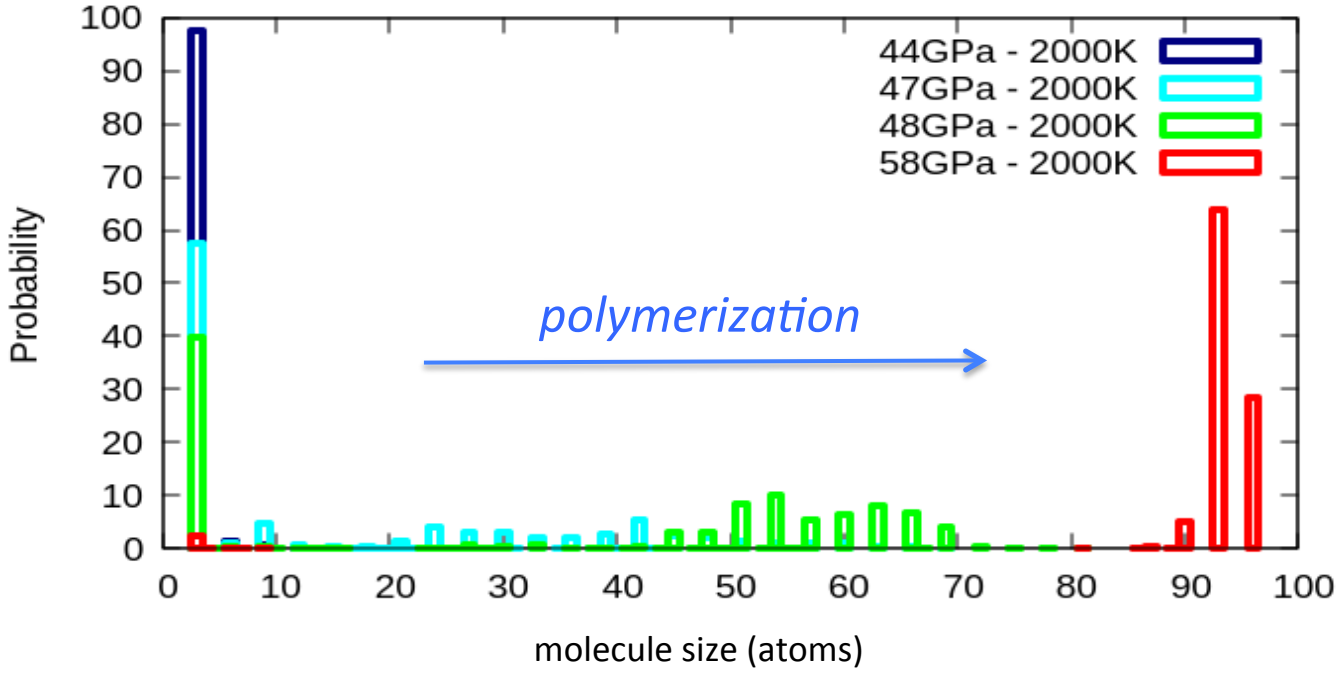
lower T favours polymerization

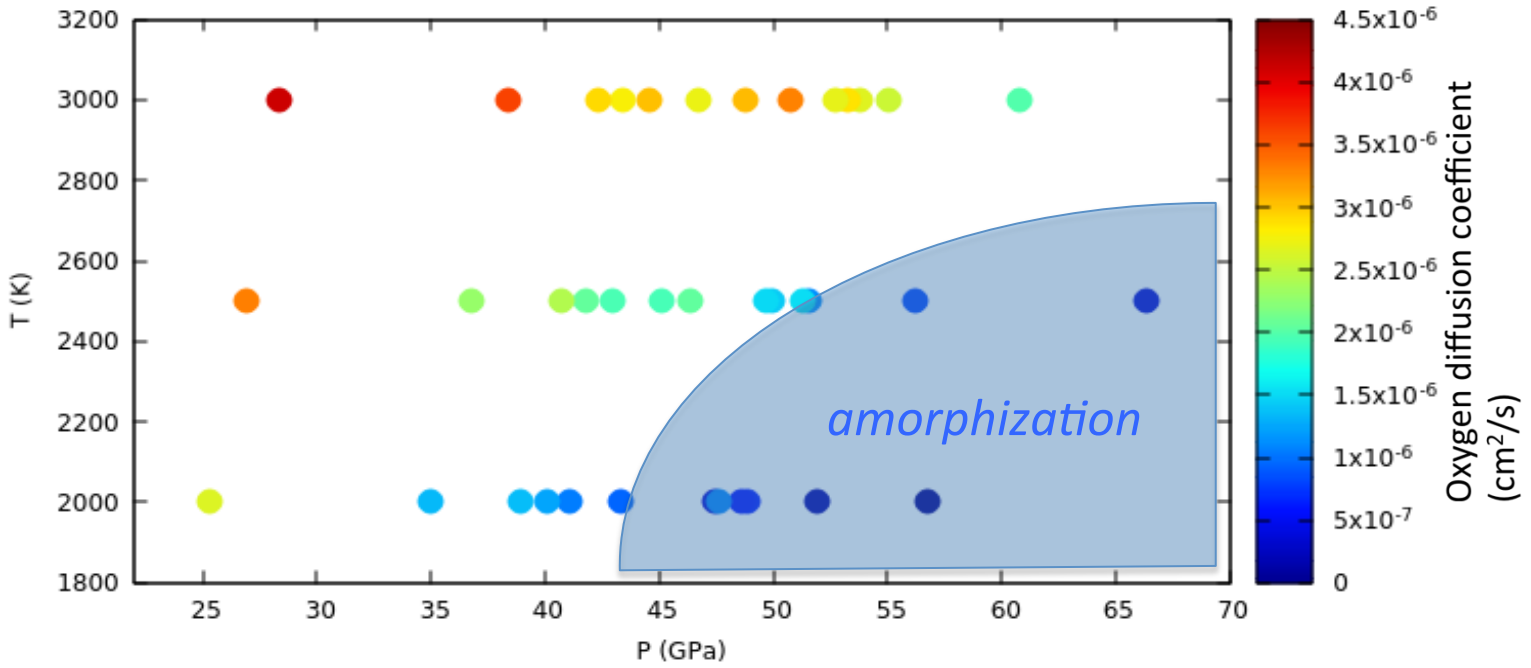




P = 25 GPa T = 3000 K
molecular fluid

P = 65 GPa T = 3000 K
polymeric fluid


44GPa - 2000K
47GPa - 2000K
48GPa - 2000K
58GPa - 2000K
polymerization
Probability
molecule size (atoms)
0
10
20
30
40
50
60
70
80
90
100

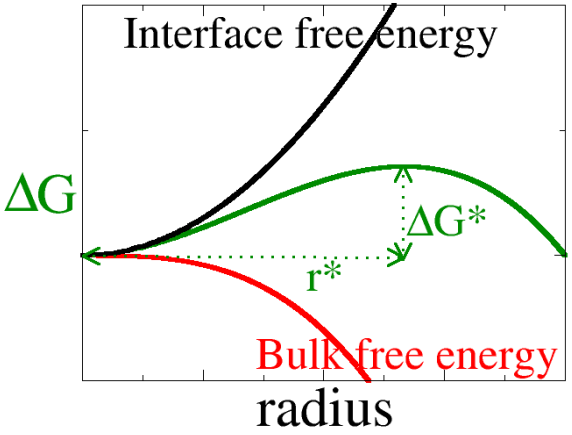

amorphization
T (K)
P (GPa)
Oxygen diffusion coefficient (cm²/s)
4.5x10⁻⁶
4x10⁻⁶
3.5x10⁻⁶
3x10⁻⁶
2.5x10⁻⁶
2x10⁻⁶
1.5x10⁻⁶
1x10⁻⁶
5x10⁻⁷
0

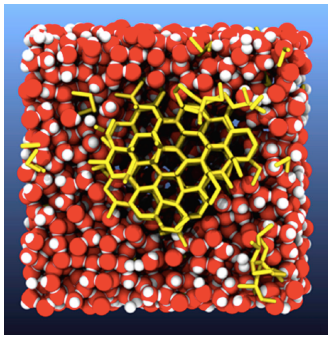
In progress: simulation of phase transitions

objective: detailed transition mechanisms, free energy barriers and kinetic rates

approach:
MD + enhanced sampling (metadynamics, umbrella sampling, transition path sampling)

Pietrucci, *Rev Phys* 2017

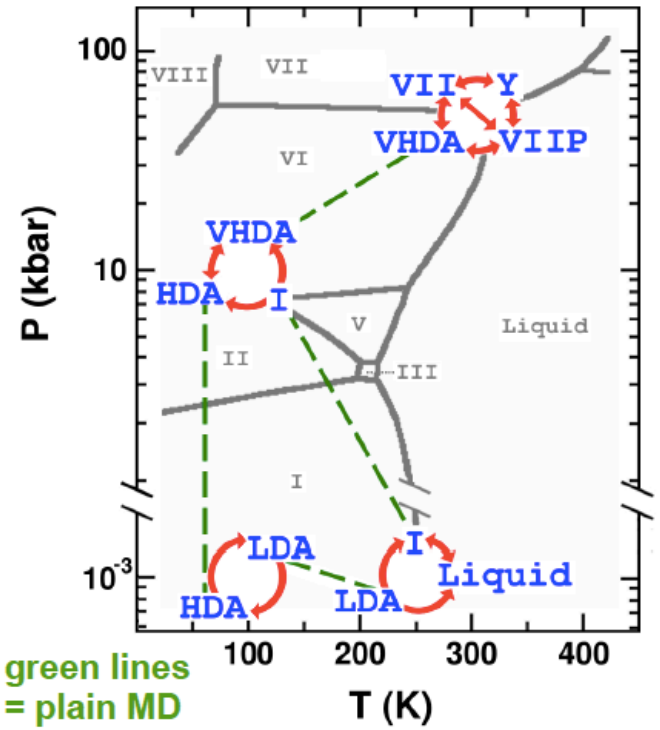


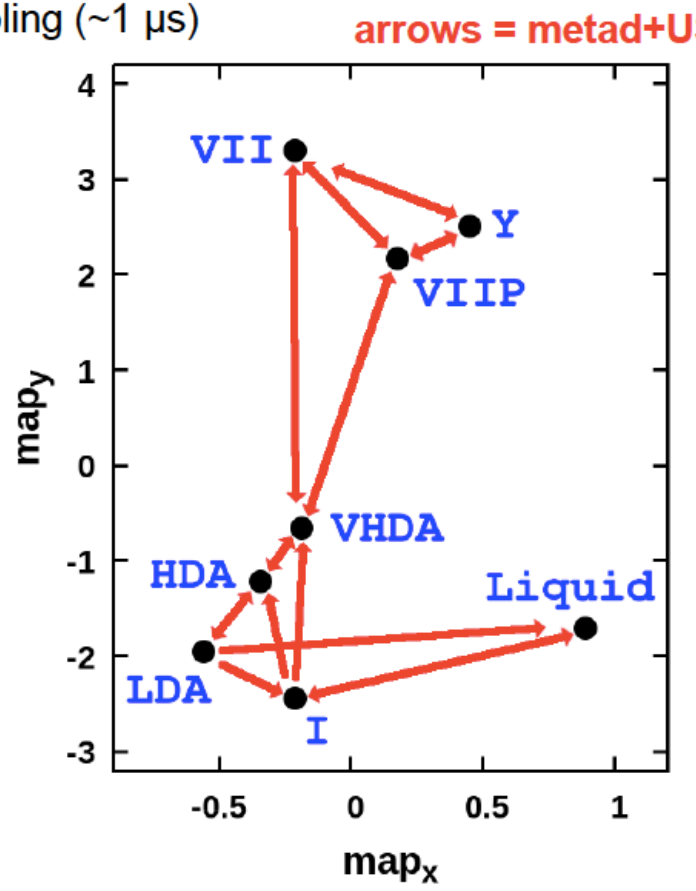


due to barriers:
huge gap between MD timescale
and experimental timescale

In progress: simulation of phase transitions

NPT MD, 800 TIP4P/2005 water molecules
metadynamics (~50 ns) + umbrella sampling (~1 μs)





Pipolo, Salanne, Ferlat, Klotz, Saitta, Pietrucci, *Phys Rev Lett* 2017
Fitzner, Sosso, Pietrucci, Pipolo, Michaelides, *Nat. Commun.* 2017

Conclusions

- *ab initio* molecular dynamics: structure and dynamics of CO_2 phases
- unprecedented system size and timescale
- important role of CO_2 dimerization process: a distinct reactive fluid
- insight into transition from molecular to polymeric fluid
- in progress: mechanisms, free-energy landscape and rates of transitions

Conclusions

- *ab initio* molecular dynamics: structure and dynamics of CO_2 phases
- unprecedented system size and timescale
- important role of CO_2 dimerization process: a distinct reactive fluid
- insight into transition from molecular to polymeric fluid
- in progress: mechanisms, free-energy landscape and rates of transitions

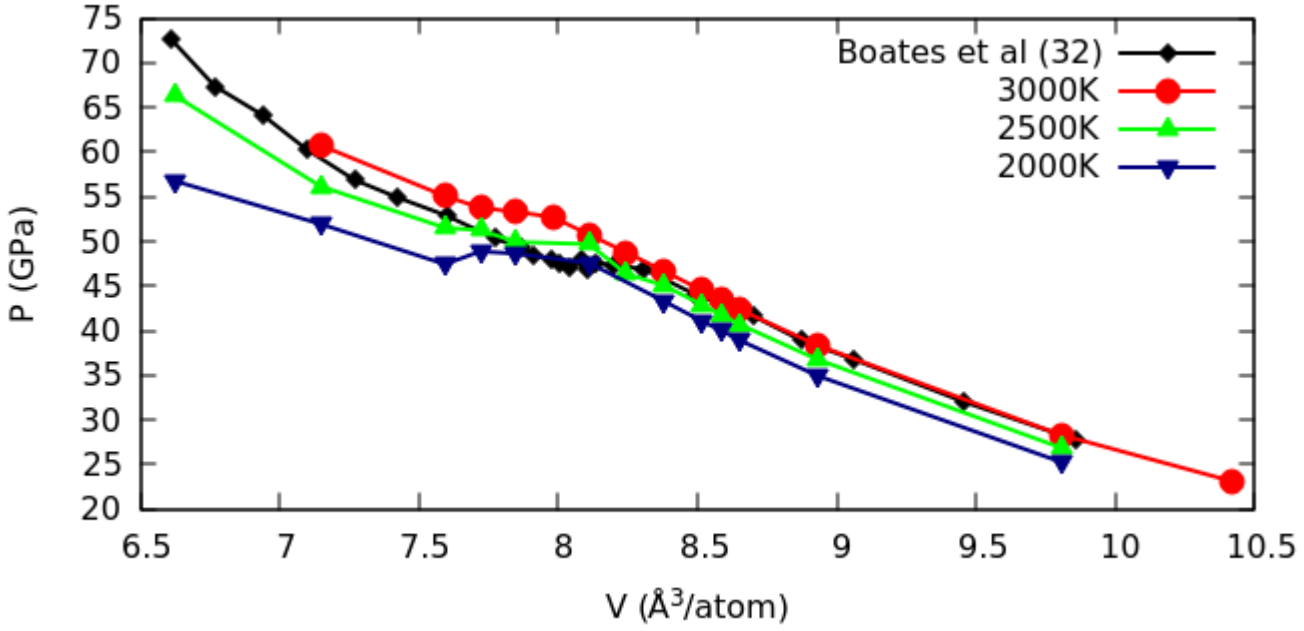
"carbon dioxide fluids at extreme conditions"

Mathieu Moog, Fabio Pietrucci, **Marco Saitta**

Le CO_2 est une molécule simple dont le comportement à haute pressions a été largement étudié ces vingt dernières années, notamment du fait de sa présence, en forme fluide, dans le manteau de la couche terrestre où il est soumis à des pressions et température extrêmes (20-100GPa, 2000K-3000K). Un grand intérêt, à la fois de type environnemental (stockage de CO_2 ou bien son dégazage dans l'atmosphère), et économique, car le dioxyde de carbone est impliqué dans le transport de métaux précieux (or, argent), et donc dans la formation de gisement de ces métaux.

Des études théoriques récentes semblent indiquer que ce système passerait d'un fluide moléculaire à un fluide polymérique dans lequel chaînes et clusters complexes. Cette transformation liquide-liquide, très exotique d'un point de vue fondamentale, et au même temps très important du point de vue géologique, reste cependant difficile à observer et caractériser expérimentalement.

Difficulté MD *ab initio* dans le cas de polymérisation de fluides moléculaires: structure désordonnée d'un liquide implique l'utilisation de cellules de simulation de taille relativement importante. Limites: la taille du système mais aussi les temps de simulations, deux facteurs qui peuvent être critiques. Dans ce projet: de l'ordre de la centaine de picosecondes et 108 molécules, ce qui **augmente d'un ordre de grandeur la longueur de simulation et double la taille du système** par rapport aux calculs qui ont déjà pu être réalisés sur ce système. étudier d'une manière bien plus quantitative cette **élusive transition de phase liquide-liquide**, permettant notamment une **comparaison directe avec les résultats expérimentaux** (obtenus dans notre équipe), et donc de potentiellement résoudre un débat très vif quant au comportement et aux propriétés du dioxyde de carbone fluide présent dans les profondeurs de la Terre.


Boates et al (32)
3000K
2500K
2000K
P (GPa)
V (Å3/atom)
75
70
65
60
55
50
45
40
35
30
25
20
6.5
7
7.5
8
8.5
9
9.5
10
10.5