UNIVERSITÀ
DEGLI STUDI
DI MILANO

High-pressure behaviour of $CaTiSiO_5$ and comparison with $CaSi_2O_5$

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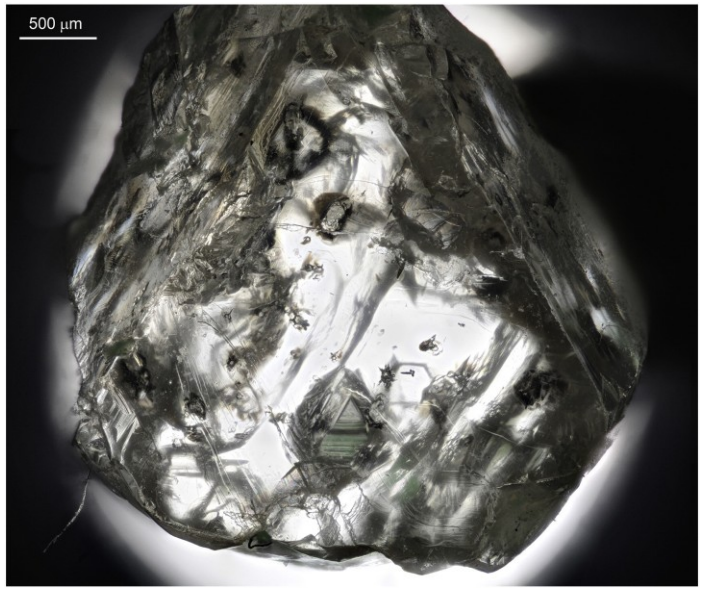
SILS school 2026

Diamond’s inclusions as a window into the Earth’s mantle

- **Super-deep diamonds** (>350 km) preserve minerals that formed in Earth’s lower mantle.

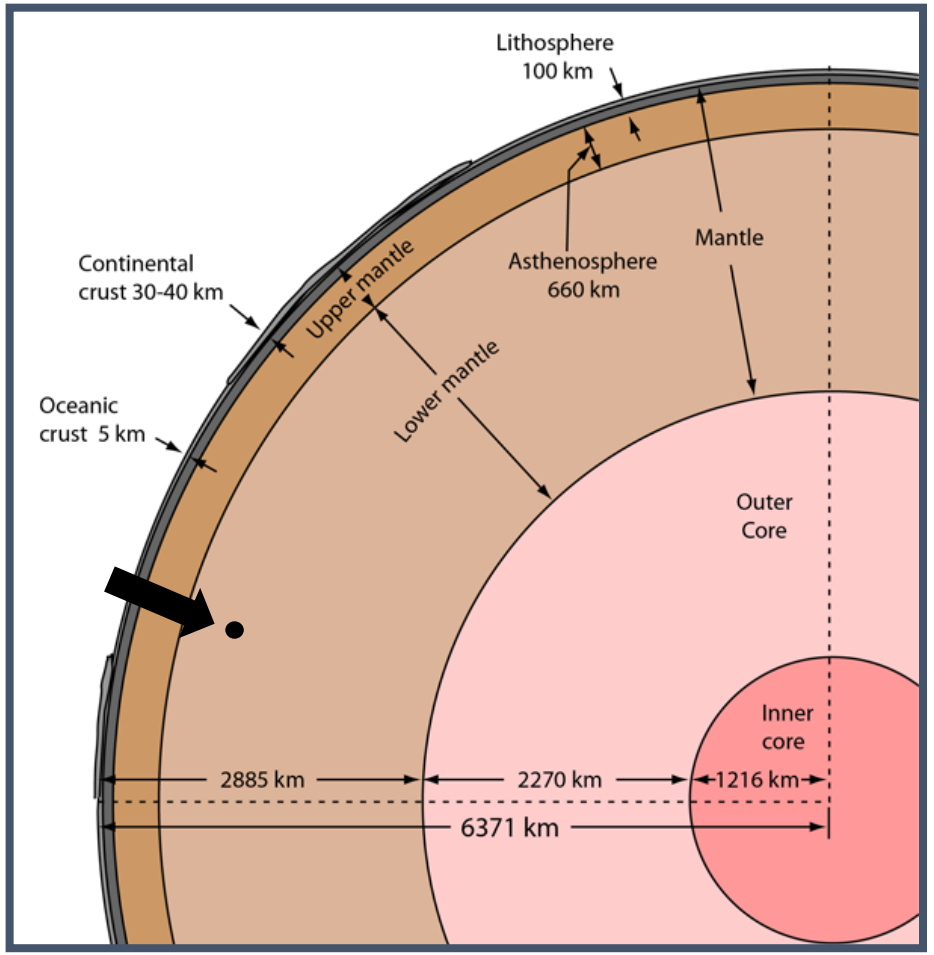
- During their journey back to the surface, some of these minerals **transform** into new phases.



RETROGRESSION PRODUCT

- These include **titanite** ($CaTiSiO_5$) and **$CaSi_2O_5$**.

EARTH’S STRUCTURE



The starting point: ab initio calculations by Char et al. (2024)

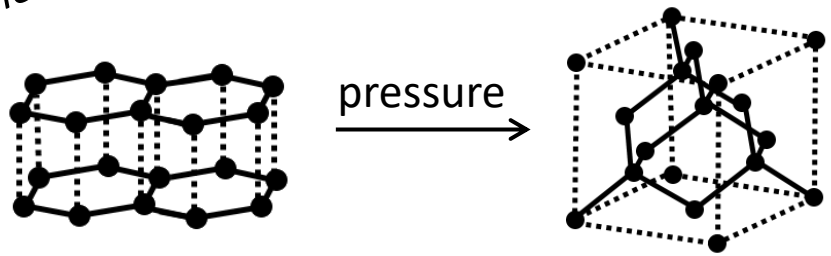
Starting from monoclinic titanite (C2/c), simulations predict **two** pressure-induced **phase transitions**:

~10 GPa	**Monoclinic C2/c → Triclinic P-1** *a displacive transition*
~18 GPa	**Triclinic P-1 → Orthorhombic Pnma** *a reconstructive transition*

Let's test these!

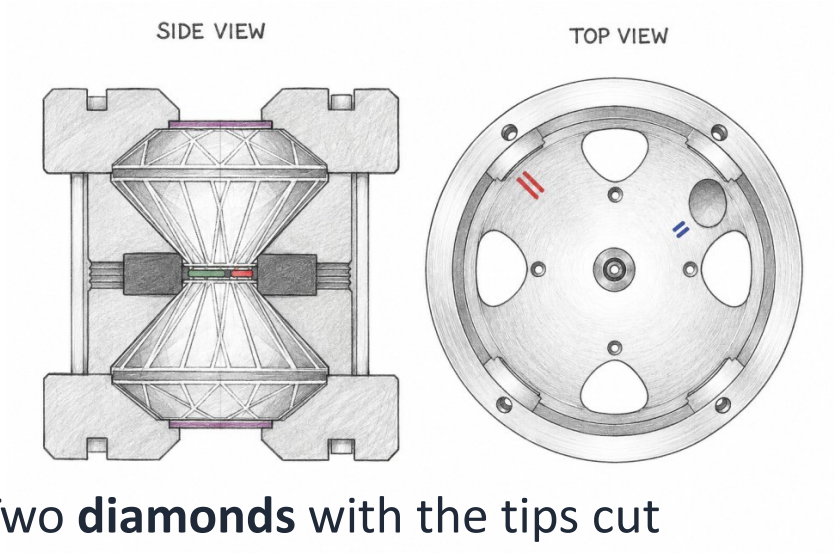
At higher pressures, all Si is predicted to adopt an **octahedral coordination,** resulting in a much denser structure.

Example:



graphite *diamond*

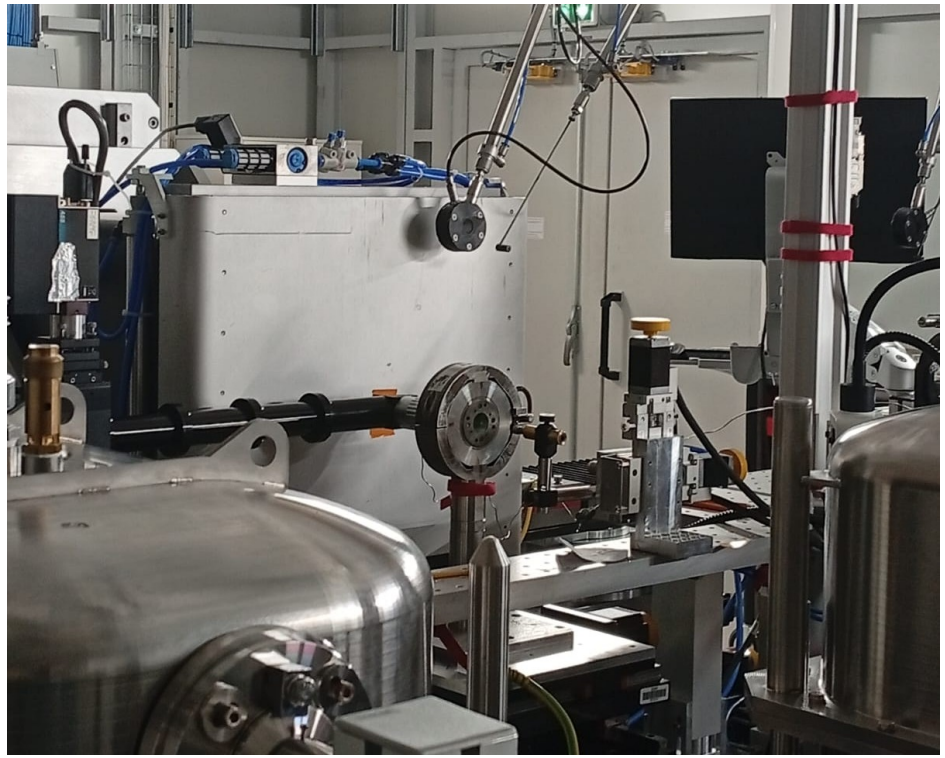
Methods: Diamond Anvil Cell (DAC) and synchrotron X-ray diffraction



- Two **diamonds** with the tips cut
- Between them sits the **gasket**: a thin metal plate with a hole at its centre, holding the **sample**
- He as the **transmitting medium** to have hydrostatic pressure
- **Pressure** is applied through four screws

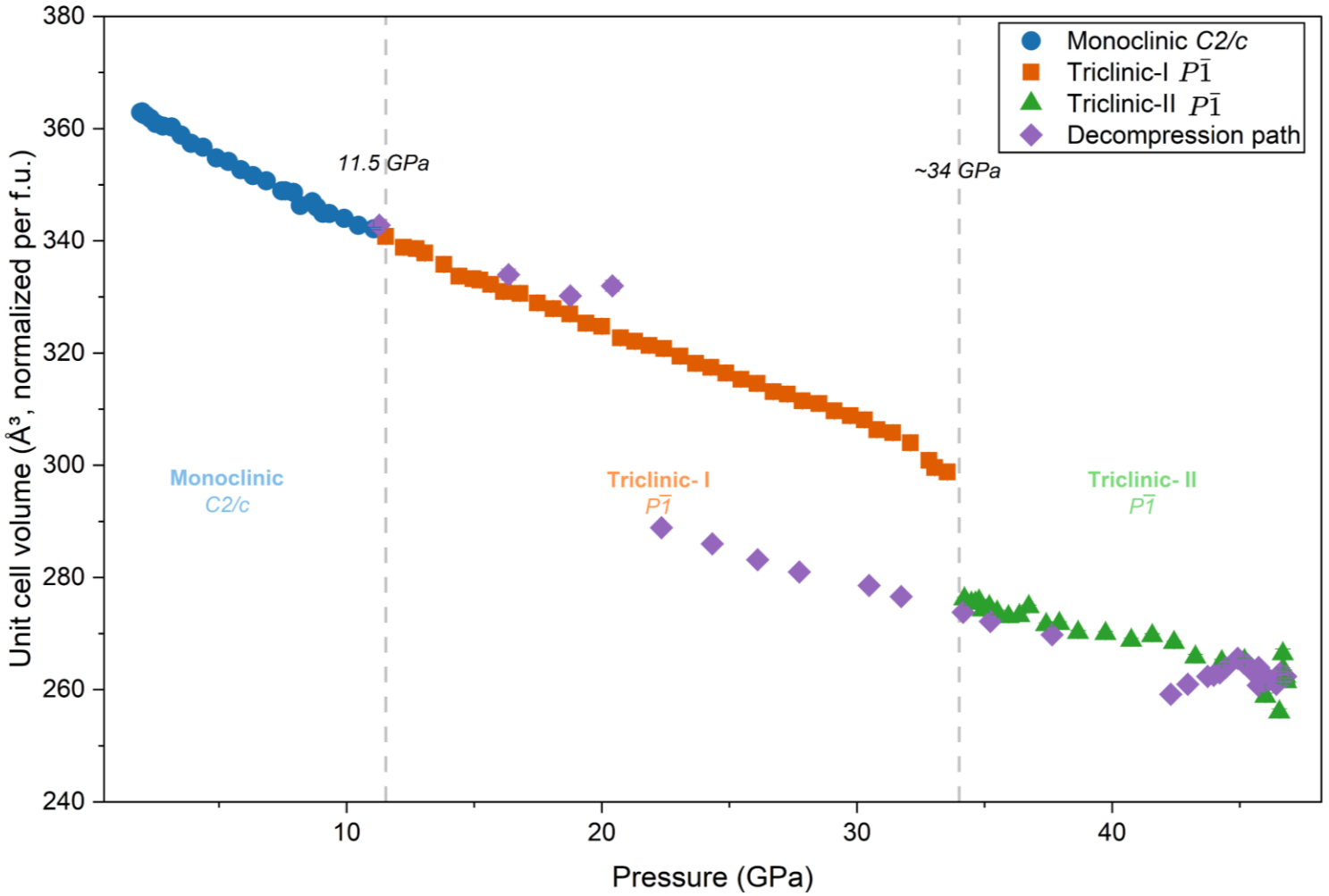
1 GPa ≈ 10 000 atmospheres → **~ 47 GPa (1200 km)**

- X-rays reveal the full atomic **structure** of the crystal



Experimental set-up at beamline ID27, ESRF (Grenoble)

Results : phase transitions in $CaTiSiO_5$



~11.5 GPa

Monoclinic → Triclinic-I

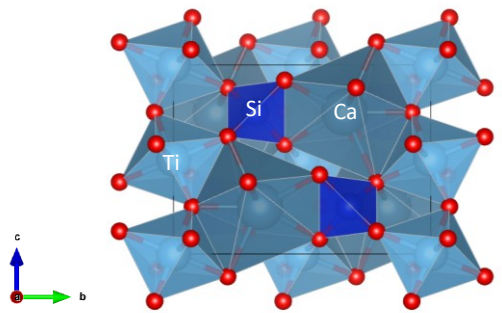
reversible, modest volume change

~34 GPa

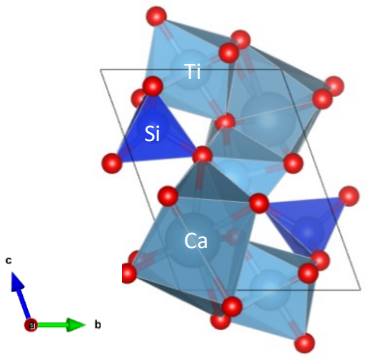
Triclinic-I → Triclinic-II

pronounced hysteresis on decompression

Monoclinic



Tri-I

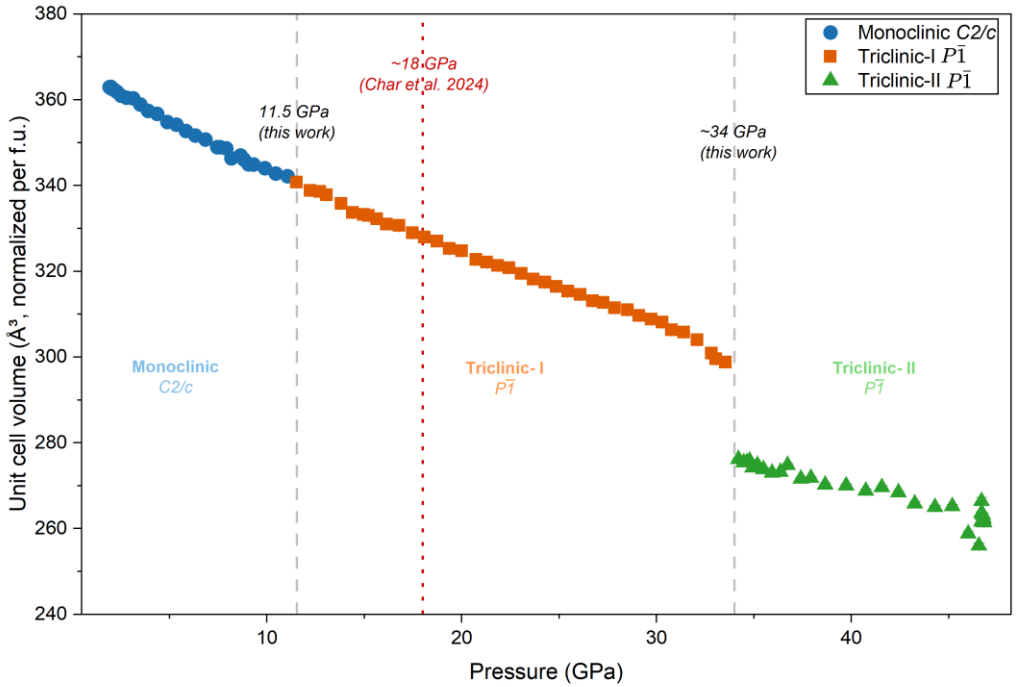


Tri-II structure was not resolved because of the low quality of the diffraction data.

Comparison with the ab initio predictions

✓ **First transition: CONFIRMED**

Predicted: **~10 GPa** → Observed: **11.5 GPa**



✗ **Second transition: NOT observed**

Predicted: orthorhombic ***Pnma*** at ~18 GPa, Si octahedral

↓

A tri-II appears instead at ~34 GPa

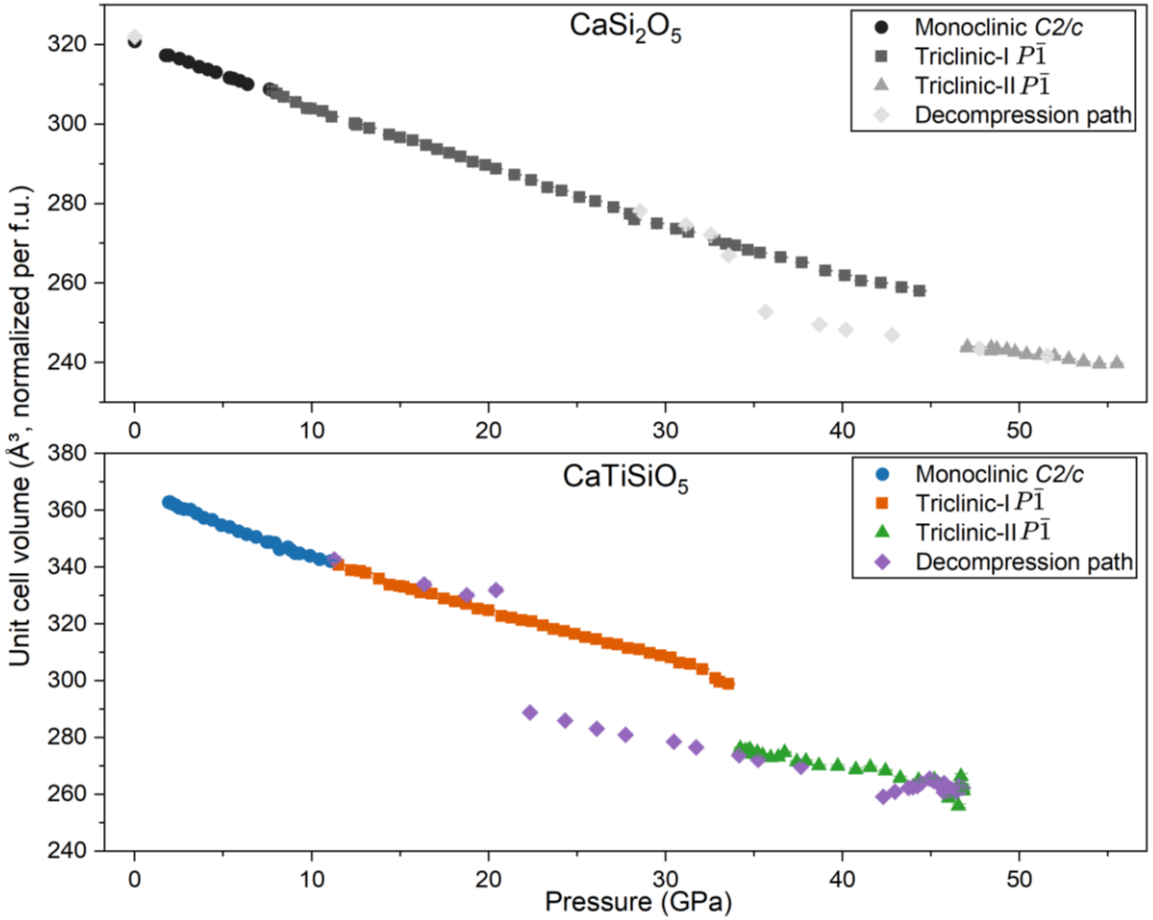
↓

The reconstructive transition is likely **kinetically inhibited** at room temperature.

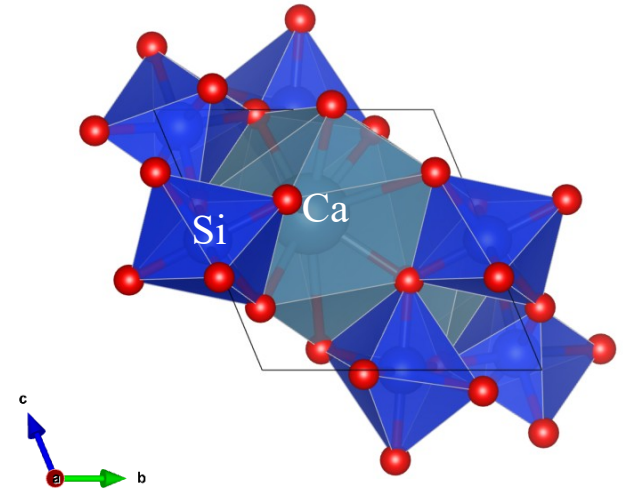
↓

Insufficient thermal energy to overcome the activation barrier.

Comparison with $CaSi_2O_5$



- At ambient pressure, **titanite's cell volume is larger** → consistent with the bigger ionic radius of Ti^{4+} compared to Si^{4+}.
- Ti^{4+} does not sit exactly at the centre of its octahedron, due to electronic (orbital) effects → a **distortion** that does not occur for Si in $CaSi_2O_5$.
- **Si reaches full octahedral coordination in tri-II**. By analogy, titanite's own tri-II is likely just as dense.



What does this mean for the diamonds?

Mono → tri-I: no depth record

This transition is reversible and involves only a modest volume change. Finding monoclinic titanite as an inclusion does not constrain the diamond's original formation pressure.

A dense tri-II: a possible depth marker

The dense, high-pressure tri-II structure could permanently deform the host diamond during growth → potentially preserving a lasting signature of deep formation, even after the diamond returns to the surface.

Future plan

- **High-temperature experiments** (in October) to test whether the orthorhombic phase is reachable.
- Repeat the high-pressure experiment, aiming for better-quality diffraction data on triclinic-II.

Thank you for the attention