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From Core to Crust: Towards an Integrated Vision of Earth's Interior

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DFT study of antigorite up to 30 GPa: implications for water transport in subduction zones

G. Capitani
Universita degli Studi di Milano Bicocca, Italy

Strada Costiera 11, 34151 Trieste, Italy - Tel. +39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it, www.

DFT STUDY OF ANTIGORITE UP TO 30 GPa: IMPLICATIONS FOR WATER TRANSPORT IN SUBDUCTION ZONES

Gian Carlo Capitani
Dip. di Scienze Geologiche e Geotecnologie, Università di Milano Bicocca,
P.za della Scienza 4, 20126, Milano, Italy.

Lars Stixrude
Department of Earth Sciences, University College London,
Gower Street, London WC1E 6BT, United Kingdom.

Marcello Mellini
Dipartimento di Scienze della Terra, Università di Siena,
Via Laterina 8, 53100, Siena, Italy.

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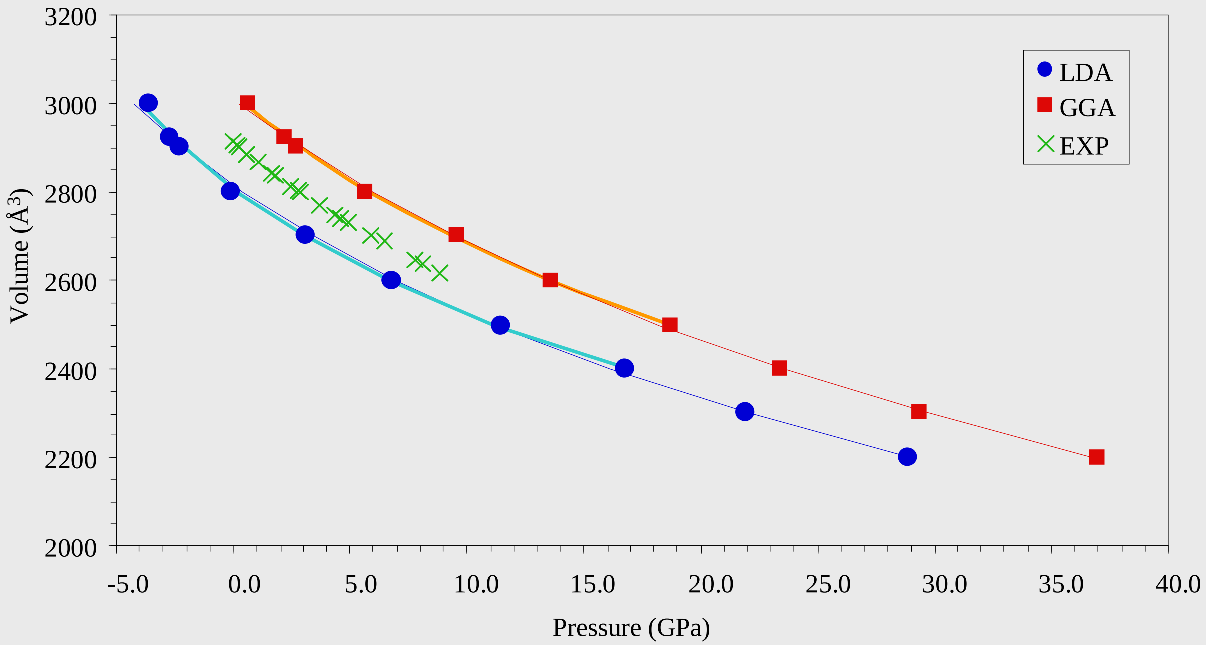
Introduction

- Antigorite [~$Mg_3Si_2O_5(OH)_4$)] is the **HP** and **HT** serpentine polymorph, and one of the major constituents of subducting slabs.
- The **structural reasons** of this higher stability field are only **poor understood**.
- Containing up to **12-13% of water** and stable up to **150-200 km**, it is the most hydrated mineral going down to the mantle during subduction.
- Its dehydration is believed to be one of the major causes of **mantle wedge hydration** and **partial melting** processes (e.g. Ulmer and Trommsdorff 1995), and of **deep focus earthquakes** (e.g. Peacock 2001).
- Powder (Hilairet et al. 2006) and single-xx (Nestola et al. 2009) DAC-XRD experiments evidence a **change in compressional** behavior at P > 6 GPa.
- The **lack of crystal structural refinements** prevents a reliable structural interpretation.
- We used **theoretical methods** to model the structural evolution of antigorite m = 17 up to a pressure **~30 GPa**.
- Results include the predicted **EoS**, **lattice parameters**, and **internal structure parameters**.

Methods

- We used **density functional theory** (DFT) (Hohenberg and Kohn 1964; Kohn and Sham 1965).
- Static calculations were performed with the **plane-wave pseudopotential** method (Heine 1970) implemented in the **VASP** code (Kresse and Hafner 1993; Kresse and Furthmüller 1996).
- We used **ultrasoft Vanderbilt pseudopotentials** (Vanderbilt 1990; Kresse et al. 1992).
- We exploit the **LDA** and **GGA** approximations to exchange and correlation (Lundqvist and March 1987; Perdew et al. 1996).
- Computations were performed in the antigorite *m* = 17 primitive unit-cell (**291 atoms**, i.e., one unit formula of $Mg_{48}Si_{34}O_{85}(OH)_{62}$).
- We used an energy cutoff of **500 eV**, and a Monkhorst-Pack (Monkhorst and Pack 1976) **1 x 2 x 2** k-point mesh.
- Convergence tests yield total energies and pressures converged within **0.6 meV/atom** and **0.4 GPa**, respectively.



EoS

LDA

V_0 =	2815.5021	Å3
K_0 =	75.8569	GPa
K' =	3.6064	

DAC

V_0 =	2913.8988	Å3
K_0 =	63.4251	GPa
K' =	5.8366	

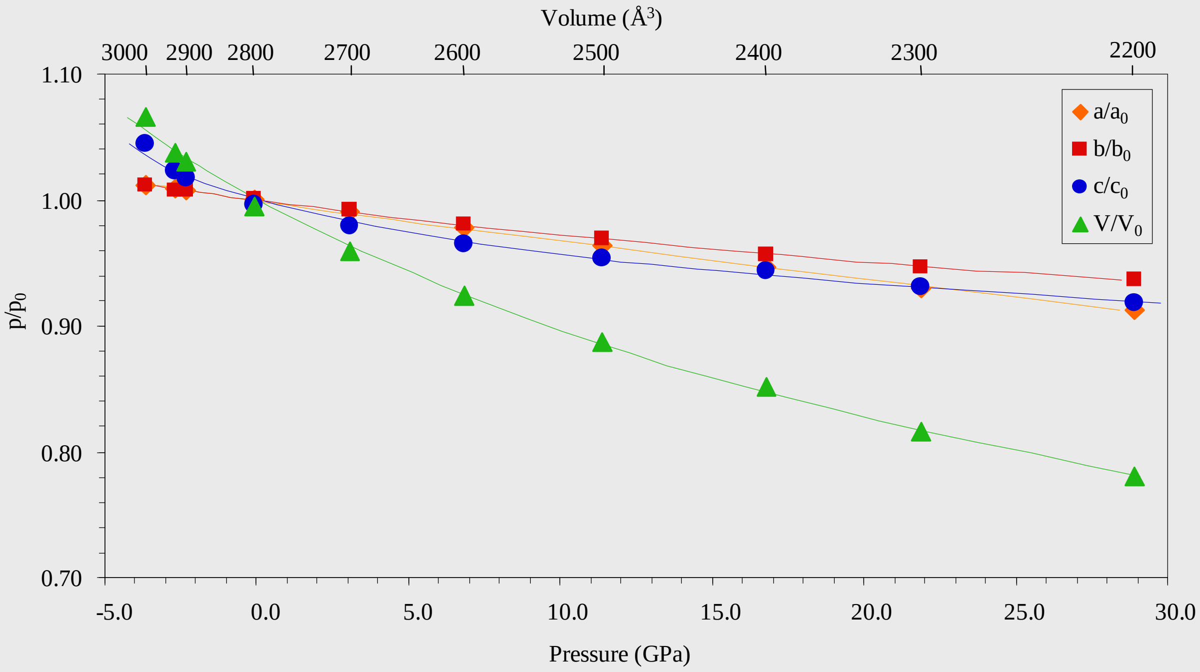
LDA up to 17 GPa

V_0 =	2806.7783	Å3
K_0 =	71.0425	GPa
K' =	5.3437	

- V_0 within LDA is **~3.7%** smaller and V_0 within GGA is **~3.0%** larger than the ambient T experimental value.
- K_0 within LDA and GGA are **19.6%** and **16.8%** larger, respectively, than that found in experiments.

- We expect **phonon excitation** to increase V_0 and to decrease K_0, thus ameliorating the agreement between LDA and experiments and augmenting the discrepancy between GGA and experiments.

Linear Compressibility



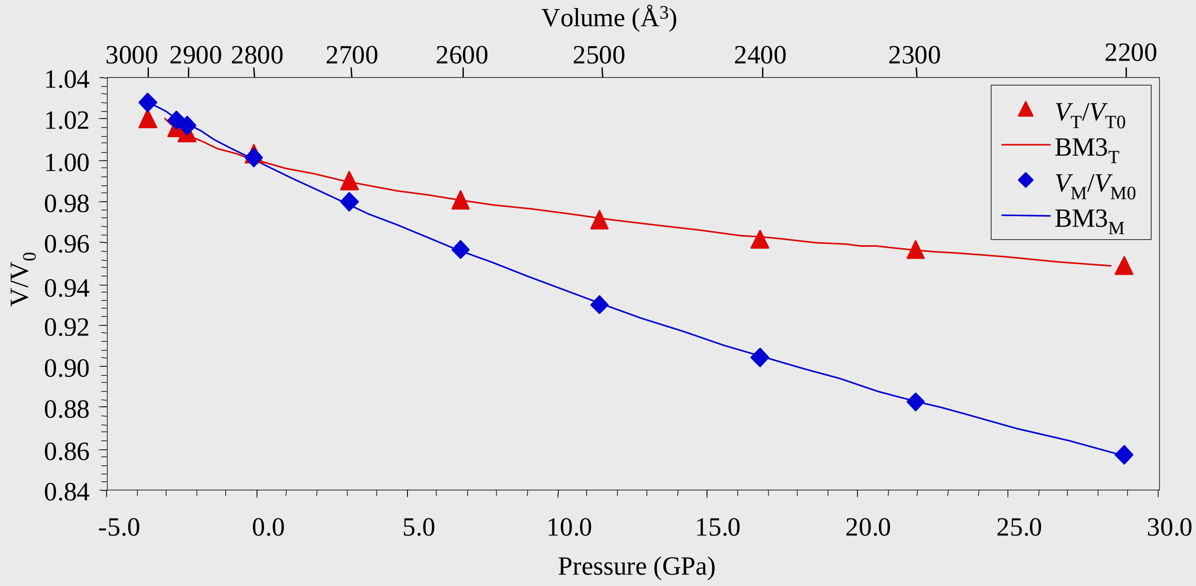
a_0 =	43.0200	Å3
Ka_0 =	93.2573	GPa
Ka' =	1.6230	

b_0 =	9.1664	Å3
Kb_0 =	103.7188	GPa
Kb' =	3.4242	

c_0 =	7.1144	Å3
Kc_0 =	50.1681	GPa
Kc' =	6.5959	

- The axial compressibility gives **β*a* : β*b* : β*c* = 1.11 : 1.00 : 2.07**.
- It appears reasonable if compared with that of lizardite **β*a* : β*c* ≈ 2.78** (Mookherjee and Stixrude 2009).
- Indeed, the compressibility of *c* in antigorite should be lower than in lizardite due to the presence of stiffer **ionic bonds** in the interlayer at reversal lines.

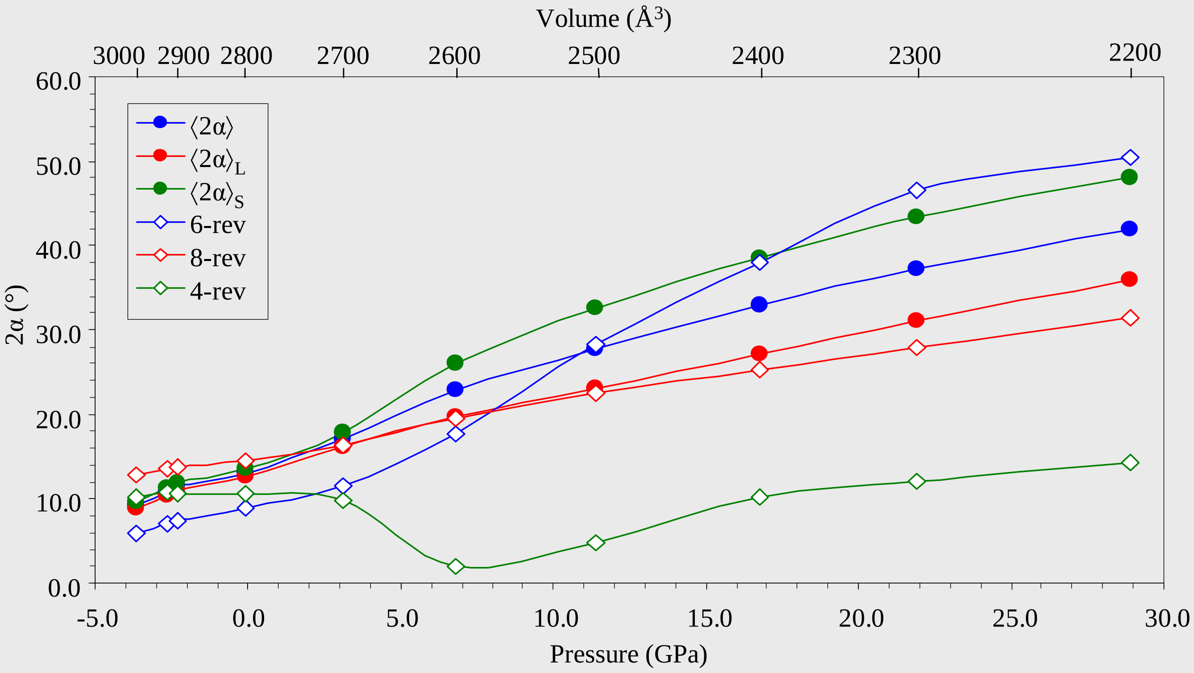
Polyhedral Compressibility



V_{M0} =	**11.565**	Å^3
K_{M0} =	**137.679**	GPa
K_M' =	**3.966**	

V_{T0} =	**2.166**	Å^3
K_{T0} =	**247.312**	GPa
K_T' =	**40.139**	

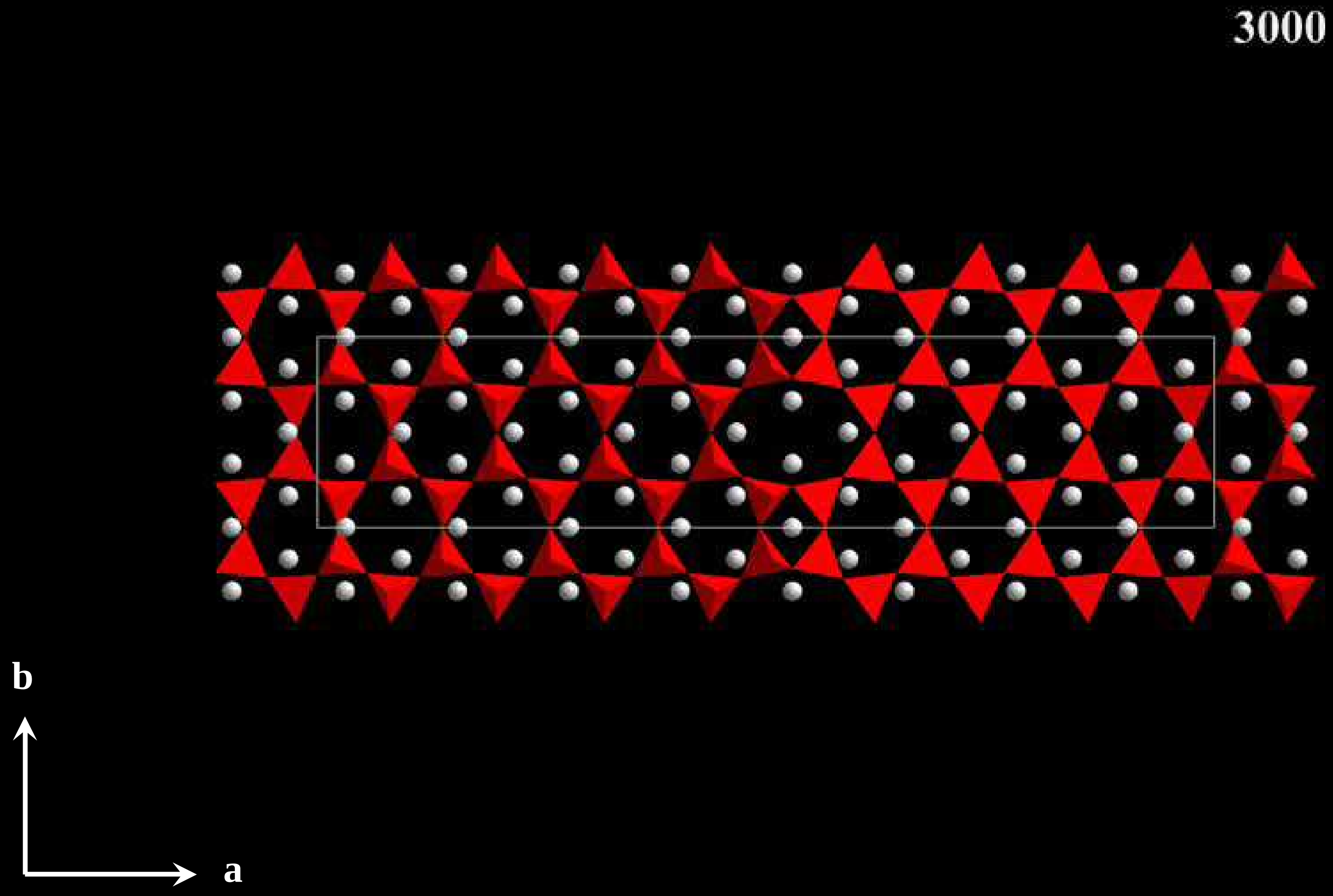
- When compared with the bulk modulus, the **polyhedral modulii** are **much larger**.
- Most of the unit-cell shrinkage is accomplished by **contraction of the interlayer**.
- This is also consistent with the observation that the **axial compressibility** is **higher across the TO-layer** than **within the TO-layer**.



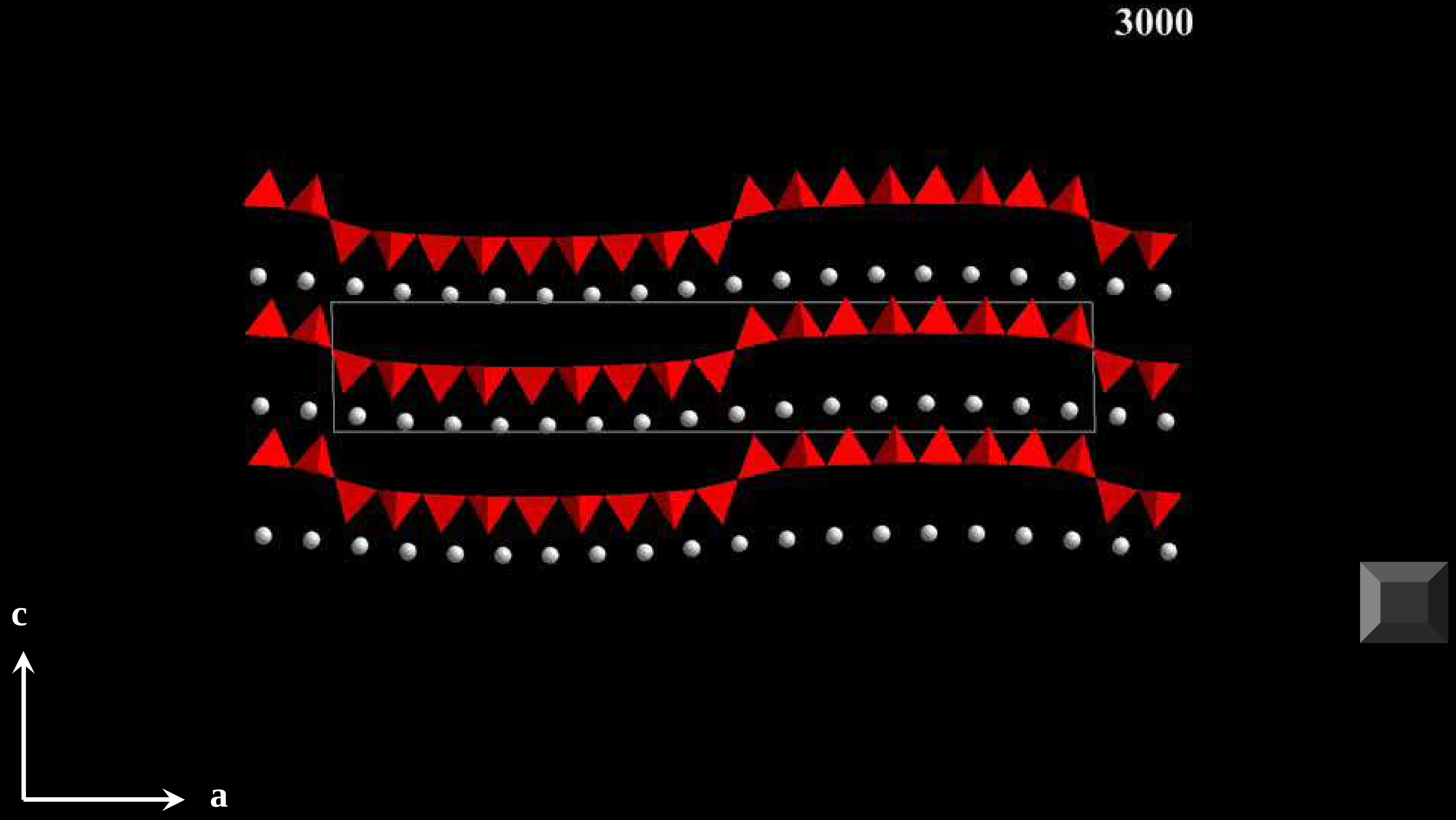
Ditrigonal Distortion

- From 3 GPa onward, the increasing ditrigonal distortion becomes more pronounced in the short-halfwave than in the long-halfwave.
- An "**anomalous ring**" with distinct shape can be recognized in the long-halfwave
- It "migrates" upon compression from the 6-reversal location towards the center of the halfwave.
- Ditrigonal distortion is thus one major mechanism by which the T-sheet readjusts to maintain the linkage with the O-sheet during compression.

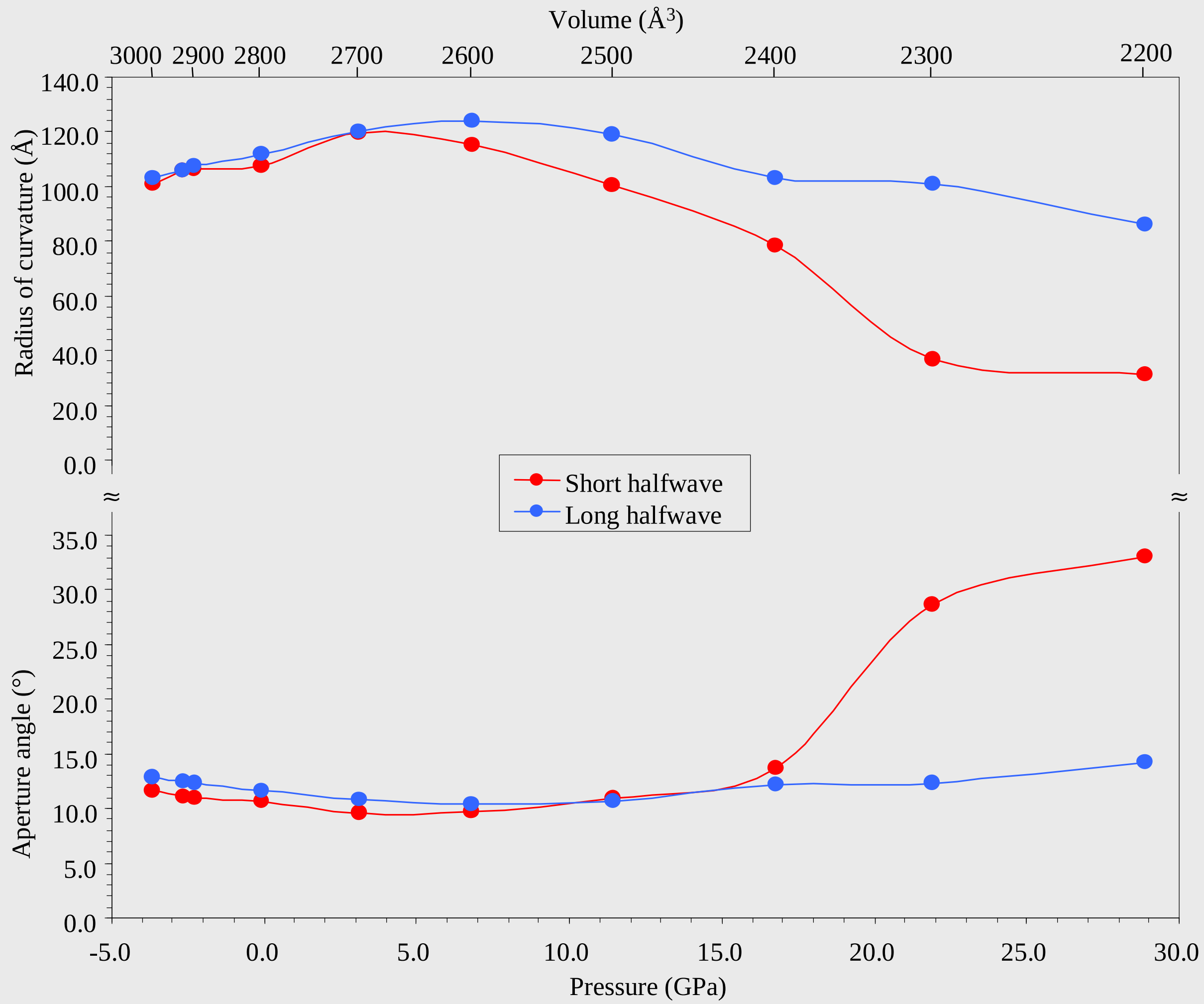
…as seen down [001]



…as seen down [010]

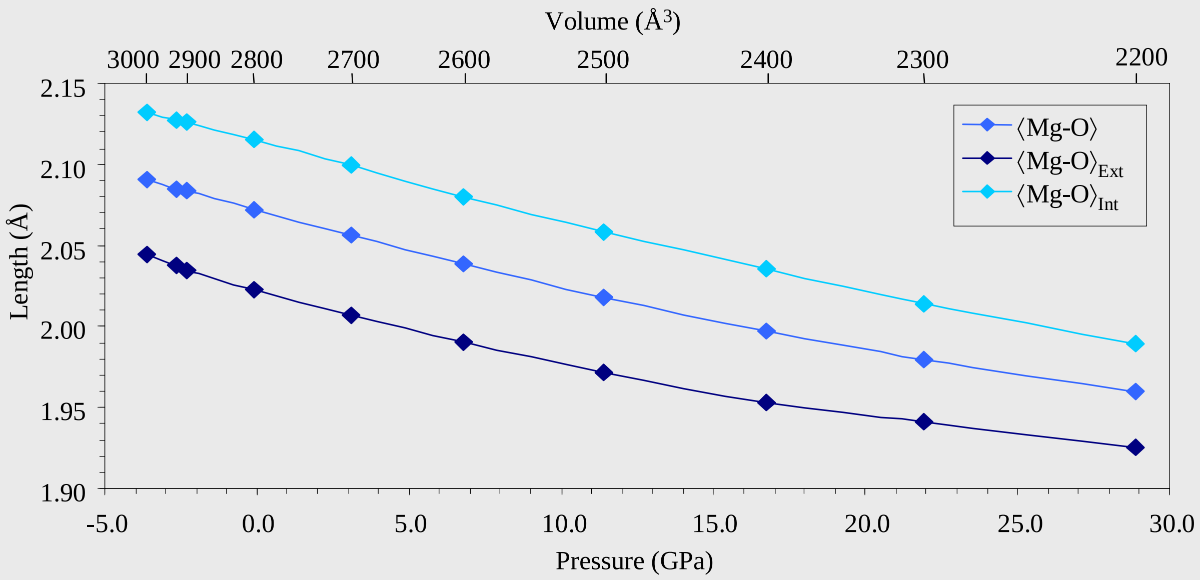


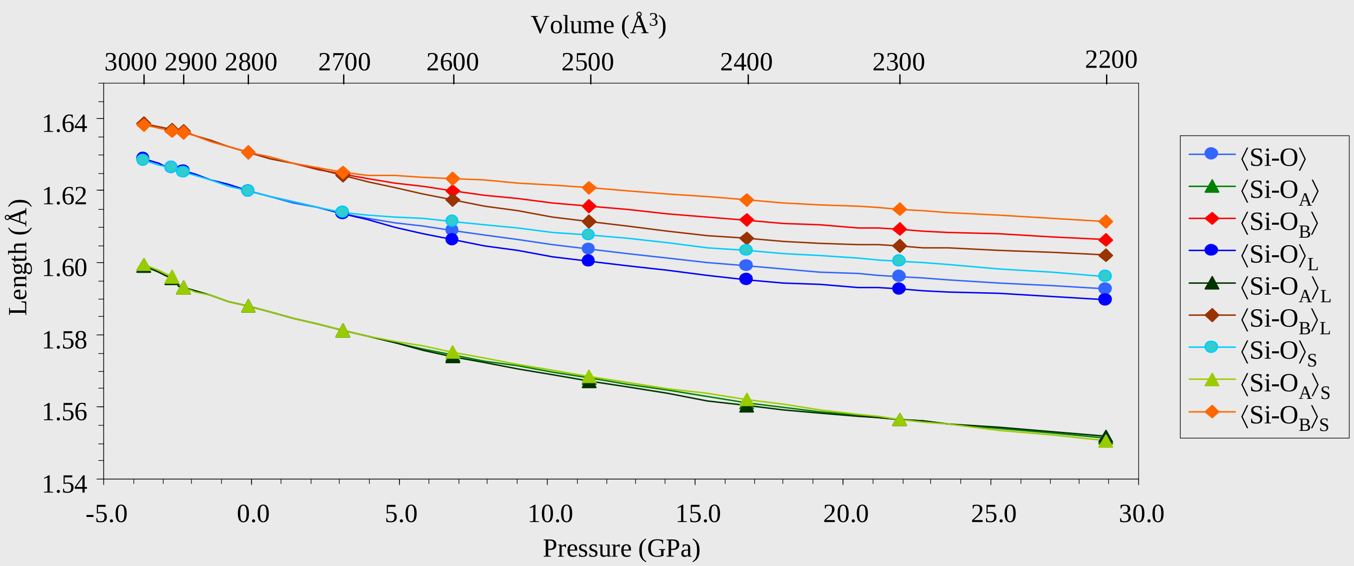
Curvature of the Halfwaves

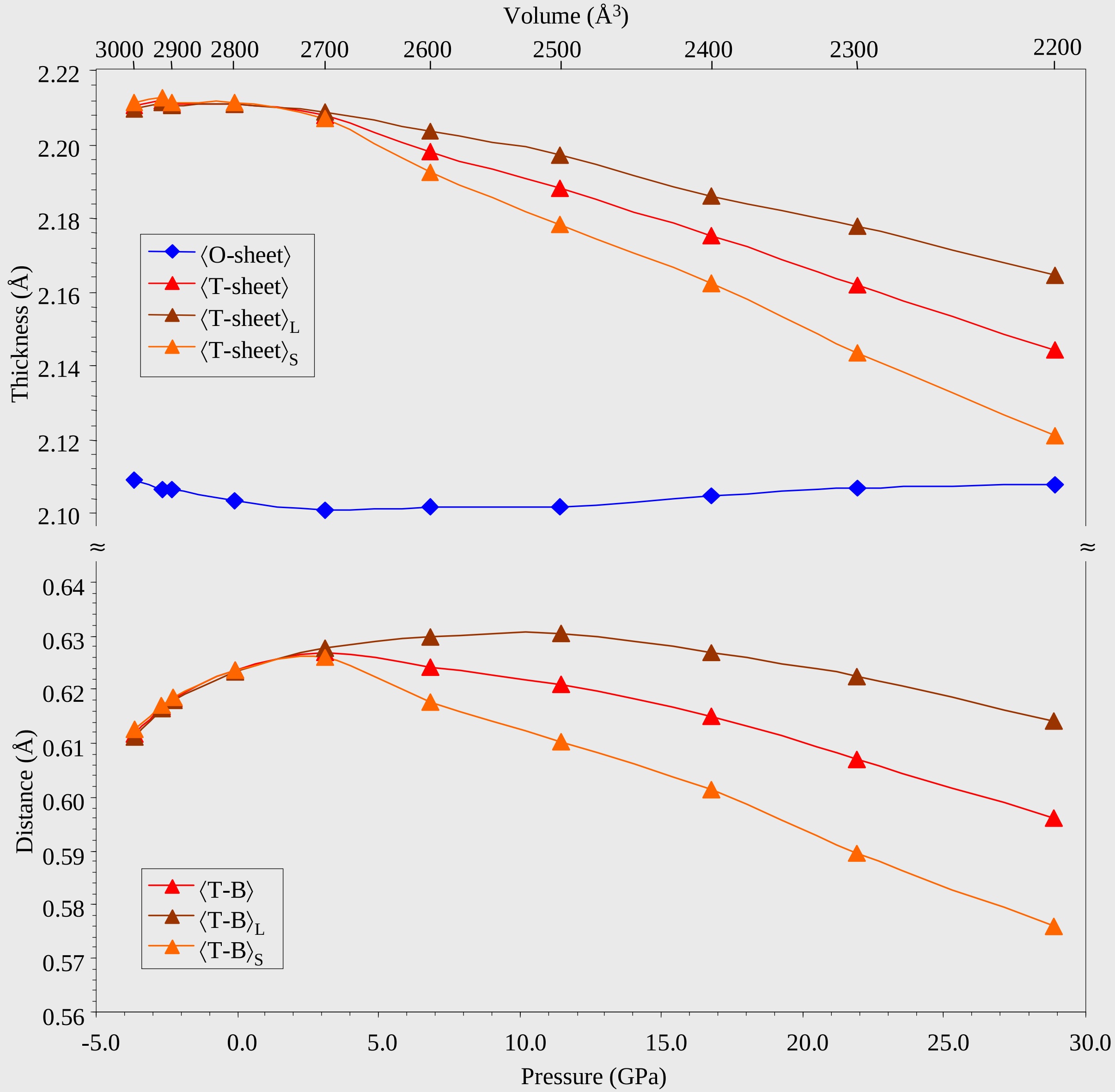


- Up to 3 GPa, the halfwaves become flatter…
- Above 17 GPa, the short-halfwave becomes very curled
- The bending of the halfwaves is thus a second major mechanism of unit-cell contraction, especially at HP, when the linear compressibility along *a* exceeds that across the TO-layer.

Bond Lengths



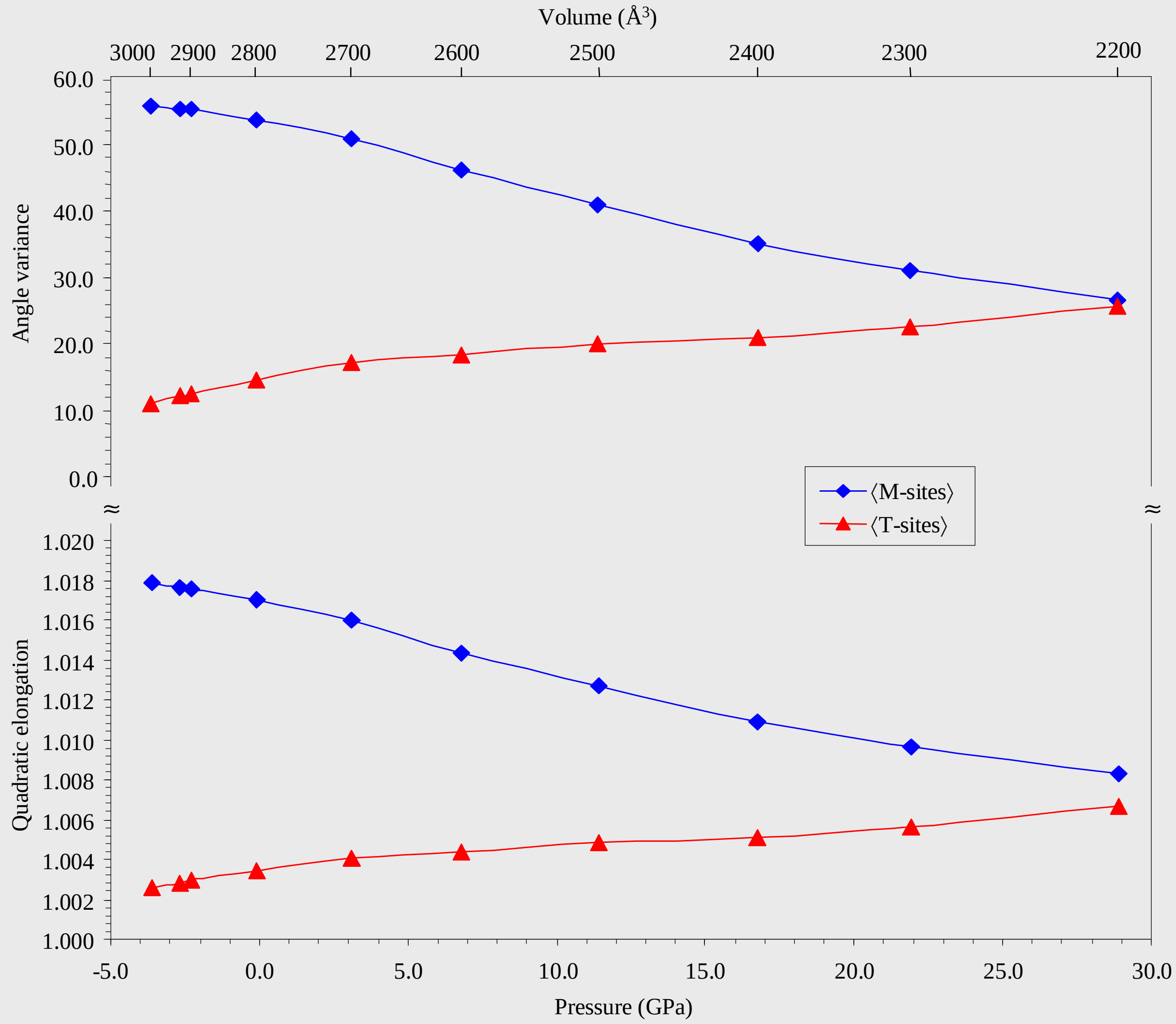


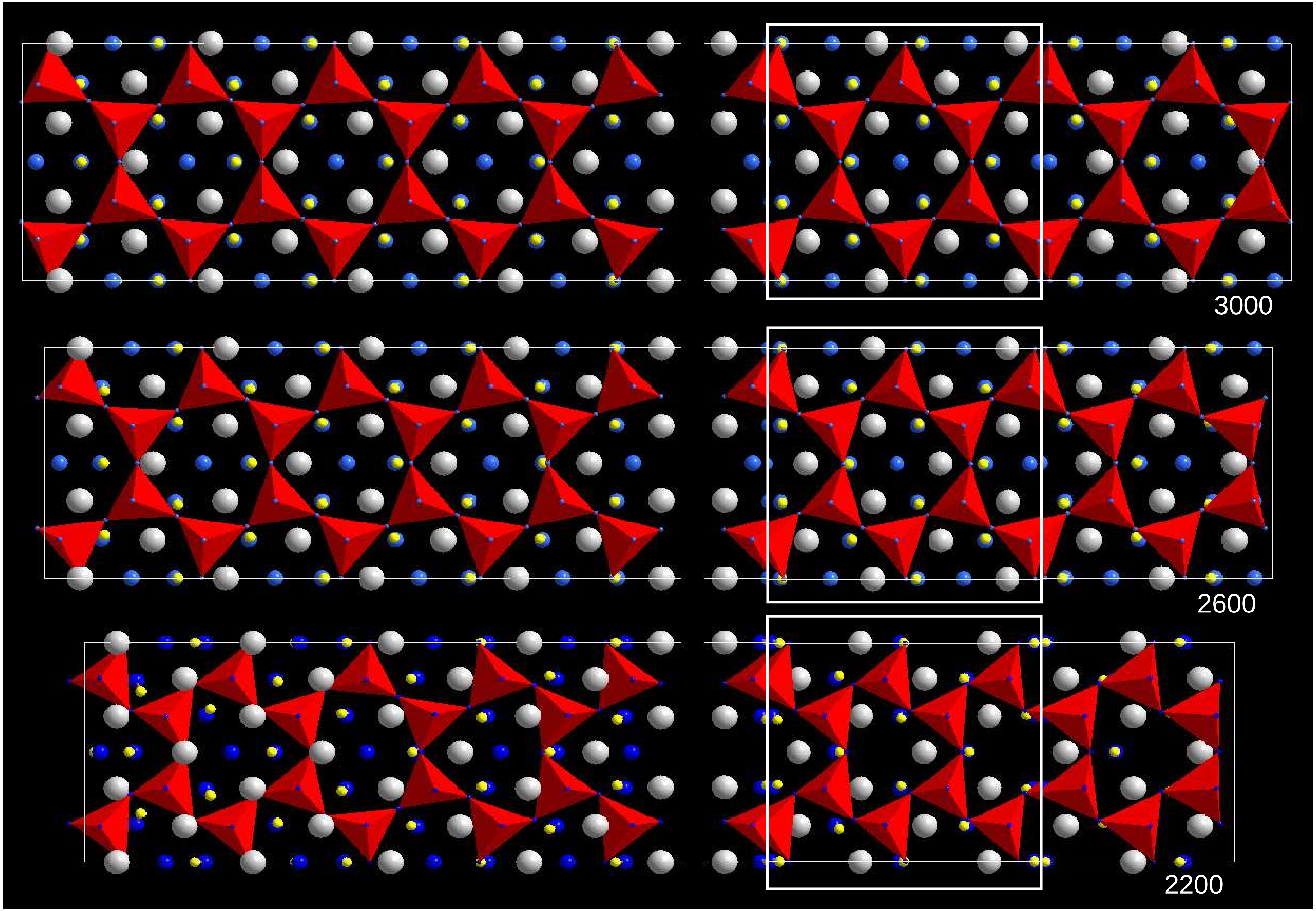


TO-sheet Thickness

- …
- Above 3 GPa, T-sheet flattening is another mechanism by which antigorite acts in response to compression

Polyhedral Distortion

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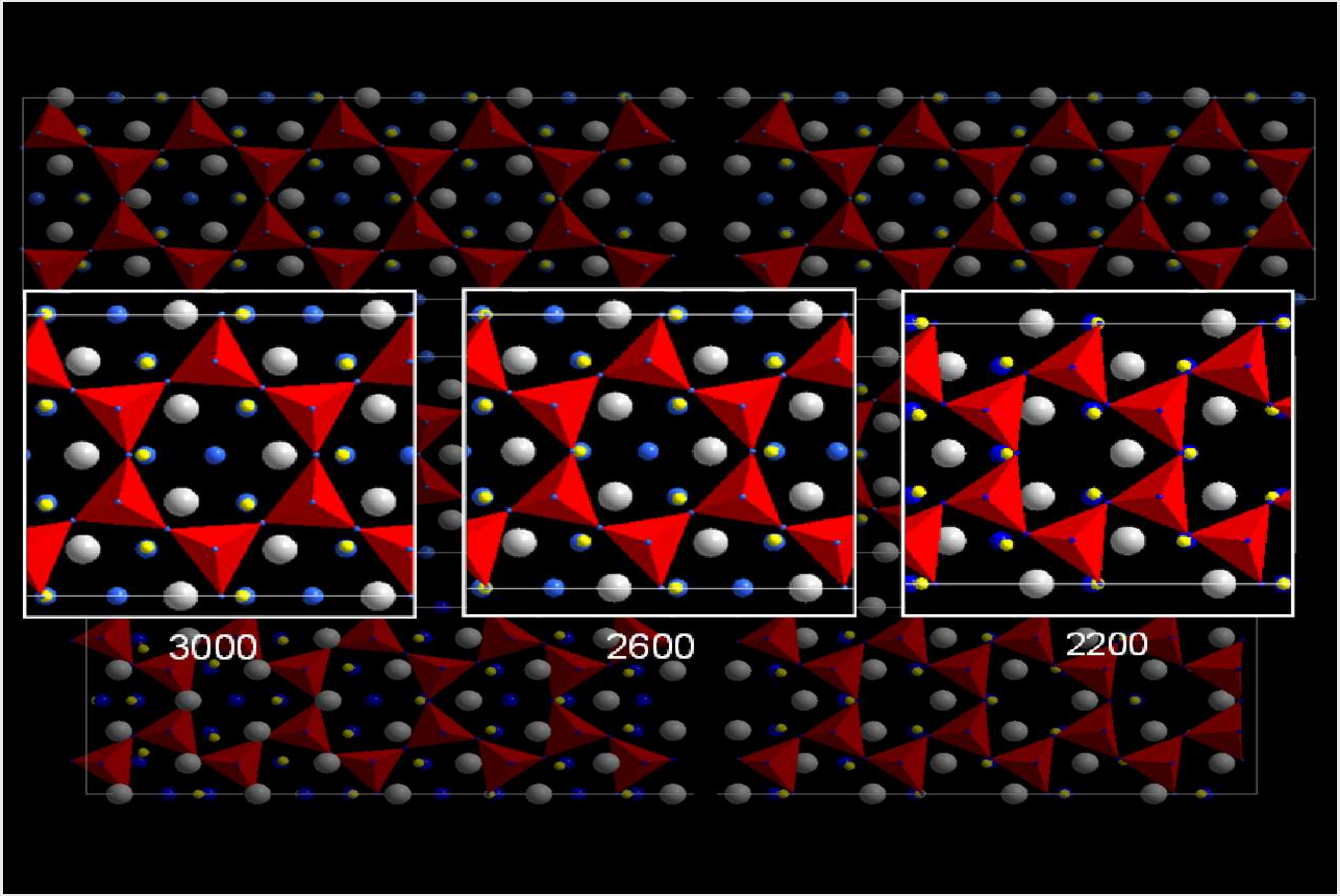
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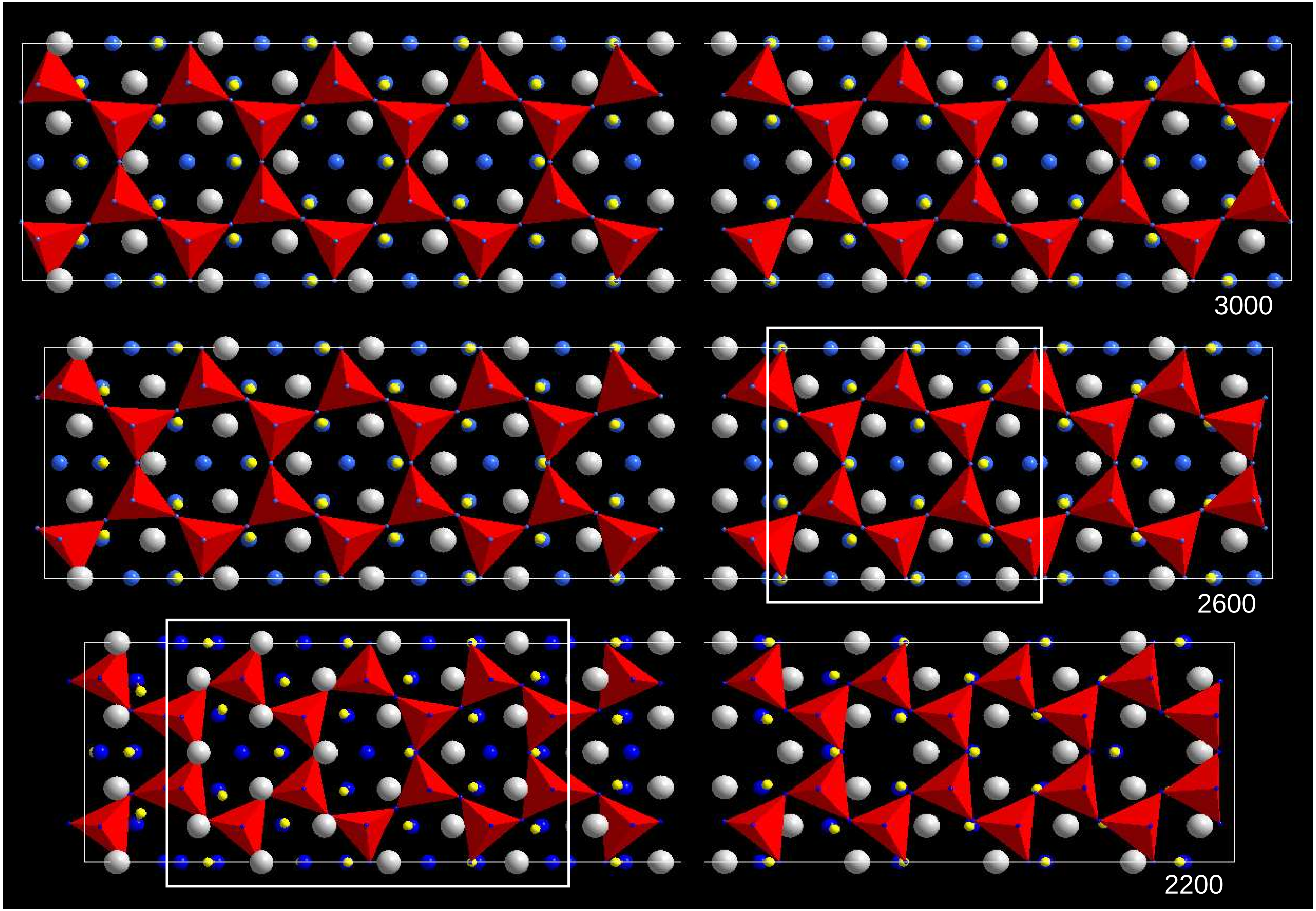
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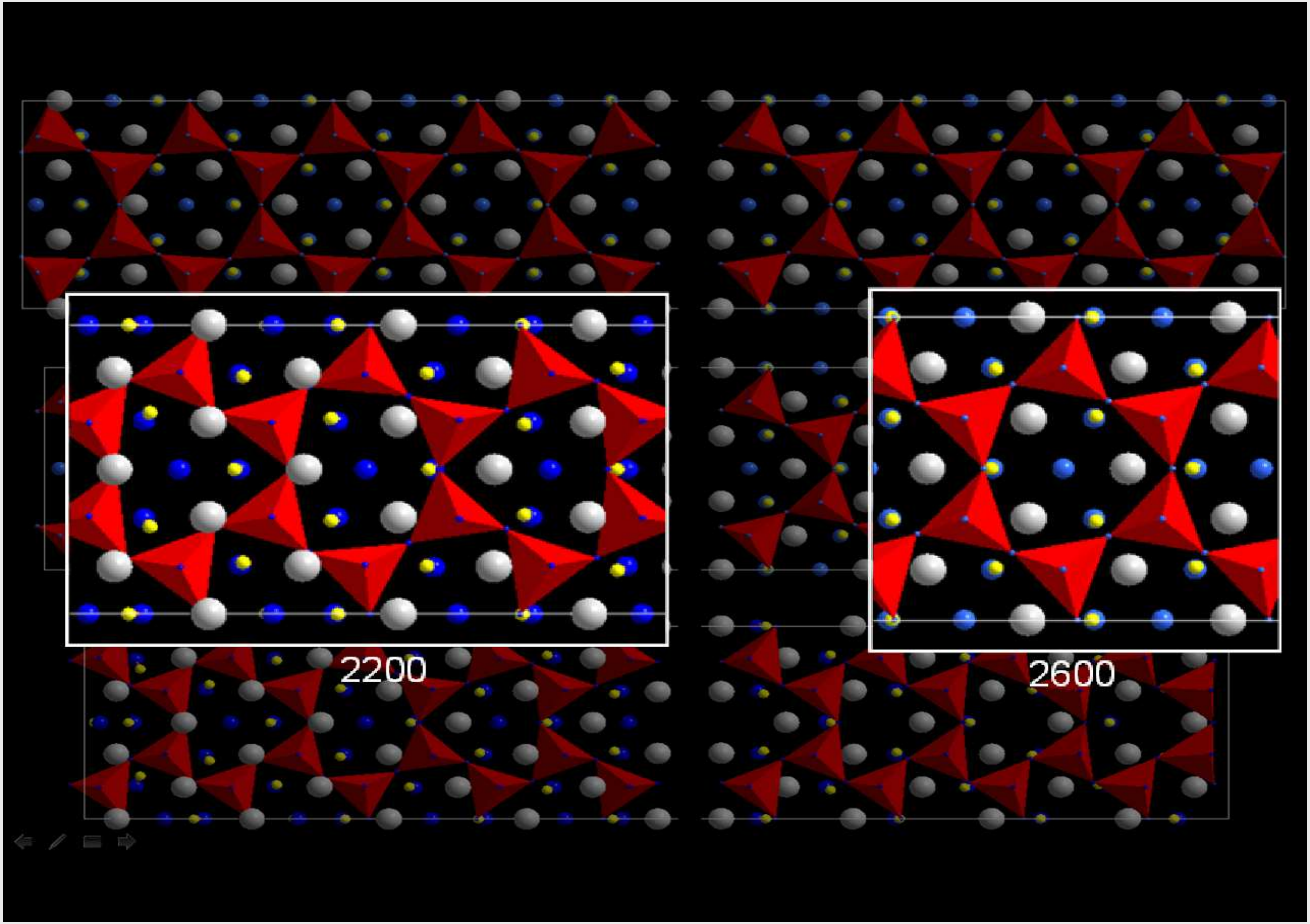
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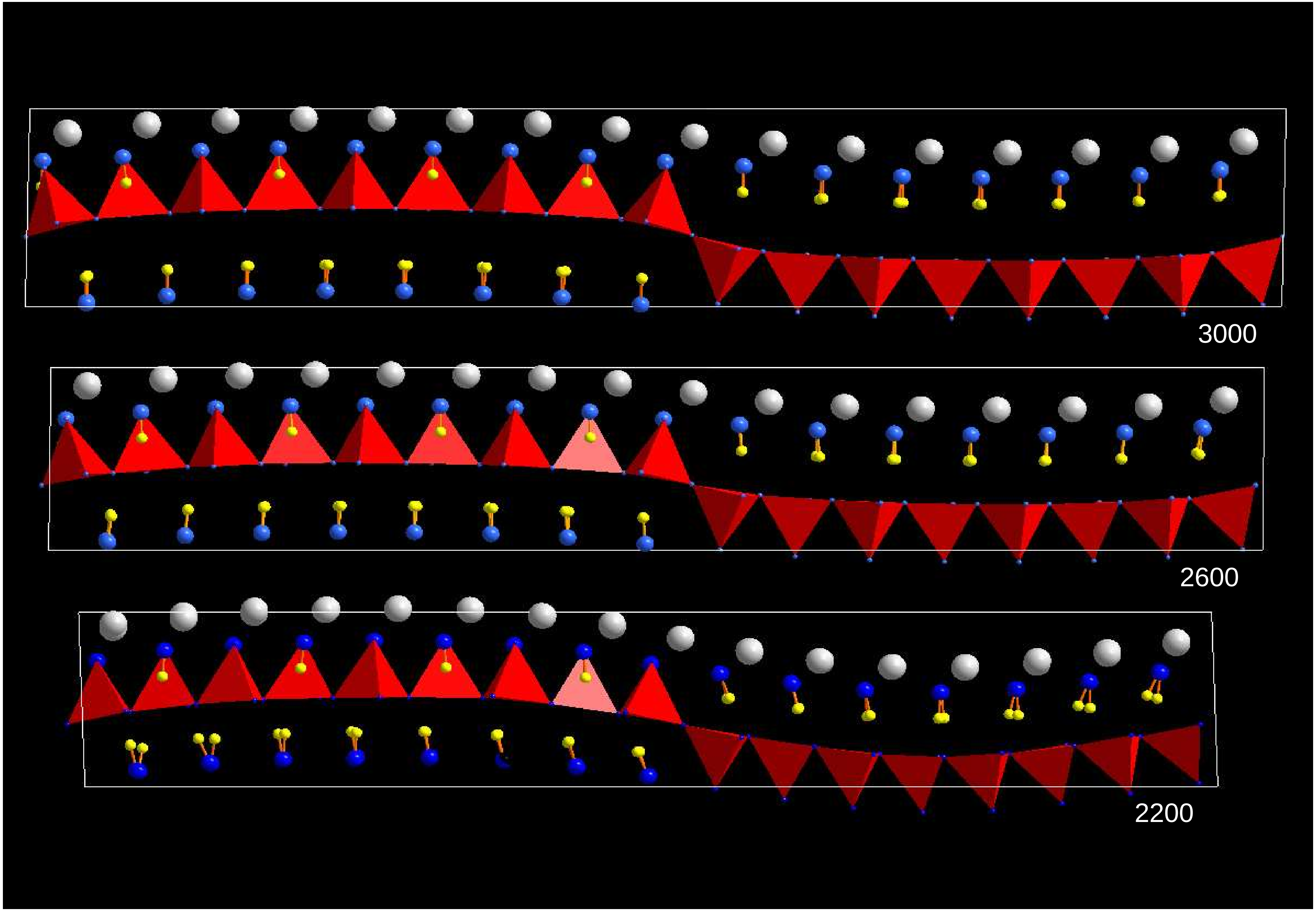
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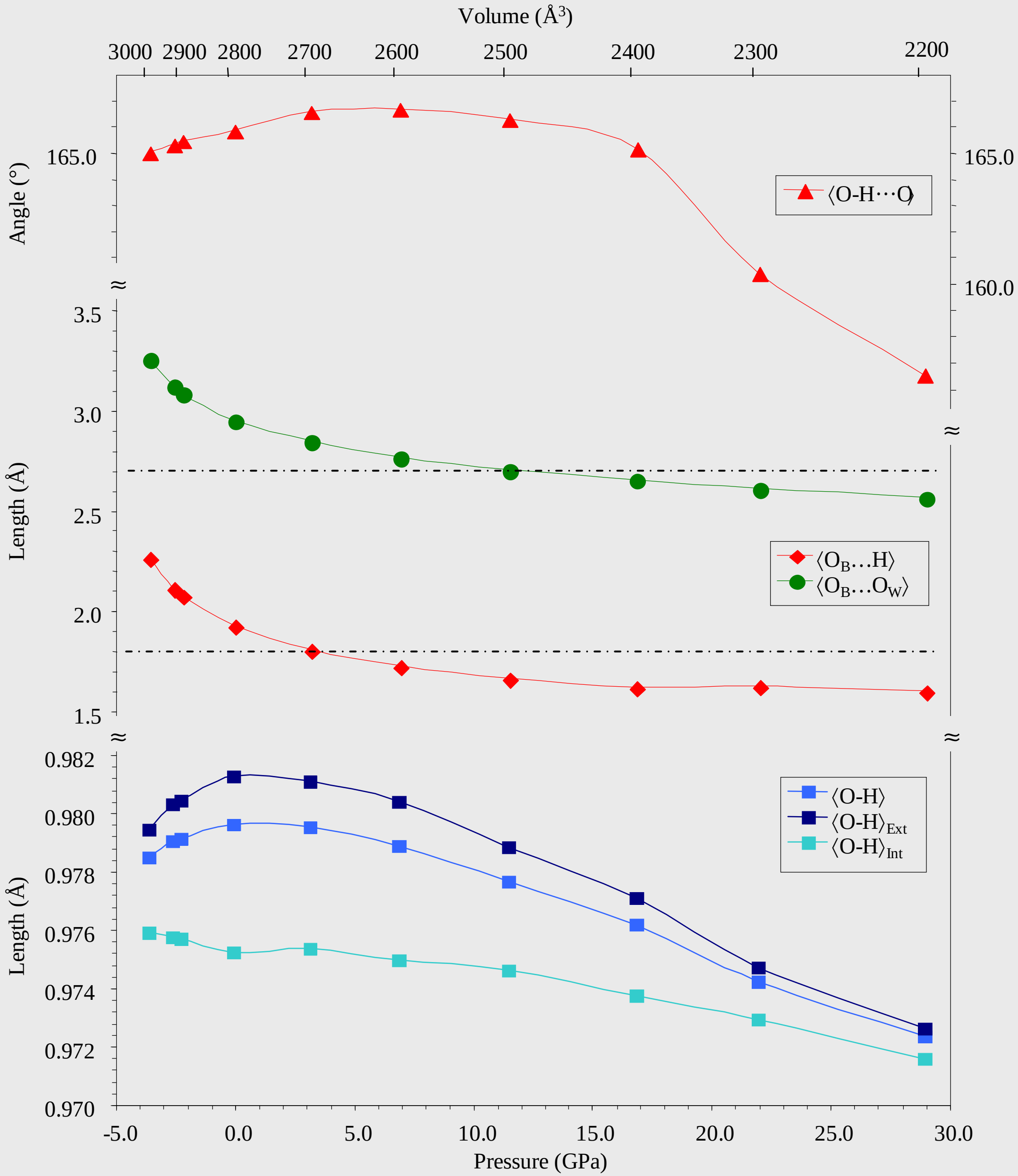


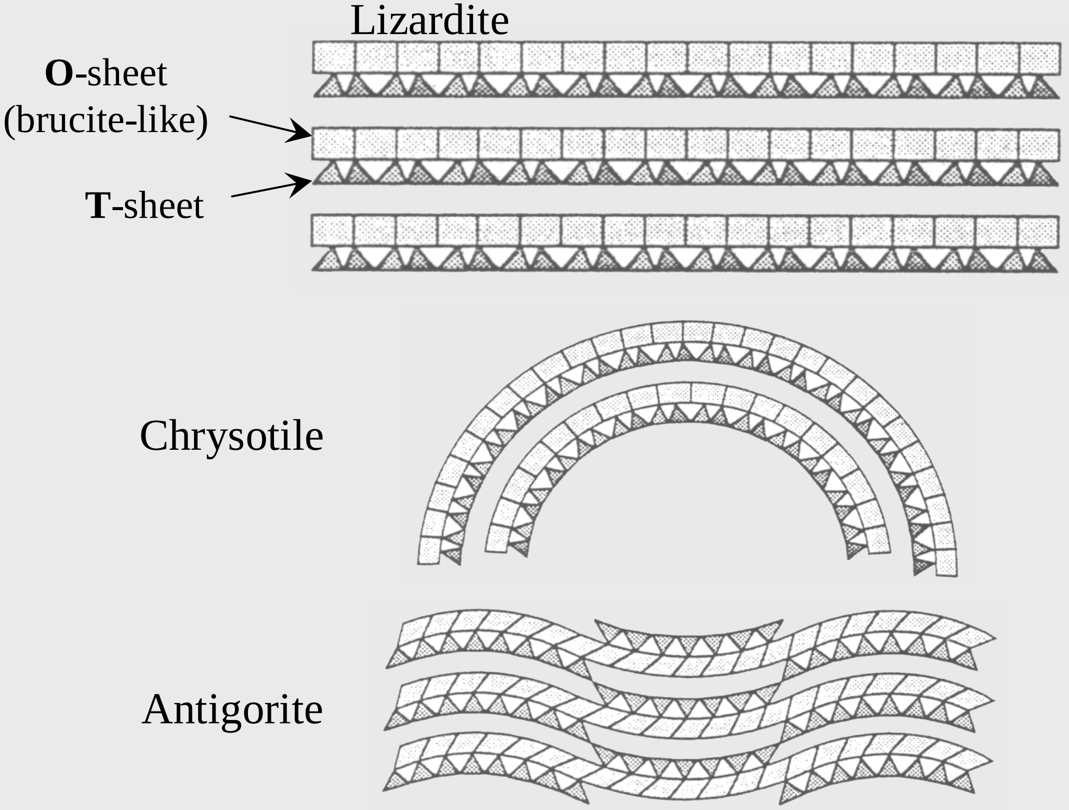
Hydrogen Bonding

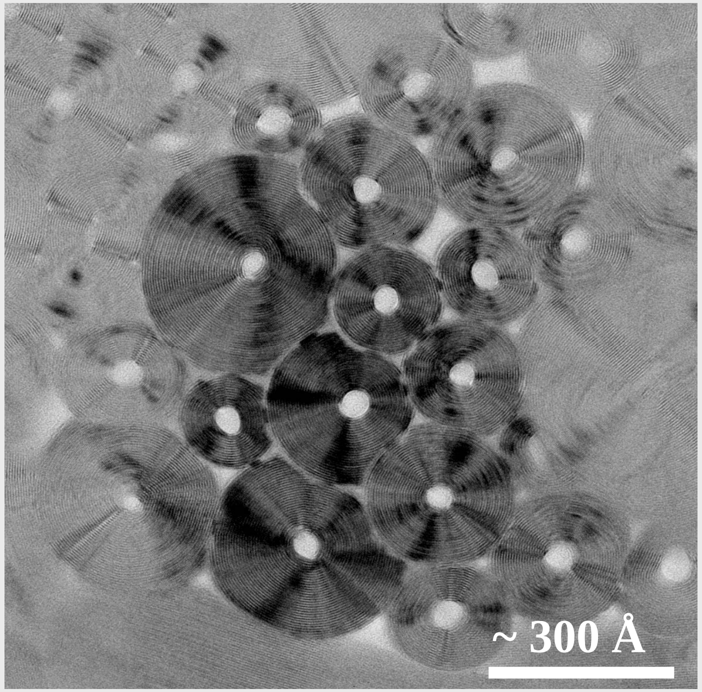
- …
- Hydrogens do not seem to change proton acceptors after discontinuity, but very locally.
- Overall, behavior indicative of a **weak hydrogen bonding** at volumes above the theoretically determined equilibrium volume, and absence of hydrogen bonding at lower unit-cell volumes.

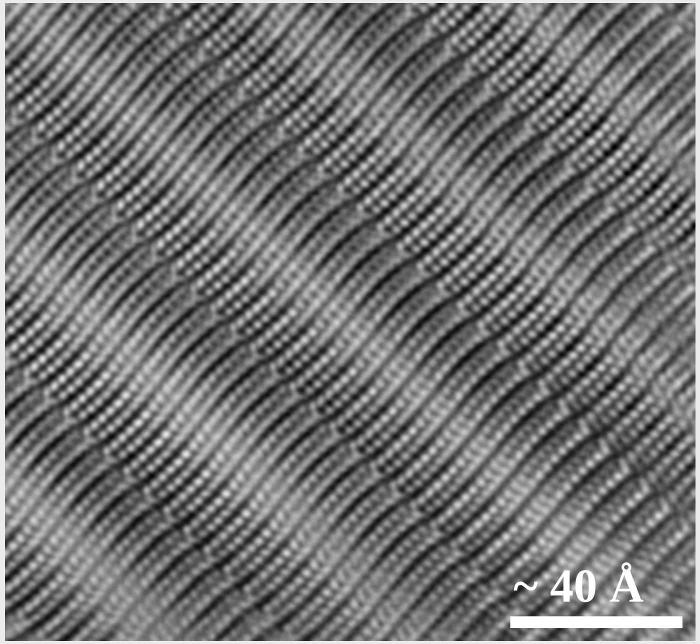
Conclusions

- Major changes in the compression behavior were identified at **~3 GPa** (4% of unit-cell volume contraction) and **~17 GPa** (8% of unit-cell volume contraction).
- Up to ~3 GPa, most of the unit-cell contraction is accomplished by **thinning of the interlayer**: the *c*-axis results much more compressible than *a* and *b*, and the halfwaves become flatter.
- This mechanism lessens progressively its effectiveness, and from 3 GPa, **ditrigonalization** of the T-sheet and halfwave **bending** are more effective.
- From 3 GPa, **short- and long-halfwave behave differently** upon compression, namely the halfwave bending, the T-O bonding, the T-sheet flattening and the H-bonding are different.
- One may wonder whether "even" antigorite polysomes with symmetrical halfwaves, as *m* = 16 for instance (Capitani & Mellini 2006), may have different structural behavior under compression and, eventually, a **different stability field** in subduction zones.
- Antigorite can rely upon **more degrees of freedom** to act in response to an increase in pressure than lizardite: the two halfwaves can bend and contract and can accommodate different degree of ditrigonal distortion. Moreover, additional strain can be accommodated at the reversals.
- These additional means to face a P increase probably contribute to the **higher stability field** of antigorite among the serpentine minerals (e.g. Evans et al. 1976).

Serpentine [$Mg_3Si_2O_5(OH)_4$)]







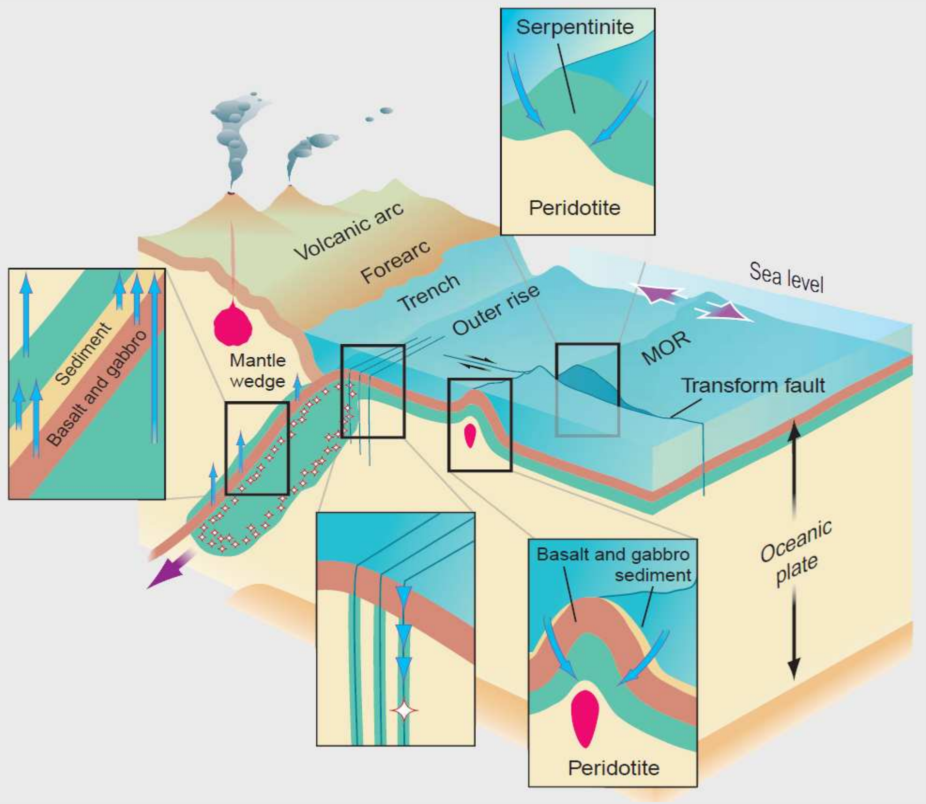
- Not a serpentine polymorph in *sensu strictu* →

  $Mg(OH)_2$ depletion

- Deviation from the serpentine composition →

  $Mg^{VI}_{3m-3}Si^{IV}_{2m}O_{5m}(OH)_{4m-6}$

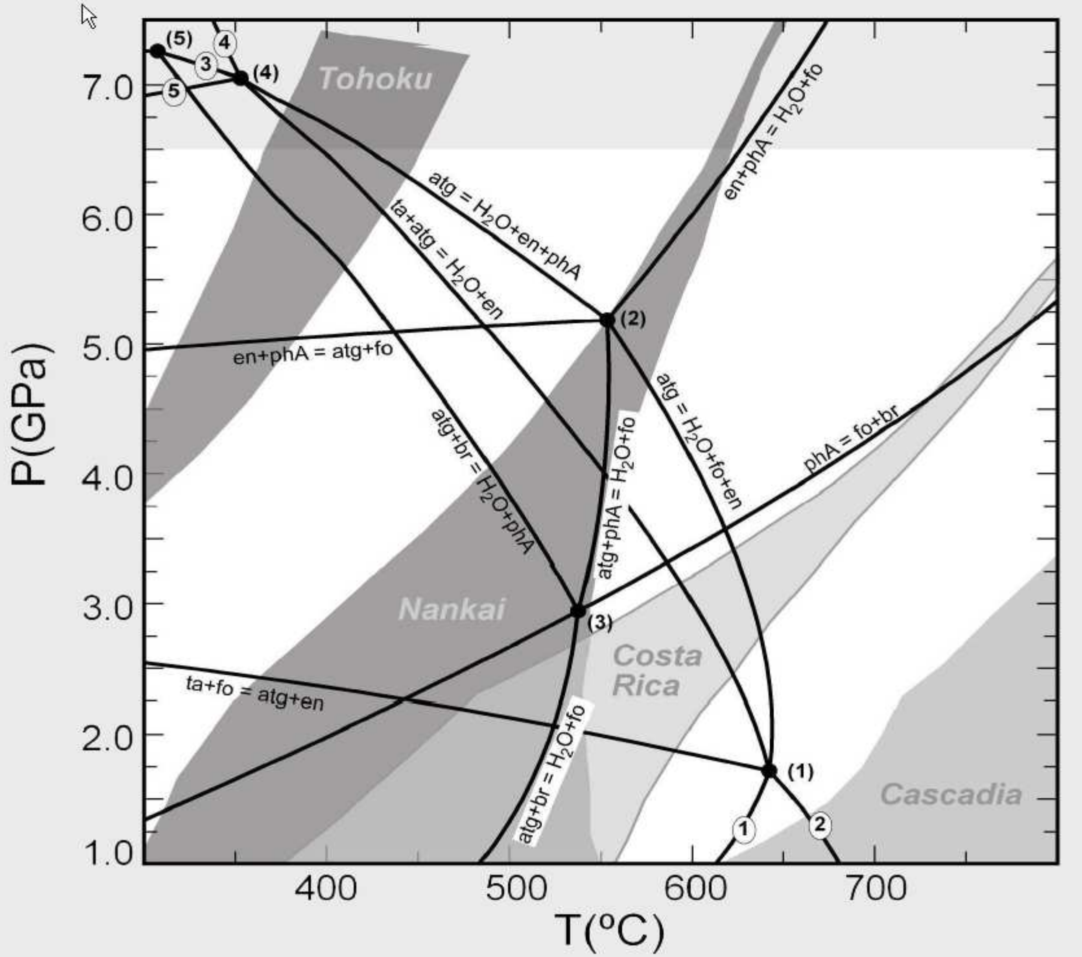
Serpentinization of Oceanic Plates



From D. Kerrick (2002) Science, 298:1344

- Serpentine is widespread in oceanic plates undergoing subduction.
- It forms by hydration of peridotite by hydrothermal circulation of seawater directly at **ocean ridges**;
- Or by seawater infiltration along deep **outer rise** faults.
- Upon subduction water is released from serpentinites by dehydration reactions.
  - Dehydration embrittlement…
  - Mantle wedge metasomatism…
  - Serpentine seamounts…
  - Calc-alkaline volcanism…

Phase Diagrams for Ultramafics



From Nestola et al. (2009) CMP, submitted