

**MATTER UNDER PRESSURE :  
DISCOVERING NOVEL CHEMISTRY  
AND NEW MINERALS IN PLANETARY  
INTERIORS**



**ARTEM R. OGANOV**

SWISS FEDERAL INSTITUTE OF TECHNOLOGY, ETH ZURICH

## **Matter Under Pressure : Expectations and Surprises**

The interiors of planets and stars are compressed by gravitational forces. The pressure at the centre of the Earth is 364 GPa, or 3.64 million atmospheres ; pressures at centres of giant planets are one order of magnitude higher. Usually, such pressures are sufficient to induce dramatic changes in the atomic and electronic structure of materials. For instance, iron (the main material of the Earth's core) loses its magnetism at 13 GPa, magnesium silicates (main materials of the Earth's mantle) undergo a sequence of structural changes, whereas fluid hydrogen and water (the major components of giant planets) become metals. In order to understand the structure and evolution of planets, such changes and the resulting properties of strongly compressed planetary matter must be understood.

One expects that under pressure highly symmetrical close-packed structures will be formed, and that, on increasing pressure, insulators will transform into semiconductors and then become metallic. It was a great surprise to find that these trends are not always followed and that many exotic and unexpected phenomena occur at high pressure – such as the breakdown of close packing under pressure, or complex structures of the elements, such as the newly discovered ionic form of boron,  $(B_2)^{0.5+}(B_{12})^{0.5-}$ .

Compressed matter can be studied experimentally, using shock-wave or static compression methods. However, such experiments are very challenging and often results suffer from large uncertainties. Theoretical studies, based on quantum-mechanical simulations, provide an attractive alternative and enable studies that would not be feasible experimentally [1]. Modern techniques, based on density functional theory or quantum Monte Carlo methods, are usually sufficiently accurate and often can be more reliable than today's experiments.

## **Towards a Quantitative Thermal Model of the Earth**

While pressure distribution in the Earth is well known, the distribution of temperature remained essentially unconstrained. Seismic tomography, in principle, allows this distribution to be determined once the

elastic properties of mantle minerals are accurately mapped as a function of temperature. This has been done [1], and resulted in unexpectedly large temperature inhomogeneity in the Earth's mantle. Such huge temperature differences (up to ~2000 K close to the core-mantle boundary region) can be maintained over geological timescales only when thermal conductivity of the mantle is very low and/or when mantle convection is very fast. This model is confirmed by the analysis of location and topography of the D'' layer [2].

### **Exotic Geochemistry of the Earth's Lower Mantle**

Traditionally, it was believed that the Earth's mantle is composed of Mg-silicates with some Fe<sup>2+</sup> impurities. However, recent experiment of D. Frost demonstrated that, instead, in the lower mantle (pressures 24-136 GPa, depths 670-2890 km) Fe<sup>2+</sup> impurities will disproportionate into Fe<sup>3+</sup> impurities and metallic iron :  $3\text{Fe}^{2+} \rightleftharpoons 2\text{Fe}^{3+} + \text{Fe}(\text{metal})$ . The coexistence of fully reduced Fe<sup>0</sup> and fully oxidised Fe<sup>3+</sup> is counterintuitive and initially raised many doubts. However, theoretical calculations [3] fully support this conclusion and provide a detailed microscopic picture of this process. The existence of free metallic iron in the mantle has important geochemical consequences : first, it results in strongly reducing conditions in the mantle. Second, if metallic iron gradually sinks into the core, it can remove a significant part of siderophile elements from the mantle.

Even more surprisingly, there are first experimental indications that xenon (inert gas at normal conditions) becomes chemically reactive under pressure. My group is currently working on this question, and it seems that xenon silicates can be stable at conditions of the Earth's mantle. This would enable xenon to remain in the Earth's interior and could thus explain why the Earth's atmosphere has ~10 times less xenon than expected from geochemical models.

### **Unexpected Mineralogy and Surprising Physics of the Earth's D'' Layer**

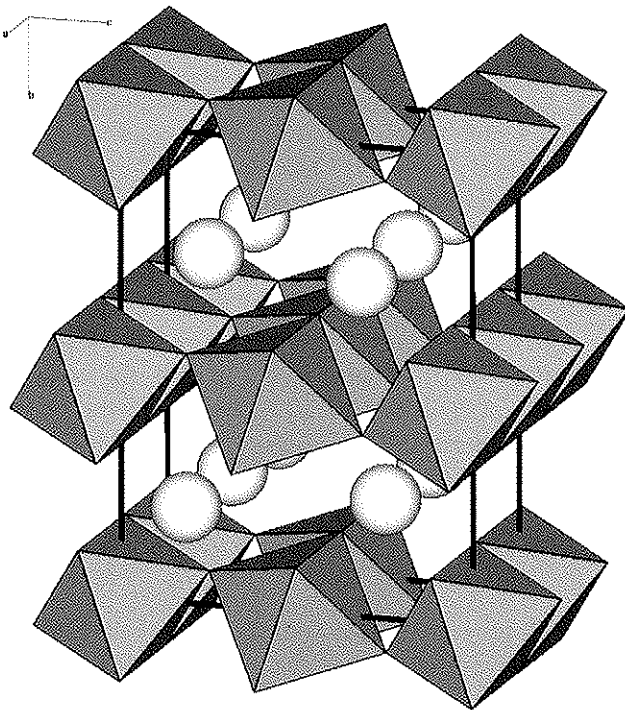
The so called D'' layer (depths from ~2700 to 2890 km) is perhaps the most complex and enigmatic region of the Earth. Seismic observations

had indicated, for a long time, that the thickness of this layer varies considerably : while in some places it is 300 km thick, in others it vanishes. Moreover, peculiar acoustic anisotropy was detected that could not be explained by properties of any known minerals. The key to the understanding of this complex layer of the Earth came from experiments of S. Ono [4], who found a new phase of  $\text{Fe}_2\text{O}_3$ , solved its structure and proposed that it might become stable also for  $\text{MgSiO}_3$ . This surprising suggestion was confirmed several months later [5,6] and had an enormous resonance among Earth scientists. The new phase of  $\text{MgSiO}_3$  has been named post-perovskite ; it is stable at pressures above 100 GPa, and its stability conditions correspond to the pressure(depth)/temperature of the D'' layer where the new mineral is thought to comprise ~70-80 volume percent. Post-perovskite has a peculiar layered structure (Fig. 1). Its calculated physical properties are quite unusual, but provide a close match to the observed properties of the D'' layer [5,7].

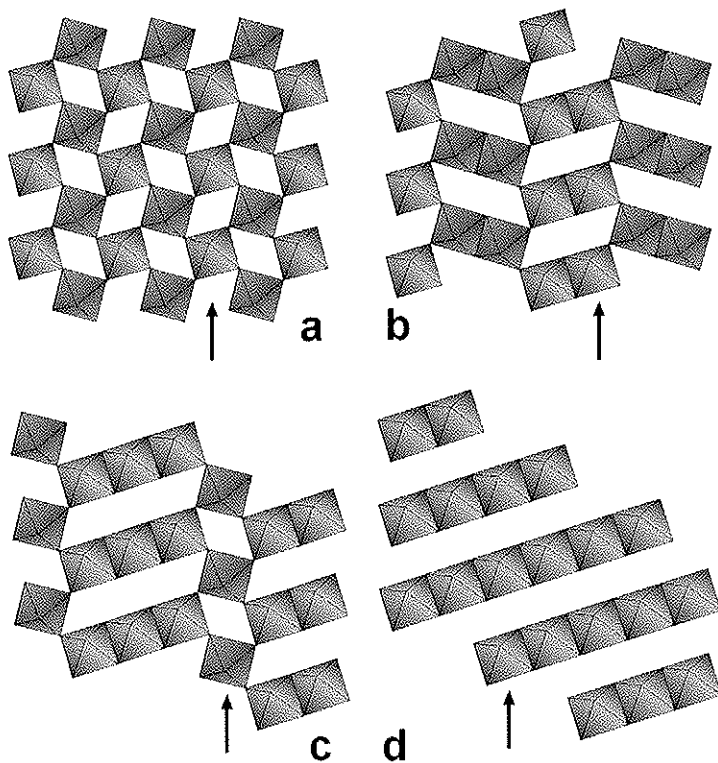
Based on the knowledge of physical properties and stability field of post-perovskite, a number of important conclusions have been made. First, post-perovskite and the D'' layer can only exist in large rocky planets – e.g. the Earth, perhaps Venus, but not smaller Mercury or Mars [5]. Second, we have predicted [5] that as the Earth cools down with time, post-perovskite D'' layer increases in thickness, i.e. grows. One can even estimate the age of the D'' layer, but the existing estimates vary widely. Third, post-perovskite has been inferred to have a high ionic conductivity [8], which might explain the observed slight periodic variations of the length of day by coupling between the Earth's magnetic field and electrically conducting D'' layer. Fourth, the existence of the post-perovskite layer should enhance dynamics of the Earth's mantle. One can expect an increase of tectonic activity of the Earth at the time when the D'' layer began to be formed.

A number of high-pressure phases with the same structure as post-perovskite have been reported. One of the most interesting cases is  $\text{Al}_2\text{O}_3$  [8] ; this system is one of clear examples of breakdown of close packing under pressure : at 0 GPa this material has a close-packed structure, but there is no geometric close packing in the high-pressure post-

perovskite form (which, nevertheless, is significantly denser). Here, nature clearly goes against simple crystallographic expectations. Another unexpected aspect is the existence of an infinite series of polytypes, with structures intermediate between perovskite and post-perovskite (Fig. 2). These are important for understanding the mechanism of plastic deformation of perovskite and post-perovskite, and the mechanism of their transformations one into another. In addition, these phases are only marginally metastable and can be stabilised by impurities and be stable minerals in the Earth's mantle. There is experimental evidence (O. Tschauner, personal communication) confirming this prediction. The predicted [7] (and more recently confirmed by several experimental studies) mechanism of plastic deformation of post-perovskite is crucial for explaining the observed acoustic anisotropy of the D'' layer.



**Fig. 1.** Crystal structure of  $\text{MgSiO}_3$  post-perovskite (after [5]). The structure contains layers of  $\text{SiO}_4$ -octahedra and Mg atoms (spheres) between them.



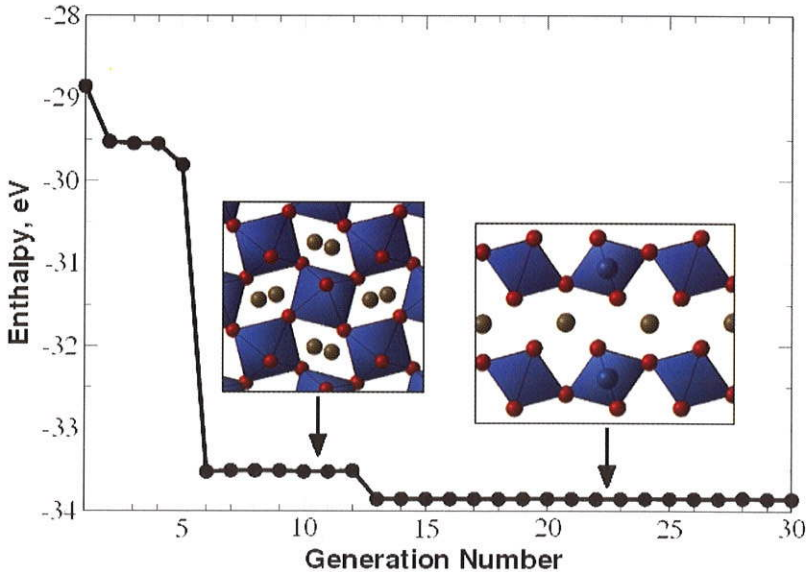
**Fig. 2.**  $\text{MgSiO}_3$  polytypes (after [7]) : a) perovskite (space group  $Pbnm$ ), d – post-perovskite ( $Cmcm$ ), b,c – predicted intermediate structures  $2 \times 2$  ( $Pbnm$ ) and  $3 \times 1$  ( $P2_1/m$ ), respectively. Only silicate octahedra are shown ; Mg atoms are omitted for clarity. These structures can be transformed one into another by plane sliding along the direction of the arrows.

## Crystal Structure Prediction : Breakthrough in Computational Materials design and Studies of Matter at High Pressure

Crystal structure is the greatest bearer of information on a compound. If one could predict the stable structure given just the chemical formula and  $P$ - $T$  conditions, it would greatly facilitate materials design and studies of materials under pressure (including planetary materials). However, this task has been traditionally viewed as impossible. As J. Maddox put it, “*One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of*

even the simplest crystalline solids from a knowledge of their chemical composition” [9].

Since 2004, I worked on solving this issue together with my exceptionally talented student Colin W. Glass. We have been able to develop a very powerful evolutionary method [10-12] that essentially solves the crystal structure prediction problem. We named our method (and code) USPEX, which stands for “Universal Structure Predictor : Evolutionary Xtallography”. Numerous tests have shown that the method has a nearly perfect success rate and structure search is so efficient that it can be routinely used in a purely *ab initio* framework. Fig. 3 illustrates the performance of this method.

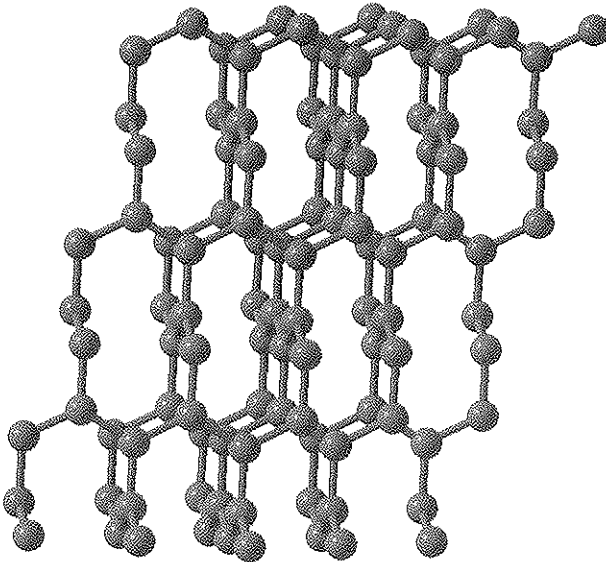


**Fig. 3.** Illustration of evolutionary crystal structure prediction (from [12]) for  $\text{MgSiO}_3$  at 120 GPa. The lowest enthalpy in each generation is shown as a function of generation. Structures of the first generation are random and have high enthalpies, but after 5 generations the perovskite structure is found, and 6 generations later the stable post-perovskite structure is produced.

With this method, a number of new phases have been predicted – including a new stable high-pressure phase of sulphur [12] and two

new high-pressure phases of  $\text{CaCO}_3$  [10], likely hosts of carbon in the Earth. We furthermore predicted [12] a new metastable phase of carbon at atmospheric pressure (Fig. 4). Bonds in this structure are as strong as in graphite (~30 % stronger than in diamond), but unlike in graphite these bonds form a 3D-framework making this structure potentially harder than diamond.

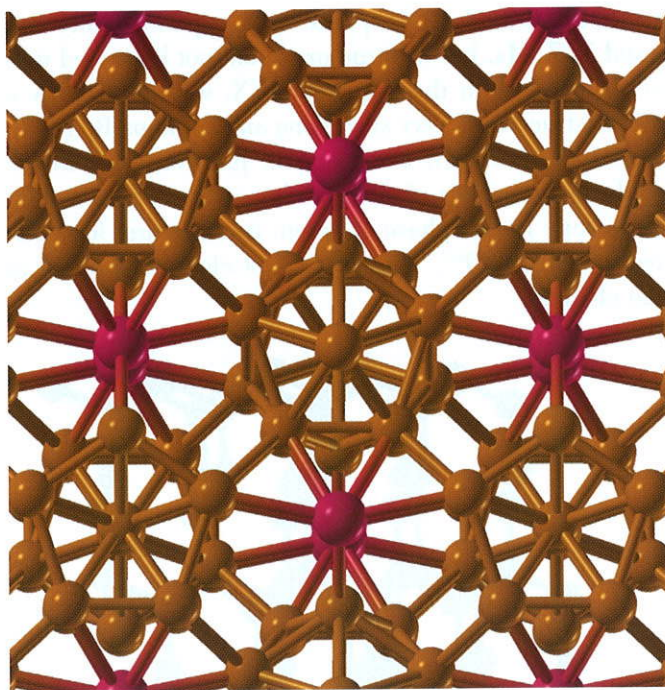
Another interesting recent result is the discovery, made jointly by theory and experiment, of a new high-pressure phase of boron (Oganov *et al.*, submitted). Initially, this phase was experimentally found by J. Chen and Y.-Z. Ma, but its structure could not be solved using only experimental data. With the use of USPEX, we could easily solve it (Fig. 5). This structure is very surprising and contains  $\text{B}_2$  and  $\text{B}_{12}$  clusters in a 3D-checkerboard arrangement, just like ions in the NaCl structure. In fact, analysis of electron density distribution shows considerable ionicity in this phase of boron, its structural formula should be written as  $(\text{B}_2)^{0.5+}(\text{B}_{12})^{0.5-}$ . This is the first clear example of an ionic form of an element.



**Fig. 4.** Newly predicted metastable structure of carbon at 1 atm. This material is likely to be harder than diamond and should be possible to synthesize.



Using USPEX, we are now systematically exploring the behaviour of elements, compounds and minerals under pressure. Such studies are laying the foundation for the understanding of planetary interiors and for a deeper understanding of chemical bonding and its response to pressure. One should expect that USPEX methodology will find application not only in high-pressure crystallography, but also in computational materials design. There is no doubt that most materials of the future will be designed using this powerful methodology.



**Fig. 5.** Structure of the newly discovered ionic high-pressure phase of boron. *Magenta* -  $B_2$ , *orange* -  $B_{12}$  sublattices.

**Acknowledgments :** I am very grateful to my collaborators, especially C.W. Glass, S. Ono, F. Zhang, D.Y. Jung, G.D. Price, R. Martonak, Y.-M. Ma, J. Chen, Y.-Z. Ma, D. Adams. This work was supported by Swiss National Science Foundation (grant 200021-111847/1), ETH Zurich (grants TH-27033 and TH-32043) and CSCS (Manno).

## References :

- [1] Oganov A.R., Brodholt J.P., Price G.D. (2001). The elastic constants of  $\text{MgSiO}_3$  perovskite at pressures and temperatures of the Earth's mantle. *Nature* **411**, 934-937.
- [2] Ono S. & Oganov A.R. (2005). *In situ* observations of phase transition between perovskite and  $\text{CaIrO}_3$ -type phase in  $\text{MgSiO}_3$  and pyrolytic mantle composition. *Earth Planet. Sci. Lett.* **236**, 914-932.
- [3] Zhang F., Oganov A.R. (2006). Valence and spin states of iron impurities in mantle-forming silicates. *Earth Planet. Sci. Lett.* **249**, 436-443.
- [4] Ono S., Kikegawa T., Ohishi Y. (2004). High-pressure phase transition of hematite,  $\text{Fe}_2\text{O}_3$ . *J. Phys. Chem. Solids* **65**, 1527-1530.
- [5] Oganov A.R. & Ono S. (2004). Theoretical and experimental evidence for a post-perovskite phase of  $\text{MgSiO}_3$  in Earth's D'' layer. *Nature* **430**, 445-448.
- [6] Murakami M., Hirose K., Kawamura K., Sata N., Ohishi Y. (2004). Post-perovskite phase transition in  $\text{MgSiO}_3$ . *Science* **304**, 855-858.
- [7] Oganov A.R., Martoňák R., Laio A., Raiteri P., Parrinello M. (2005). Anisotropy of Earth's D'' layer and stacking faults in the  $\text{MgSiO}_3$  post-perovskite phase. *Nature* **438**, 1142-1144.
- [8] Oganov A.R., Ono S. (2005). The high pressure phase of alumina and implications for Earth's D'' layer. *Proc. Natl. Acad. Sci.* **102**, 10828-10831.
- [9] Maddox J. (1988). Crystals from first principles. *Nature* **335**, 201.
- [10] Oganov A.R., Glass C.W., Ono S. (2006). High-pressure phases of  $\text{CaCO}_3$ : crystal structure prediction and experiment. *Earth Planet. Sci. Lett.* **241**, 95-103.
- [11] Glass C.W., Oganov A.R., Hansen N. (2006). USPEX – evolutionary crystal structure prediction. *Comp. Phys. Comm.* **175**, 713-720.
- [12] Oganov A.R., Glass C.W. (2006). Crystal structure prediction using evolutionary techniques: principles and applications. *J. Chem. Phys.* **124**, art. 244704.