

# UNDERSTANDING PHASE TRANSITIONS IN THE EARTH'S INTERIOR: CONTRIBUTIONS FROM AN ANALYSIS OF THE CATIONIC ARRAY IN POST-PEROVSKITE PHASES

**Maria Ondina Figueiredo**

CENIMAT/I3N, Mat. Sci. Dept., Fac. Sci. Technology, New University of Lisbon, Campus de Caparica, 2829-516 CAPARICA & LNEG, Unit of Min. Resources & Geophys. Apart. 7586, 2610-999 AMADORA

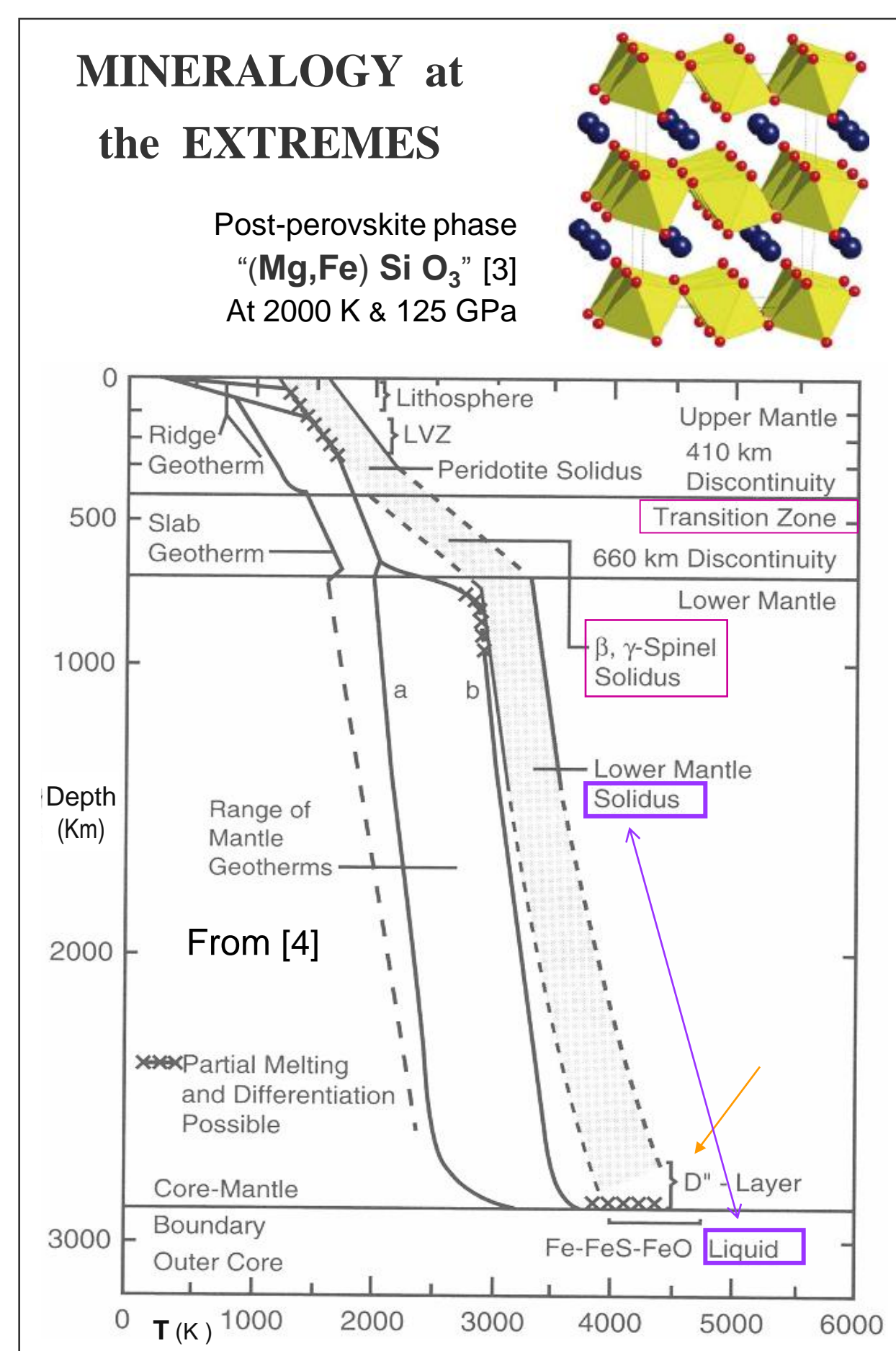
## Problematic

Predicting and modelling the high pressure & high temperature (HP-HT) behaviour of mineral crystal structures has become a major target for mineralogical crystallographers and material scientists dealing with matter under extreme conditions [1].

The structural role played by the anionic array (close packing) and by the geometry of anion coordination polyhedra around cations were for long recognized. Conversely, the topology of the bulk array of cations – the cationic structural fraction (TSK, from *Teilstruktur Kationen*) – was comparatively overlooked. The interest increasingly focused on phase transformations in the Earth's interior along the last decades has brought these features to the first rank of priorities in the analysis of structural features.

Geophysical implications of displacive, iso-symmetrical transitions – originating cryptopolymorphism through the formation of closest-packed analogues of chain and sheet silicates [3] – and of symmetry-breaking transformations are revisited, further focusing on phases with general formulae  $ABO_3$  – pyroxenes, perovskites and other double oxides like ilmenite – and  $A_2BO_4$  – spinelloids and perovskite derivatives.

Possible implications of the structural relationship between ilmenite and calcite are considered in relation to the way carbon may be hosted deep inside the earth. More abridging questions are addressed, particularly about the very state of matter under the extreme HP-HT conditions estimated for the deep earth's mantle.



## Perovskite and its structural derivatives

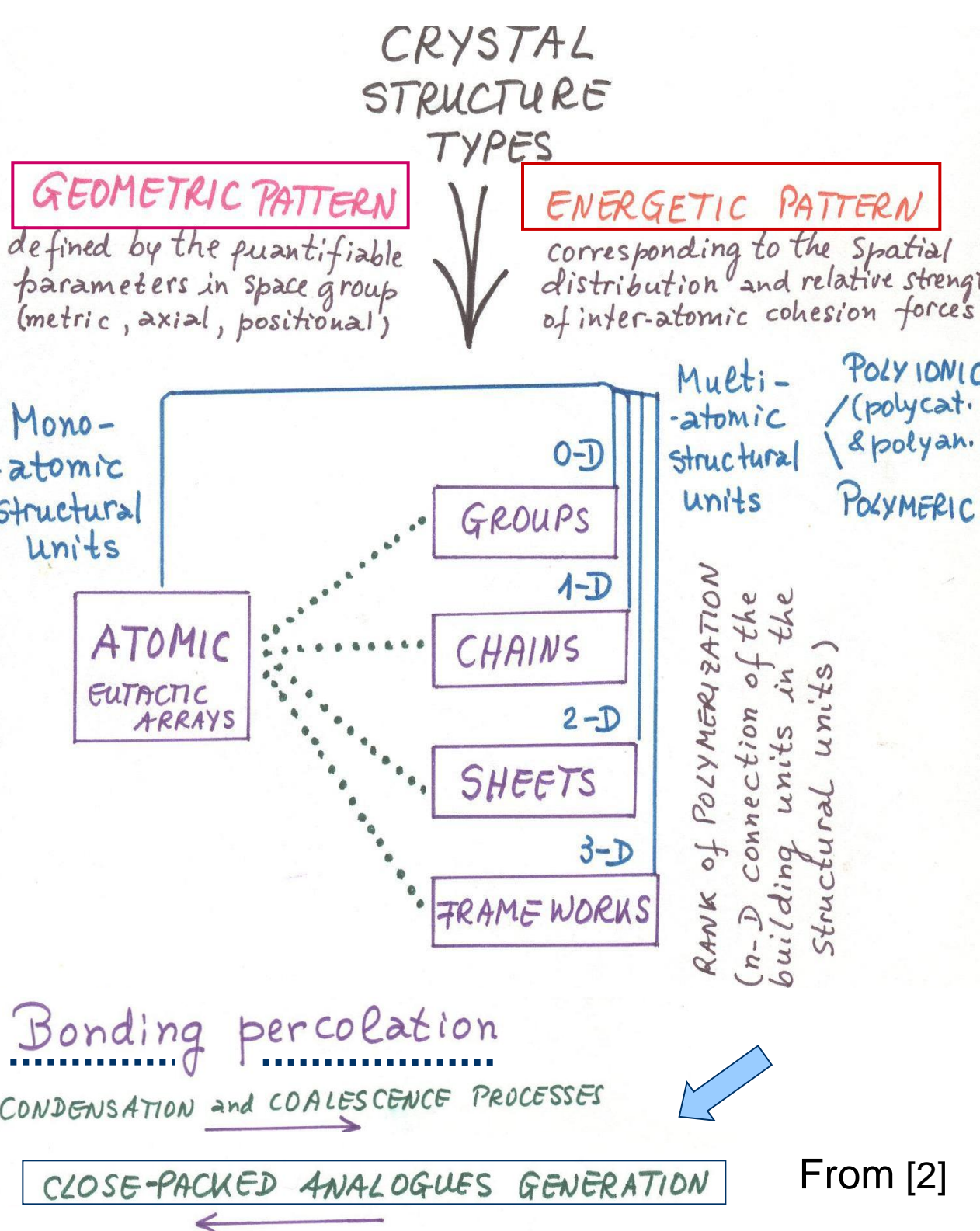
When considering octahedral plus large cations within **cubic perovskite** (crystal chemical formula  $A^{\circ}[B^{\circ\circ}O_3]T^c$ , space group  $Pm\bar{3}m$ ) – that is, metal ions occupying Wyckoff sites (1a) plus (1b) in the crystal structure – the obtained bulk cationic structural fraction (TSK) configures an “I” lattice-complex (body-centred cubic array). The metal-metal environment then gathers a higher number of neighbours (8 closer neighbours forming a cube plus 6 a slightly further, figuring an octahedron) by comparison with a true cubic closest-packing (12 close neighbours arranged as a cuboctahedron), an “F” lattice-complex.

**Symmetry-breaking transformations** may occur in perovskites without breaking the octahedral framework by processes of *tilting*, *rotation* & *cation off-centring* following symmetry sub-group relations, either keeping the unit cell (*Translationen-gleich* sub-groups) or the symmetry class (*Klassen-gleich* sub-groups). The crystal structure of neighborite ( $NaMgF_3$ ) illustrates the first process of transformation [5].

Slicing perovskite structure into *octahedral-layer slabs* is another way of generating *derivative structures*:  $K_2NiF_4$  [6] is an example.

Despite containing also an octahedral layer,  $CaIrO_3$  structure [7] displays a distinct interlinking of octahedra: chains of edge-sharing octahedra are interconnected by corners to form such layer.

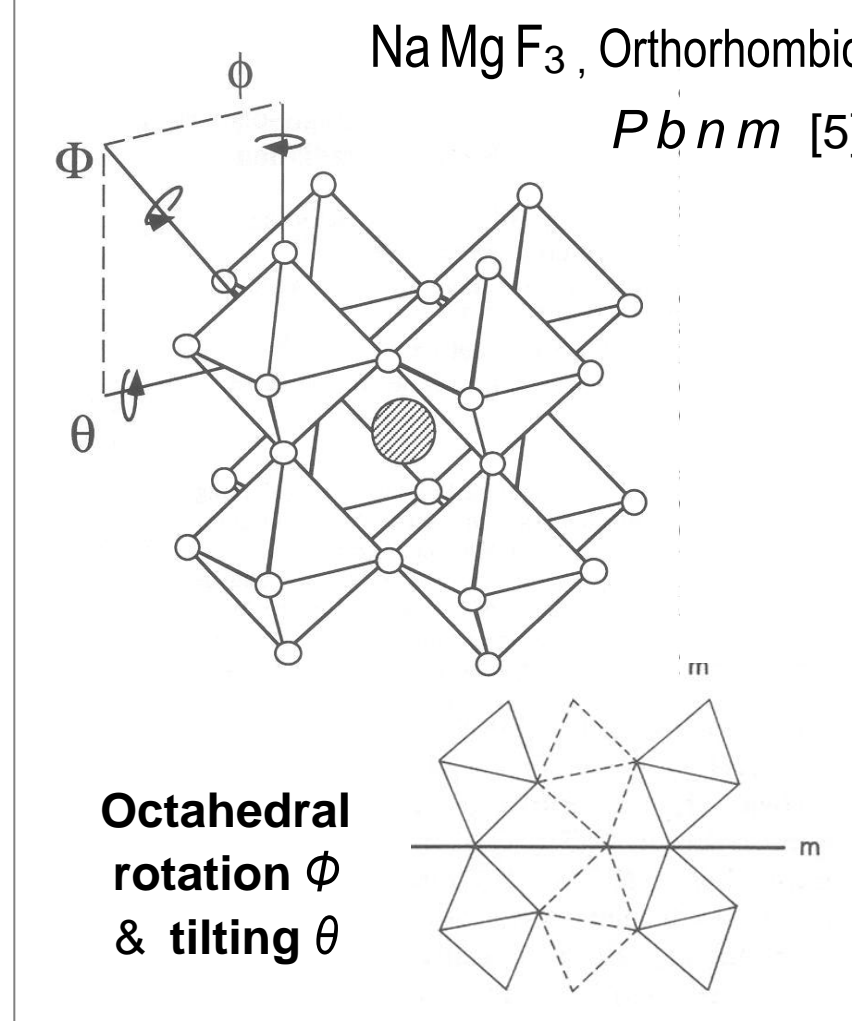
## ENERGY vs. GEOMETRY: INTERCONVERSIONS BETWEEN CRYSTAL STRUCTURE-TYPES (STP's)



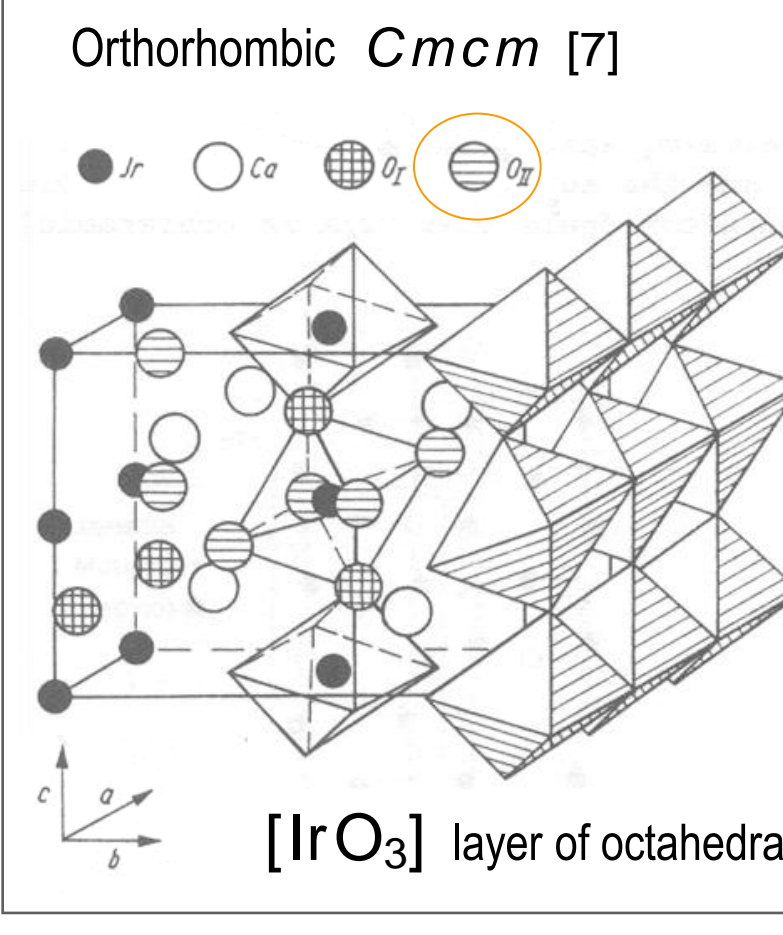
## Geometrical aspects

The geometrical compliance of crystal structure with mechanical stresses may be achieved by out-of-plane polyhedral tilting (observed for octahedra in perovskites) or by more complex interconversions between plane nets (like those figured out by the atomic layers in close-packed structures). The topology of tetrahedral interconnections in silicates allows for a suitable geometrical compliance by trigonalization of hexagonal rings (in micas) or chain shrinkage (in pyroxenes). *Isocompositional crystallographic shear* [1] is often adopted by closest-packed arrays (e.g., by spinelloid phases) to comply with mechanical stresses.

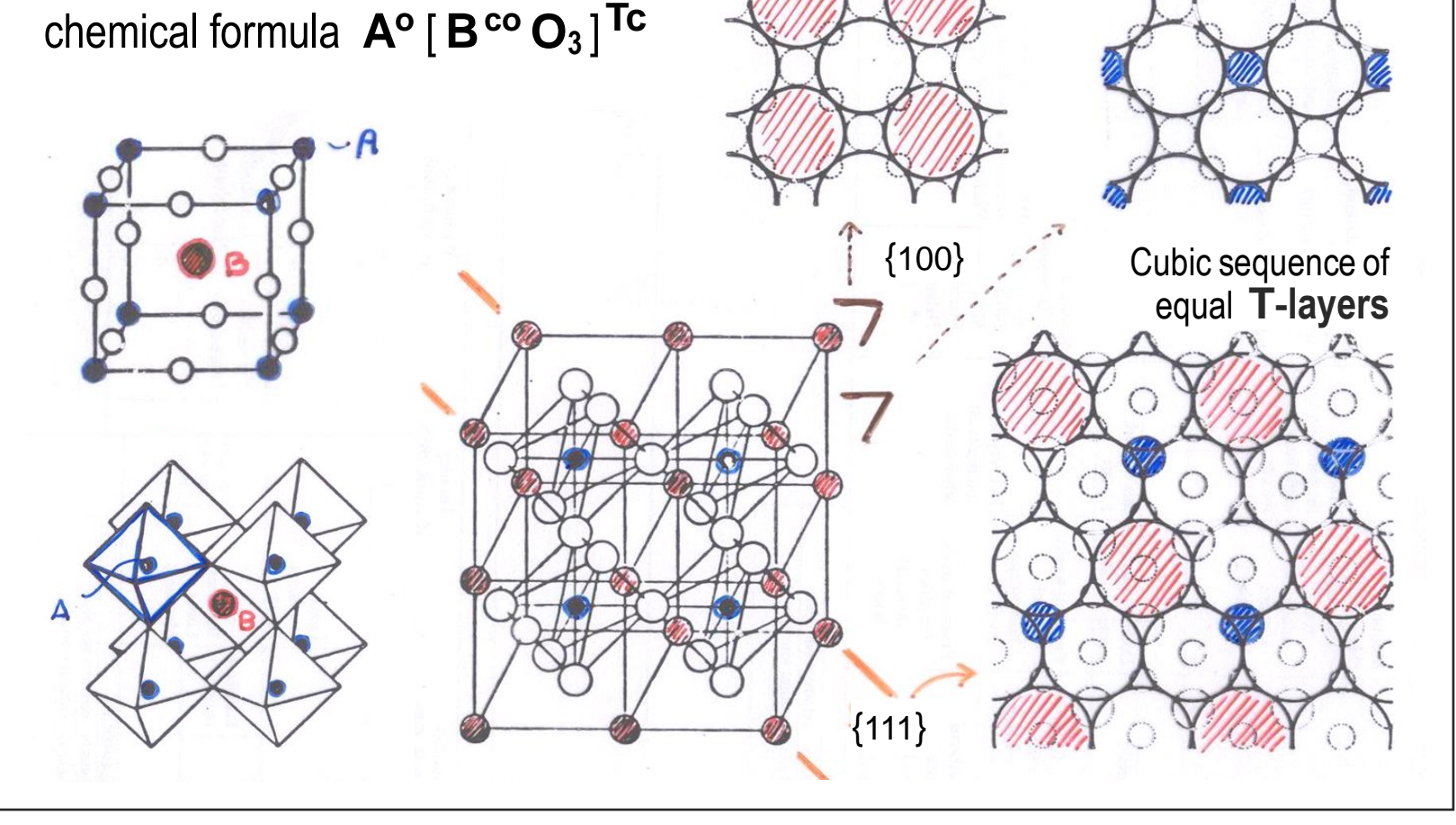
## Crystal structure of NEIGHBORITE, $NaMgF_3$ , Orthorhombic $Pbnm$ [5]



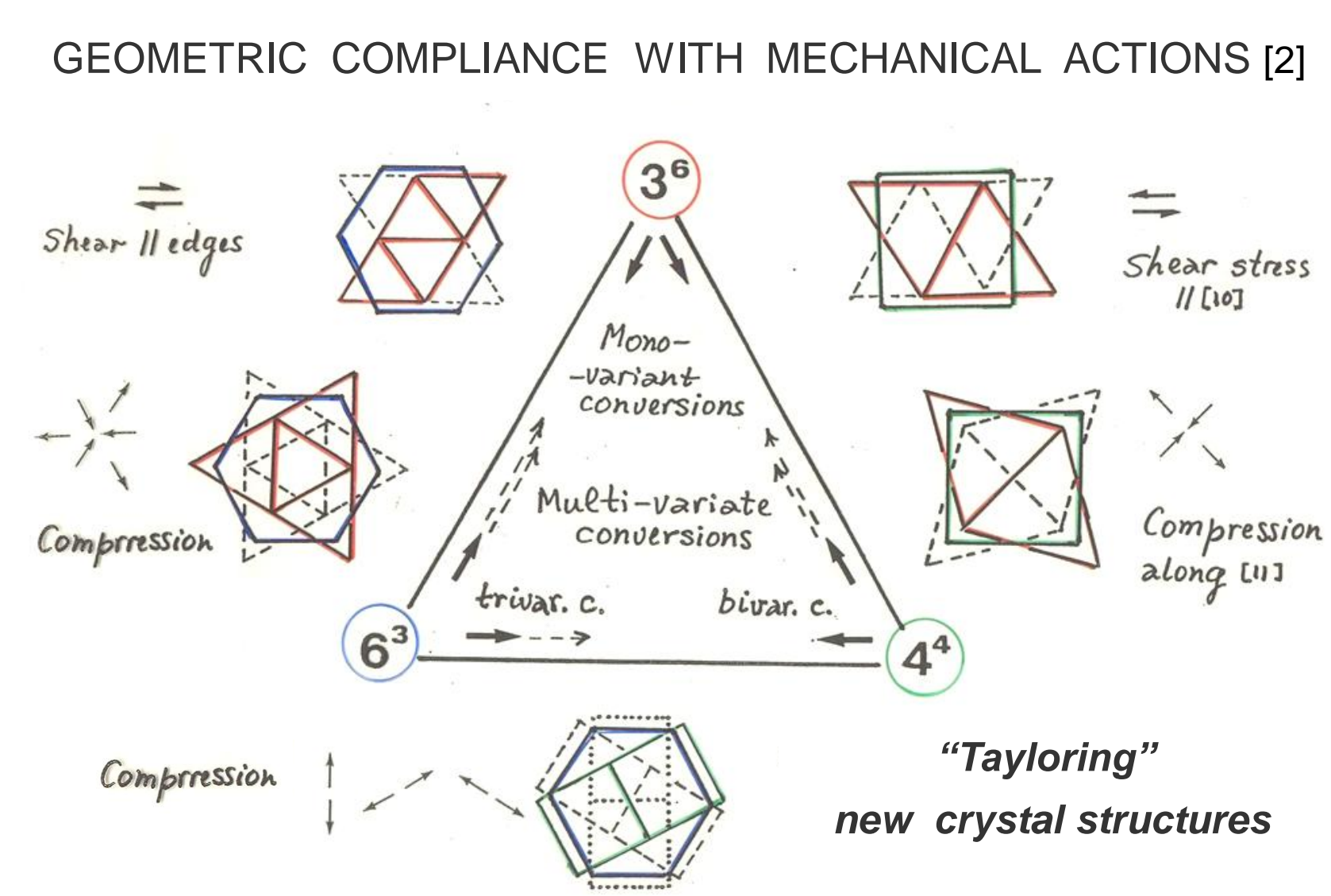
## Crystal structure of $CaIrO_3$ , Orthorhombic $Cmcm$ [7]



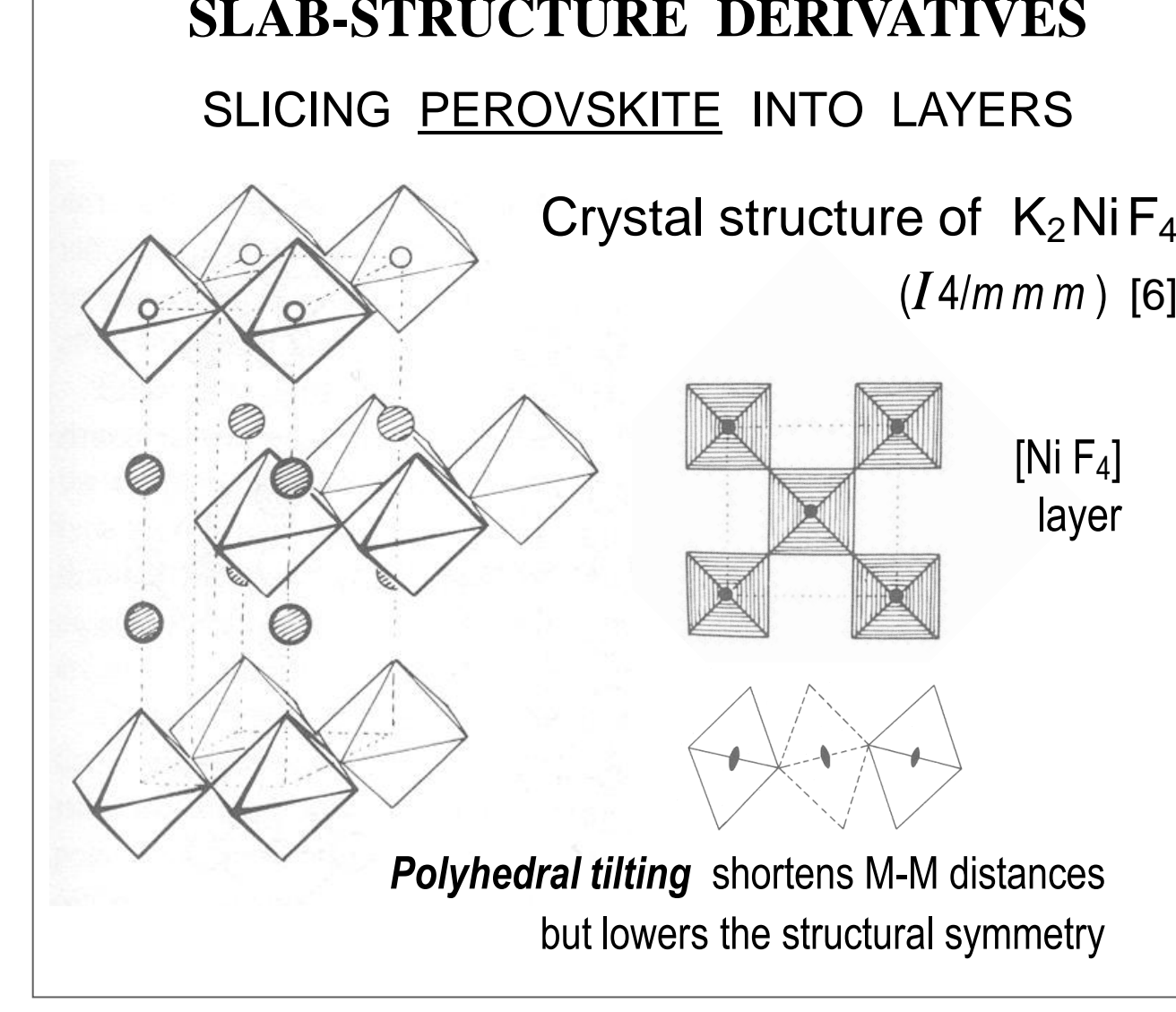
## PEROVSKITE: crystal chemical formula $A^{\circ}[B^{\circ\circ}O_3]T^c$



## INTERCONVERSIONS of REGULAR TESSELLATIONS



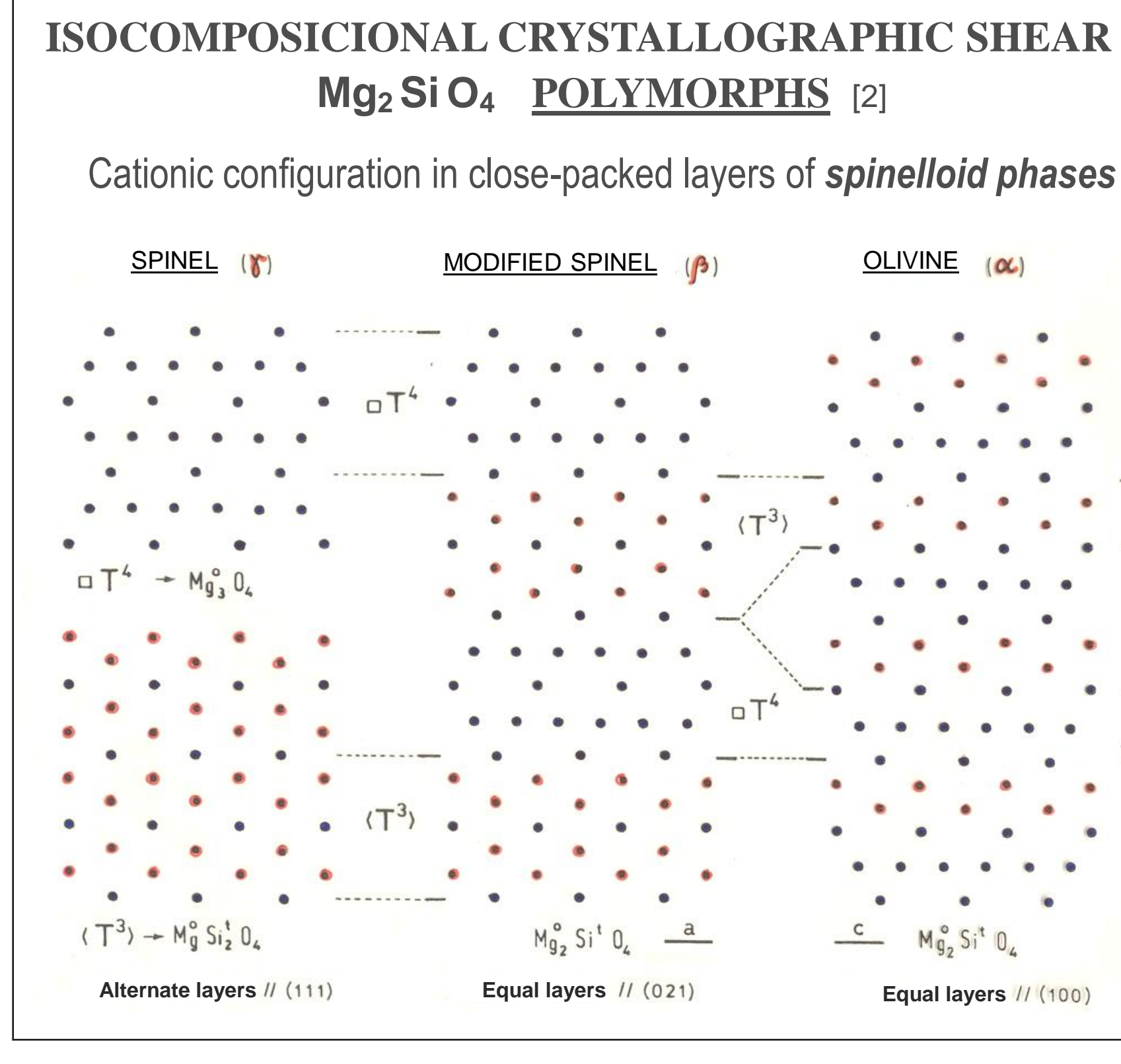
## SLAB-STRUCTURE DERIVATIVES



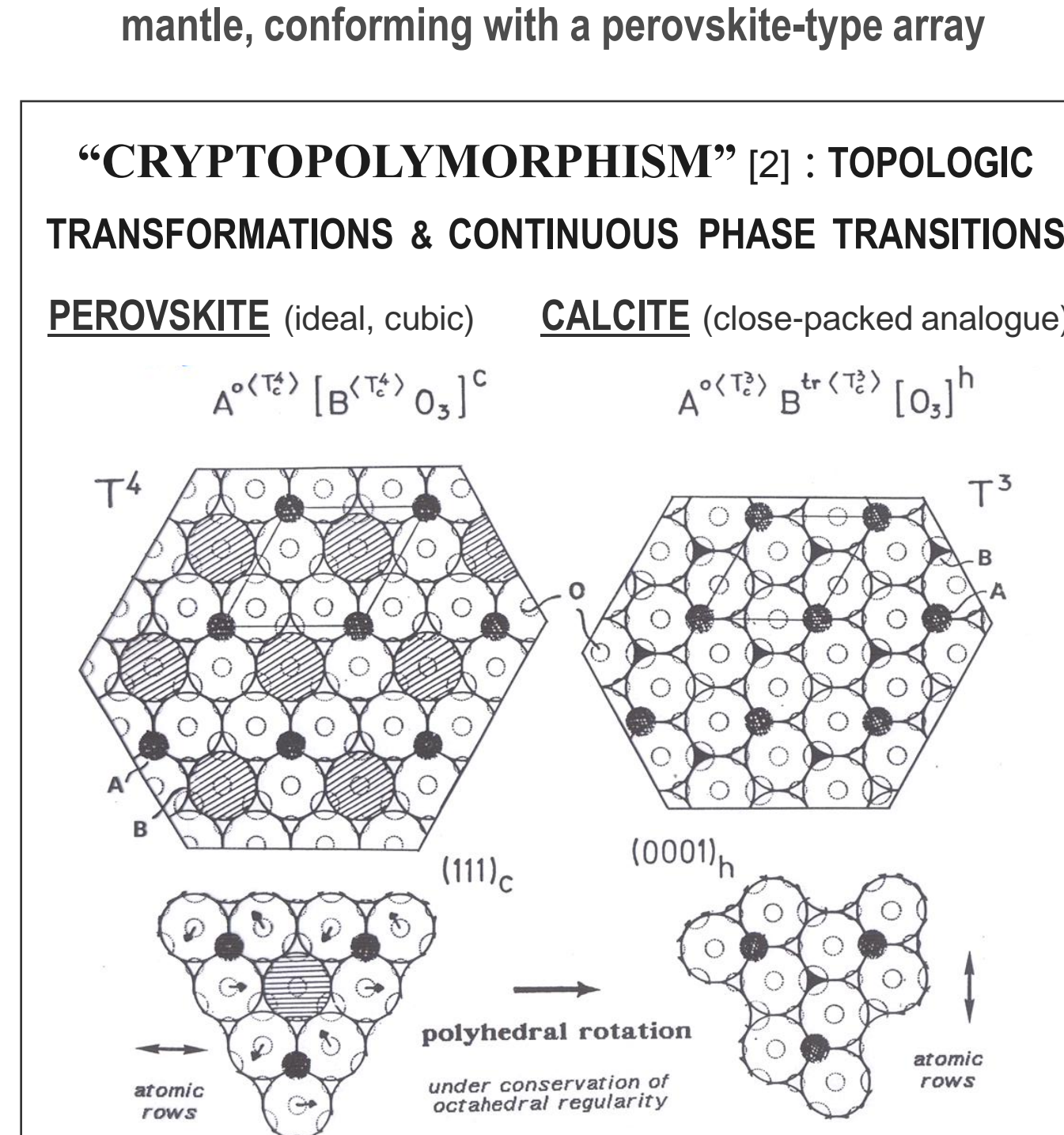
## References

- [1] T.S. DUFFY (2008) Mineralogy at the extremes. *Nature* 451, 269-270.
- [2] M. O. FIGUEIREDO (1994) Mechanisms of structural transformations in minerals and their geological implications. In *Relación entre la estructura y las propiedades de los materiales VI Symp. Grupo Esp. Cristalogr.*, Univ. Pais Vasco, Edts. M.I. Arriortua, J.L. Pizarro & M.K.Urtiaga, Dept.-Legal nº BI-1422-94, pp. 155-169.
- [3] — (1988) The generation of closest packed analogues by polygonal interconversions of plane nets. *Zeit. Krist.* 185, 281 (abstr.).
- [4] T.S. DUFFY (2005) Synchrotron facilities and the study of Earth's deep interior. *Rept. Progr. Phys.* 68, 111.
- [5] Y. ZHAO *et al.* (1994) High pressure crystal chemistry of neighborite,  $NaMgF_3$ . *Amer. Min.* 79, 615-621.
- [6] B. BALZ (1953) Über die Struktur des  $K_2NiF_4$ . *Naturwiss.* 40, 241
- [7] F. RODI & A. BABEL (1965) Ternäre oxide der Übergangsmetalle 4. Erdalkali-Ir (IV)-oxide. Kristallstrukturen von  $CaIrO_3$ . *Zeit. Anorg. Allgem. Chemie* 336, 17-23.
- [8] C. MARTIN *et al.* (2006) Phase transitions and compressibility of  $NaMgF_3$  (neighborite) in perovskite- and post-perovskite-related structures. *Geophys. Res. Letters* 33, L11305.

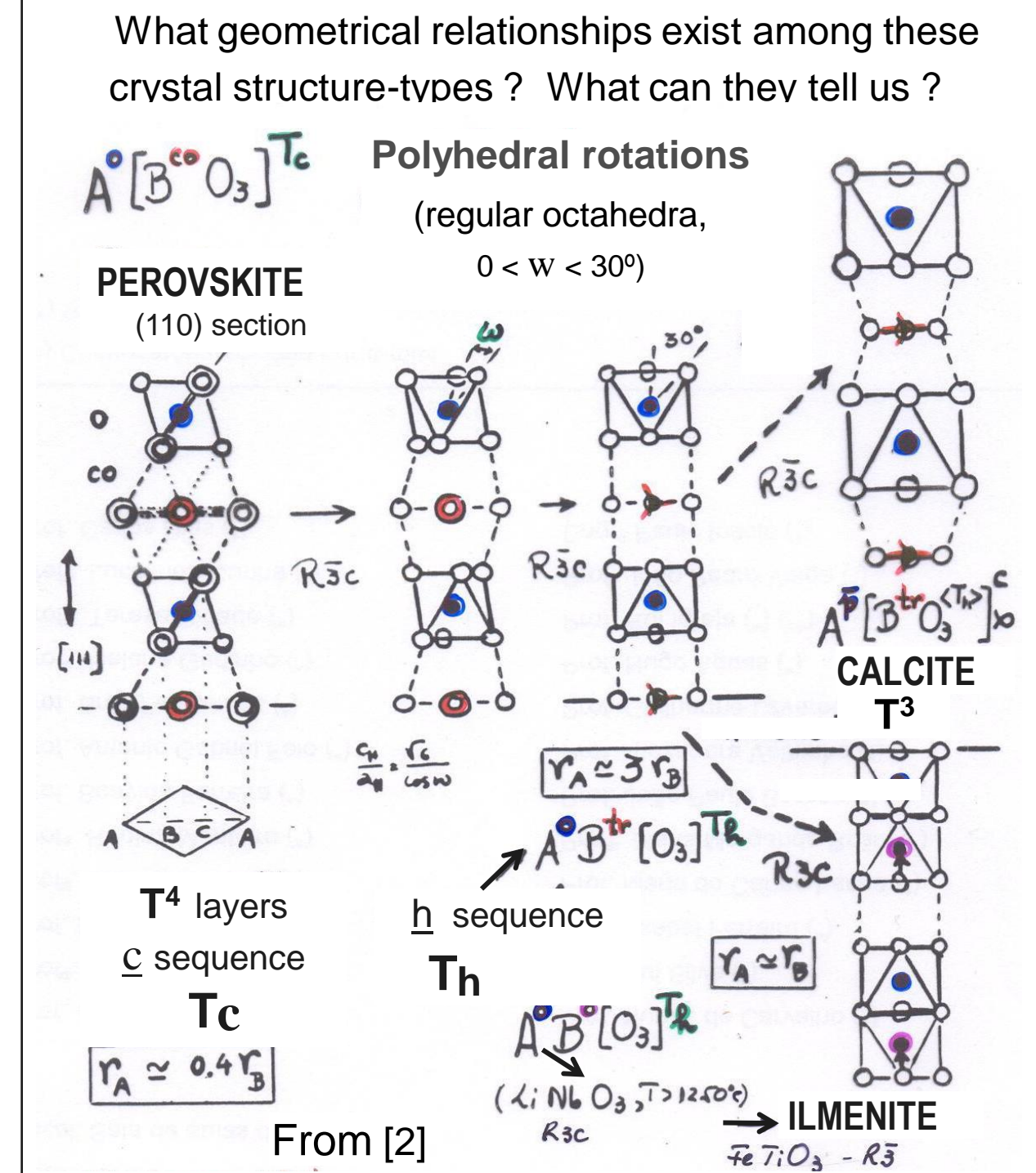
## SHEAR DERIVATIVES FROM CLOSEST PACKINGS: ISOCOMPOSICIONAL CRYSTALLOGRAPHIC SHEAR & $Mg_2SiO_4$ POLYMORPHS [2]



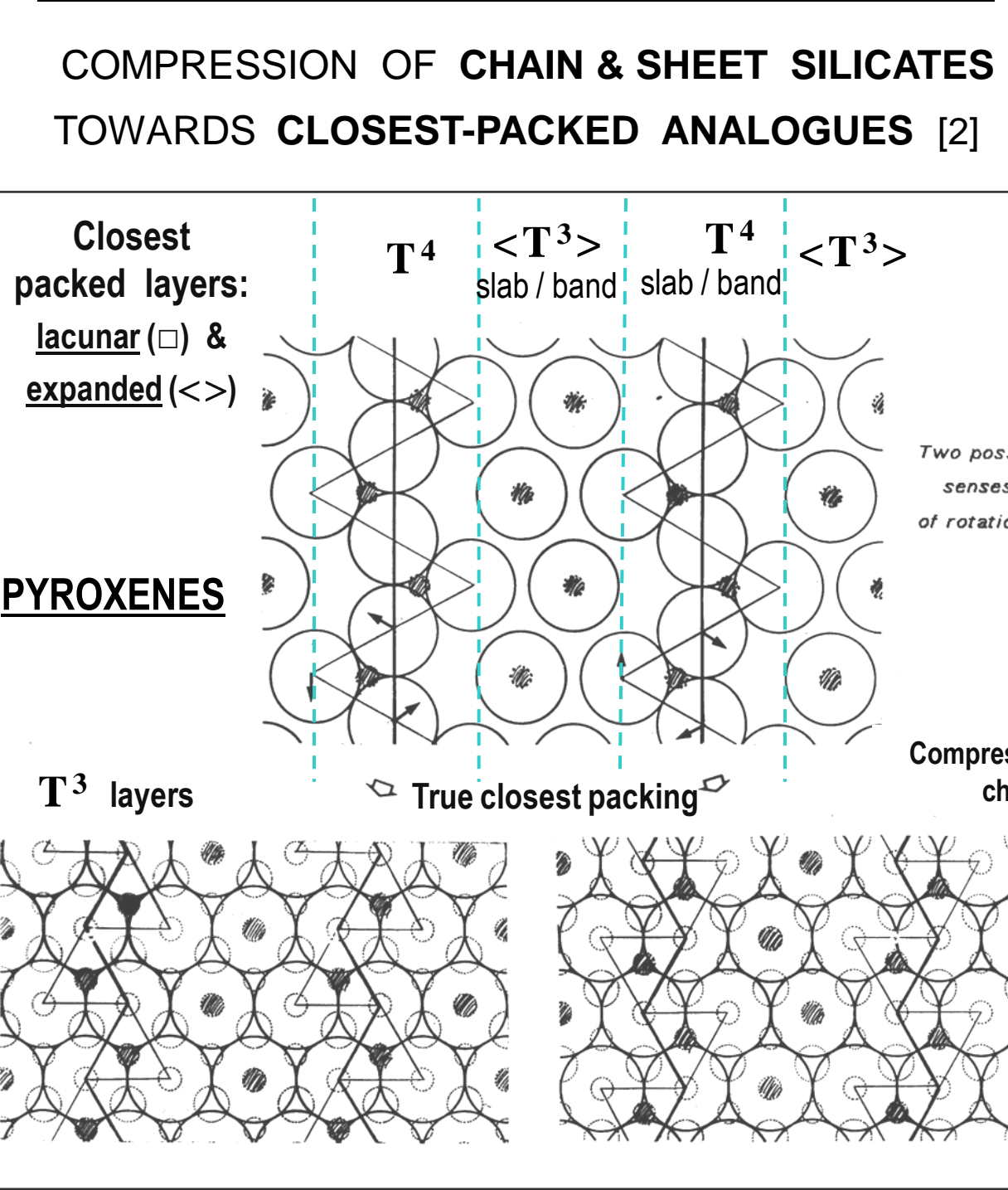
## Unravelling the way carbon is hosted in the inner Earth's mantle, conforming with a perovskite-type array



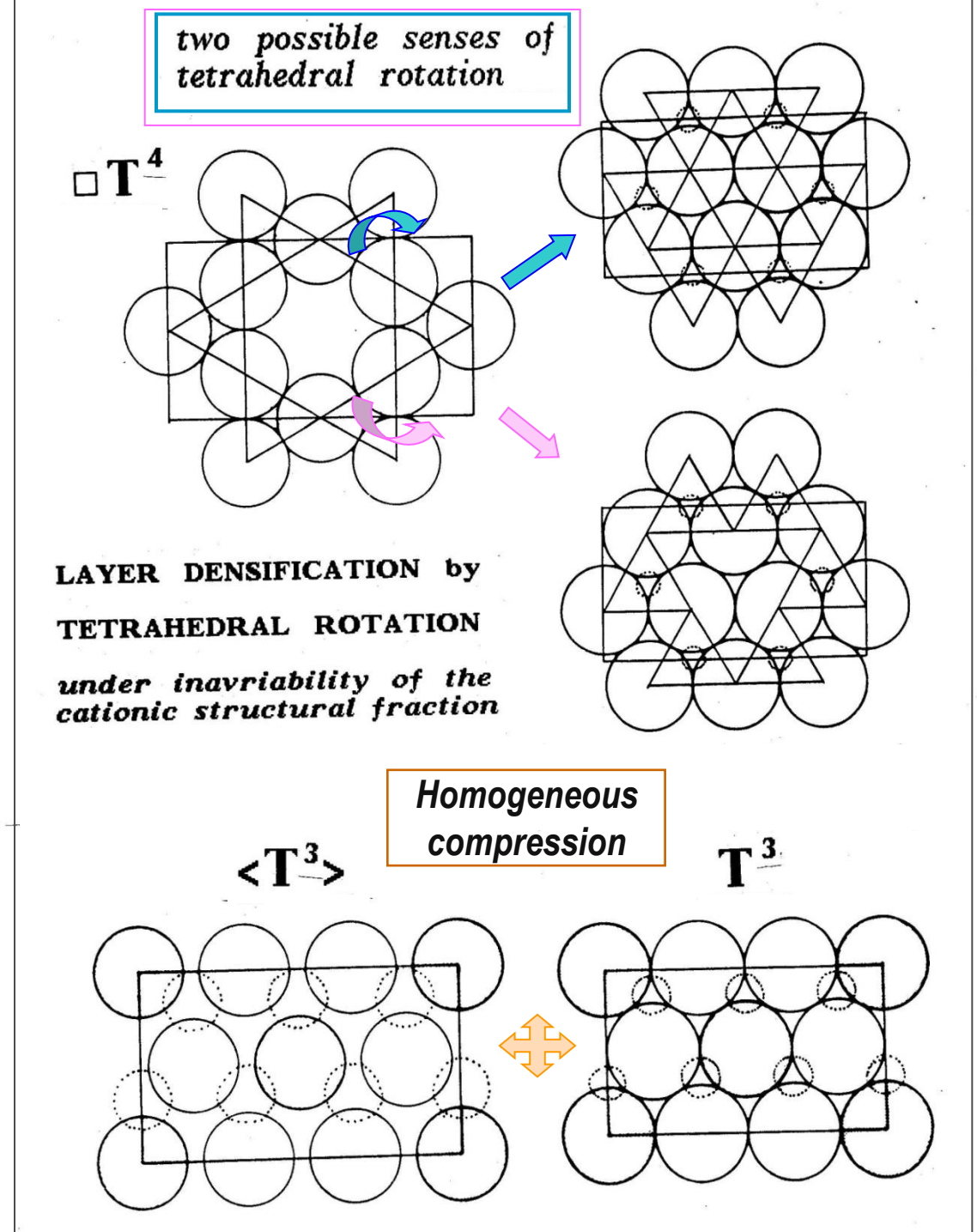
## PEROVSKITE, ILMENITE, CALCITE



## ISO-SYMMETRIC TRANSFORMATIONS



## MICAS & allied PHYLLOSILICATES



## Final comments

This overview unravels motivating prospective issues susceptible of contributing to understand the phase evolution in the earth's interior, namely, the structural compression processes complying to external pressure, along with a suggestion about how carbon may efficiently stay hosted deep in the earth's mantle. The analysis of the bulk cationic array in post-perovskite phases emerges as a potential means of interpreting phase sequences. Furthermore, from the present analysis it becomes clearly opportune to question the very state of matter under the extreme (P,T) conditions of earth's core-mantle boundary.