Crystal structure prediction as a tool to probe planetary interiors

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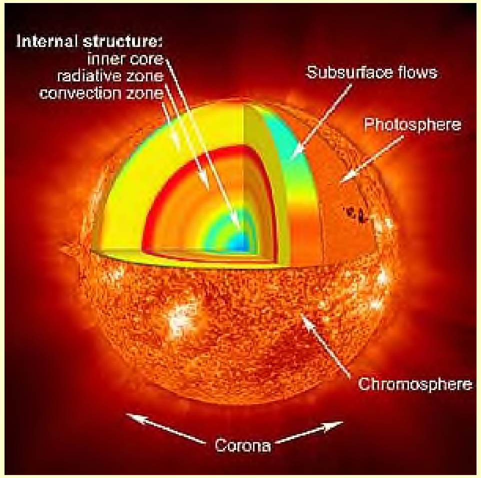
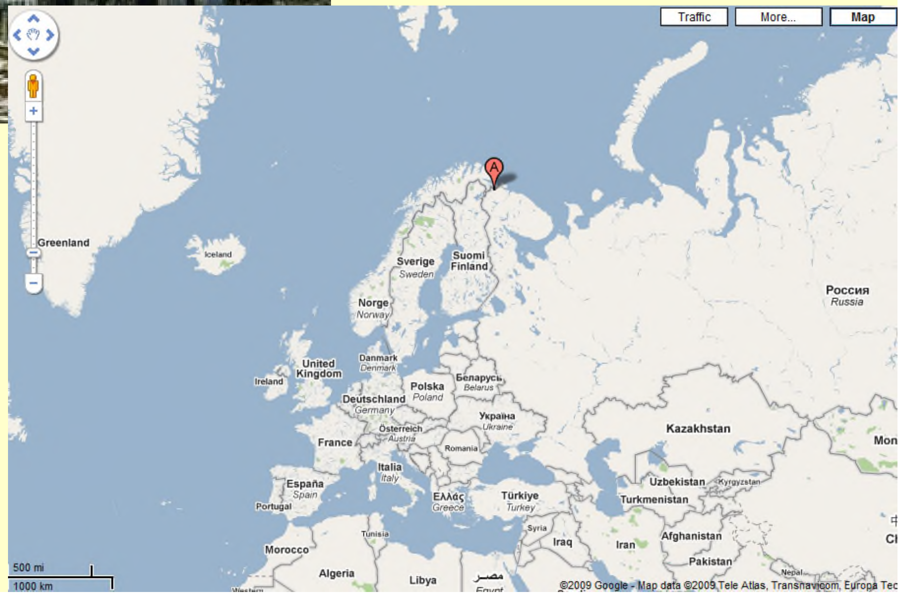
What is the Earth made of?



Model based on non-volatile part of the solar photosphere and CI chondrites

Element	Universe	Earth	Earth's crust	Earth's mantle
O	20.10	3.73	2.9	3.68
Mg	1.08	1.06	0.09	1.24
Al	0.08	0.09	0.36	0.12
Si	1	1	1	1
Fe	0.9	0.9	0.11	0.16

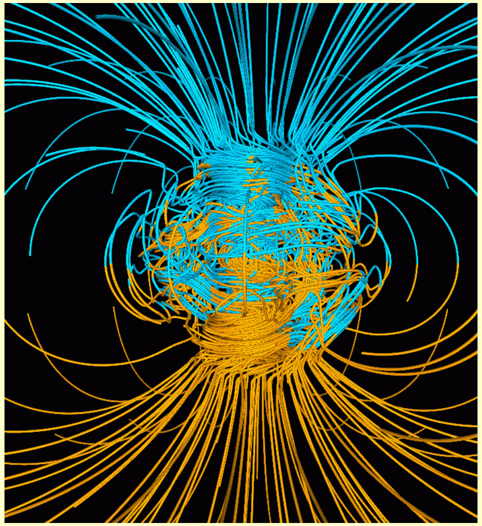
Earth's radius = 6371 km. The deepest borehole – Kola Superdeep (12.3 km), less than 1/500 of the Earth's radius...



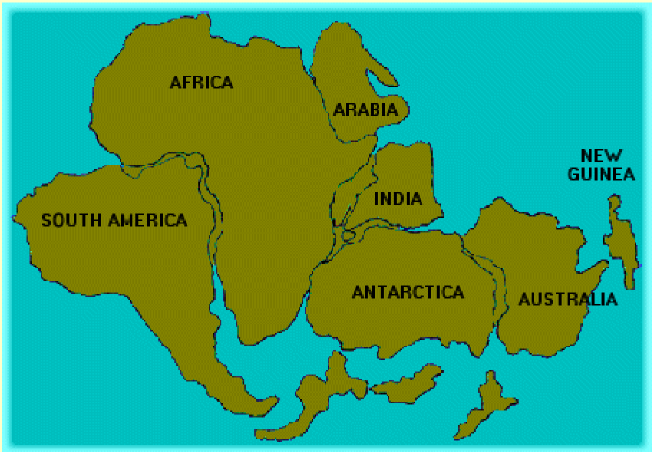
Earth's interior matters

Earthquakes

Volcanism

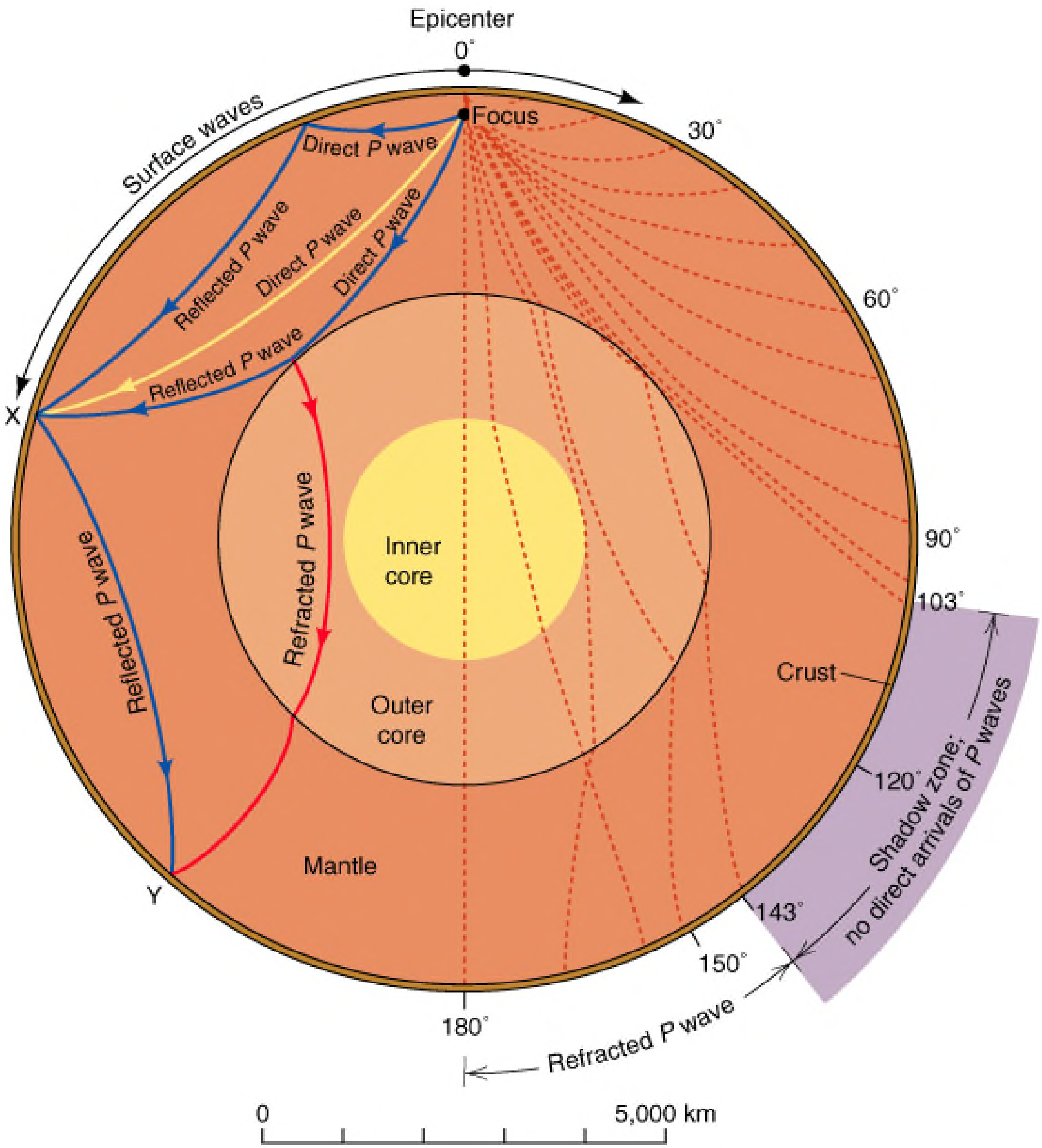


Magnetic field – generated in the core, protects life from solar wind



Continental drift

Earth's interior cannot be probed directly, we rely on seismology and mineral physics



1906: Oldham discovers liquid core.

1914: Guthenber determines depth of core-mantle boundary

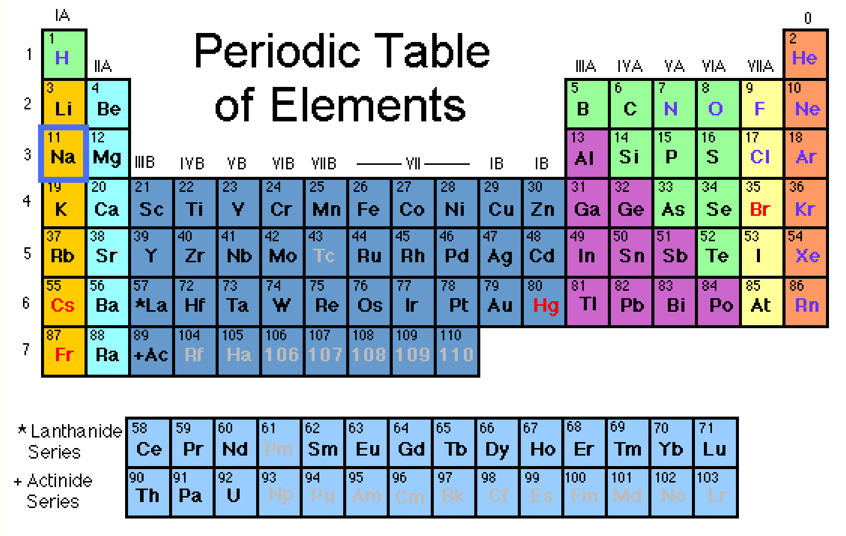
1936: Lehmann discovers solid inner core

1981: Dziewonski creates reference Earth model

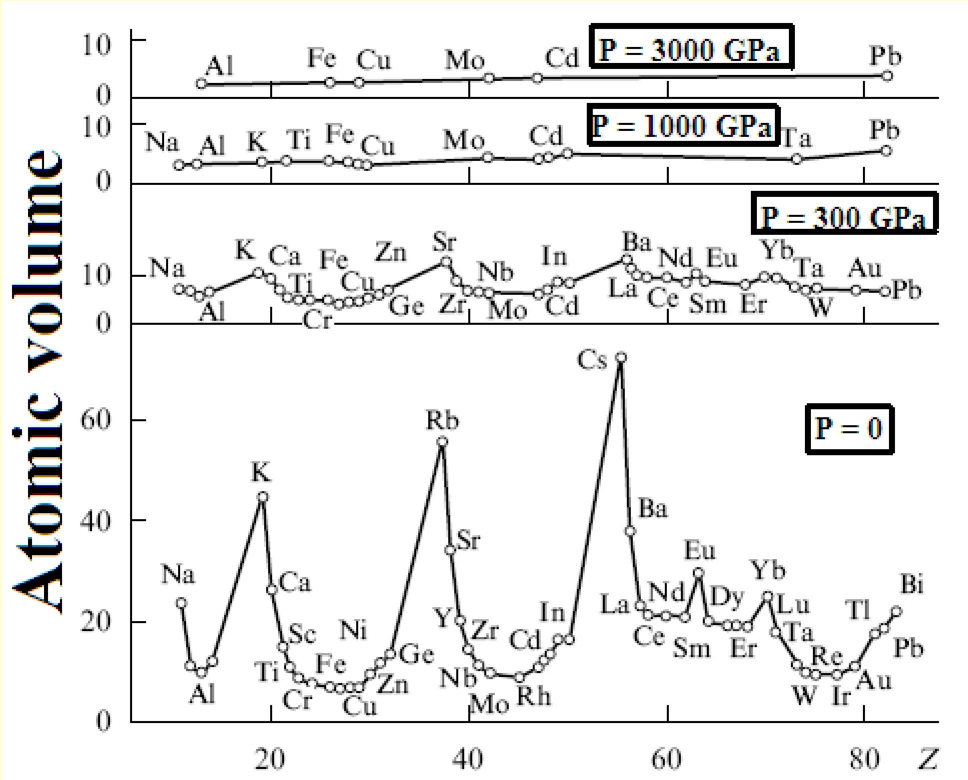
2002-2003: Discovery of the innermost core (Ishii, Beghein)

Pressure in Earth's center = 364 Gpa, temperature ~6000 K.

Chemistry fundamentally changes under pressure

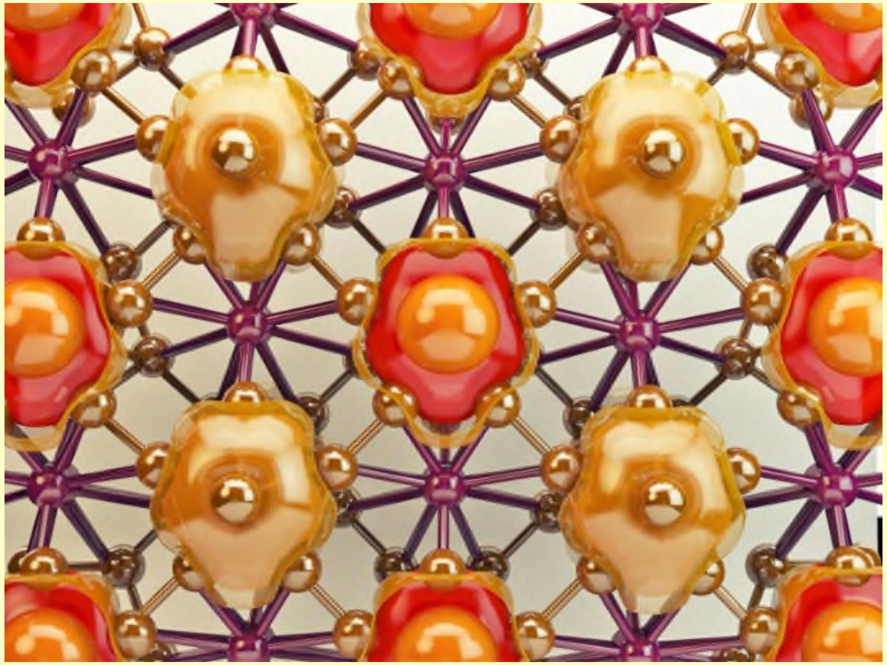


At 100 GPa oxygen becomes a superconductor!

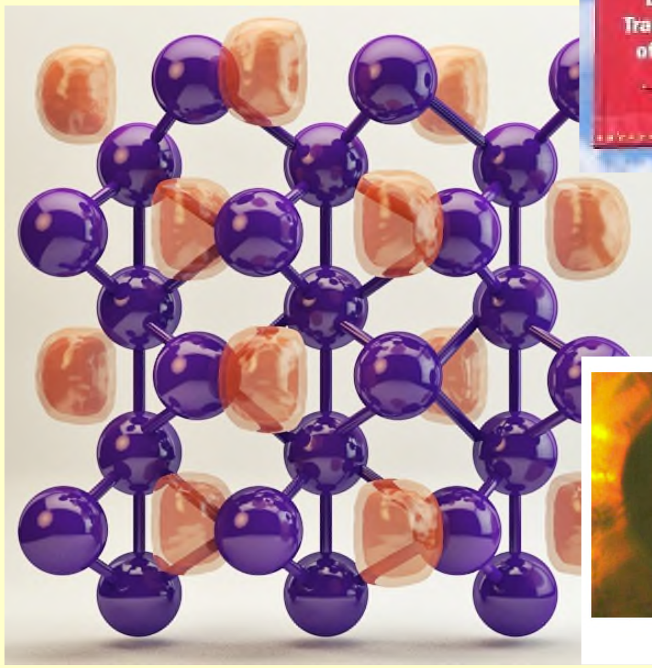


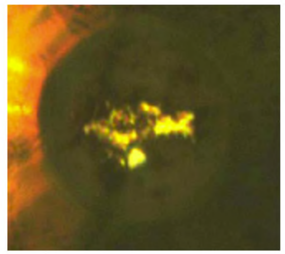
Periodic Law disappears at ultrahigh Pressures (Al'tshuler, 1999)

Novel chemistry of the elements under pressure



New superhard structure of boron
(Oganov et al., *Nature*, 2009)





199 GPa

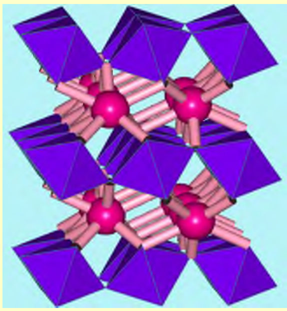
High-pressure transparent
allotrope of sodium
(Ma & Oganov, *Nature*, 2009)

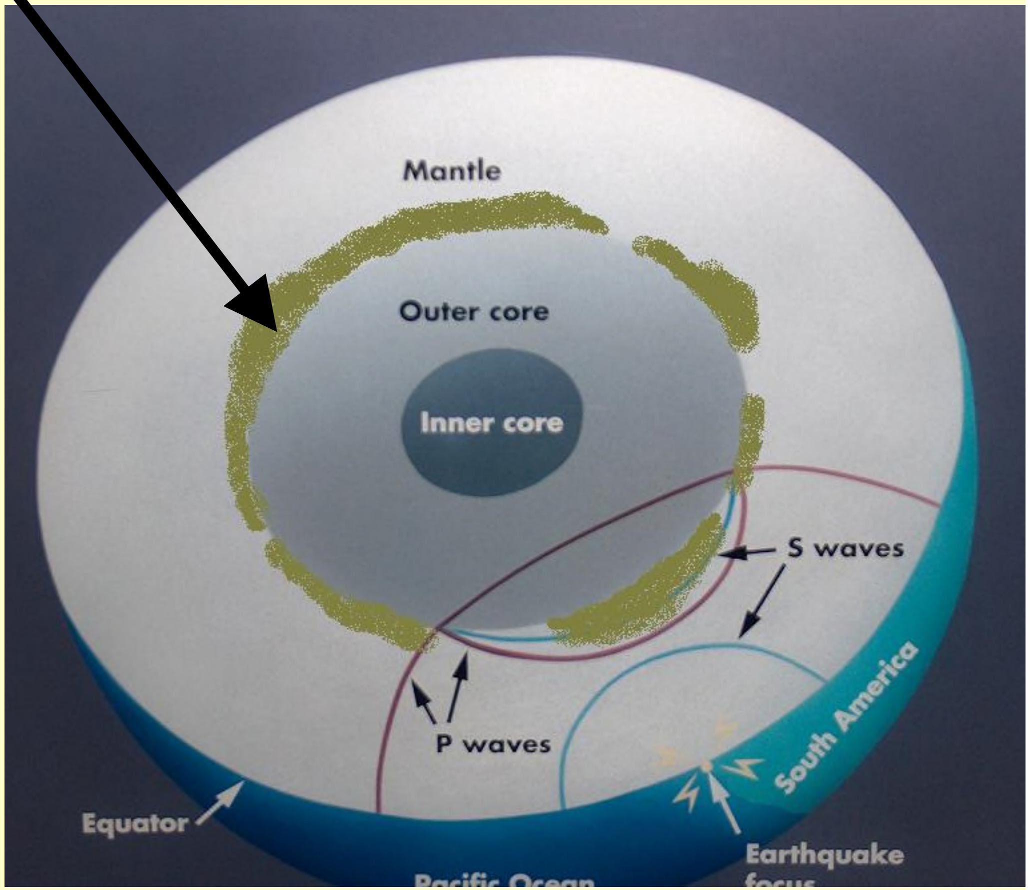
Properties of D" layer (2700-2890 km) were explained by $MgSiO_3$ post-perovskite

D" – root of hot spots

$MgSiO_3$ makes ~75 vol.% of lower mantle

Anomalies of D":
seismic discontinuity,
anisotropy





Discovery of post-perovskite has motivated us to develop crystal structure prediction

Post-Perovskite Phase Transition in $MgSiO_3$

Motohiko Murakami,[1*] Kei Hirose,[1*] Katsuyuki Kawamura,[1] Nagayoshi Sata,[2] Yasuo Ohishi[3]

22 January 2004; accepted 29 March 2004

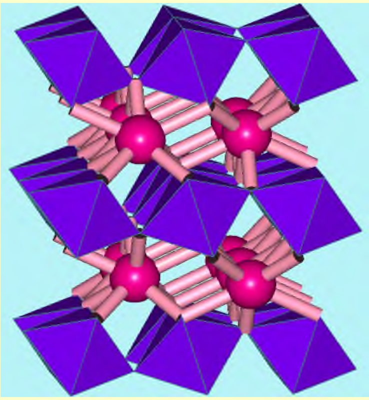
www.sciencemag.org SCIENCE VOL 304 7 MAY 2004 855

Theoretical and experimental evidence for a post-perovskite phase of $MgSiO_3$ in Earth's D″ layer

Artem R. Oganov[1] & Shigeaki Ono[2]

NATURE | VOL 430 | 22 JULY 2004 | www.nature.com/nature 445

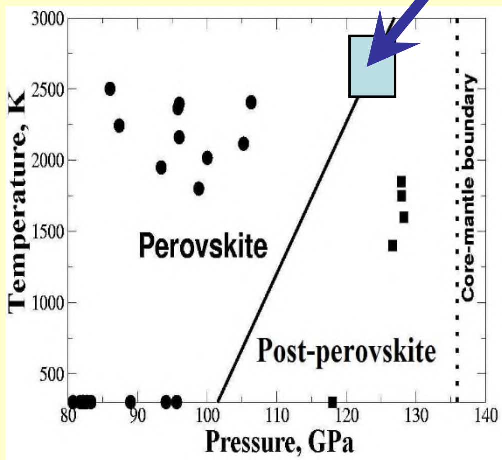
Received 24 March; accepted 27 May 2004; doi:10.1038/nature02701.



$MgSiO_3$
пост-перовскит

Phase diagram of $MgSiO_3$

D" discontinuity

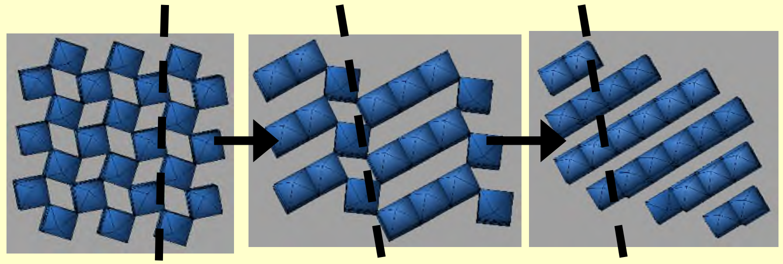


Explains existence of D", allows to determine its temperature. Explains variations of its thickness. Explains variations of the length of day. Predicts that D" grows with time as Earth cools down.

nature Vol 438|22/29 December 2005|doi:10.1038/nature04439

Anisotropy of Earth's D″ layer and stacking faults in the $MgSiO_3$ post-perovskite phase

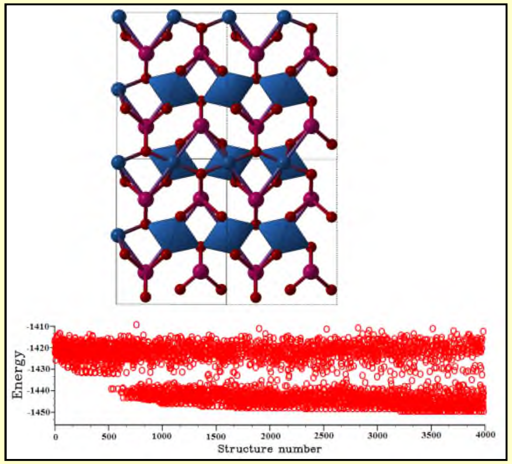
Artem R. Oganov[1], Roman Martoňák[2], Alessandro Laio[2], Paolo Raiteri[2] & Michele Parrinello[2]



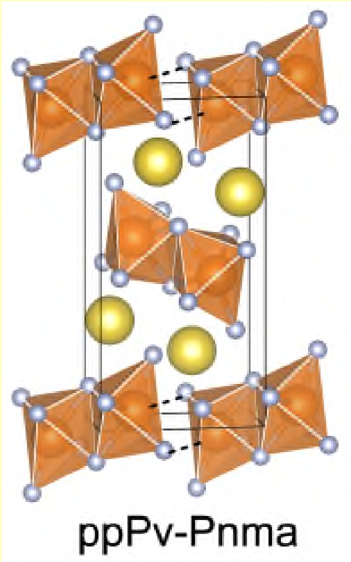
Predicted a new family of minerals.

Confirmation – Tschauner (2008)

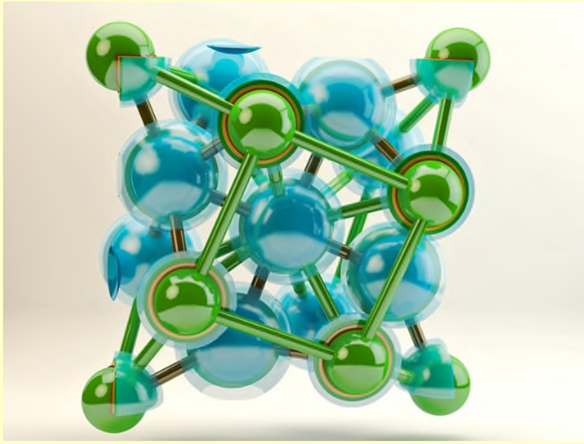
With novel predictive methods, we get a powerful tool to look inside the planets



1. Predicting crystal structures by evolution



2. Predicting planetary mineralogy



3. Predicting planetary chemistry

Acc. Chem. Res. **1994**, *27*, 309−314

Are Crystal Structures Predictable?

ANGELO GAVEZZOTTI*

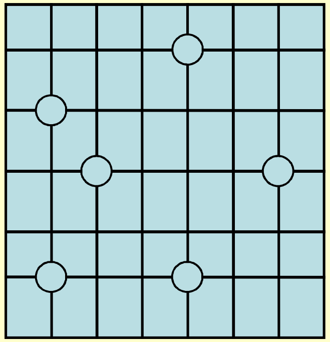
"No": by just writing down this concise statement, in what would be the first one-word paper in the chemical literature, one could safely summarize the present state of affairs

J. Maddox (*Nature*, 1988)

Need to find GLOBAL energy minimum.

Trying all structures is impossible:

$$C = \frac{1}{(V/\delta^3)} \frac{(V/\delta^3)!}{[(V/\delta^3) - N]!N!}$$



N_{atoms}	Variants	CPU time
1	**1**	**1 sec.**
10	**10^{11}**	**10^{3} yrs.**
20	**10^{25}**	**10^{17} yrs.**
30	**10^{39}**	**10^{31} yrs.**

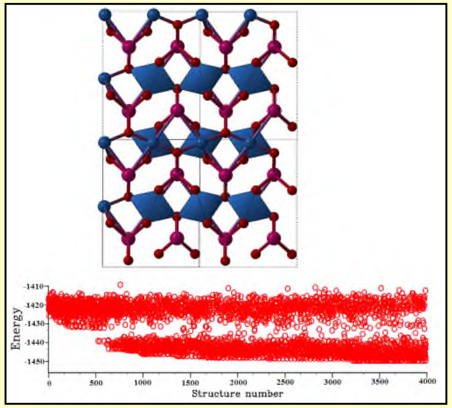
RESEARCH NEWS

Crystal structure prediction – evolutionary or revolutionary crystallography?

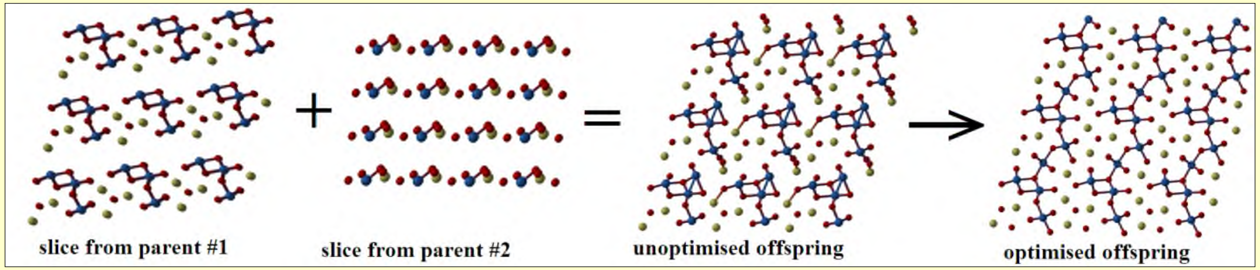
S. L. Chaplot and K. R. Rao   CURRENT SCIENCE, VOL. 91, NO. 11, 10 DECEMBER 2006

Overview of USPEX (Oganov & Glass, *J.Chem.Phys.* 2006)

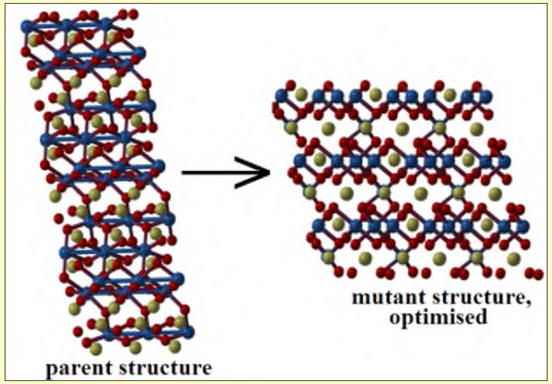
USPEX
(Universal Structure Predictor: Evolutionary Xtallography)



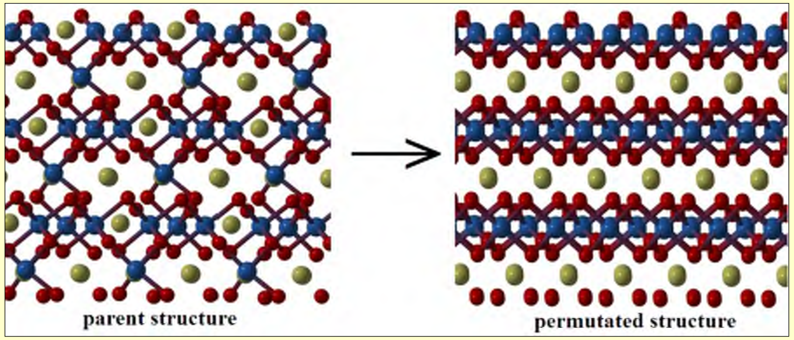
- (Random) initial population
- Evaluate structures by relaxed (free) energy
- Select lowest-energy structures as parents for new generation
- Standard variation operators:



(1) Heredity (crossover)

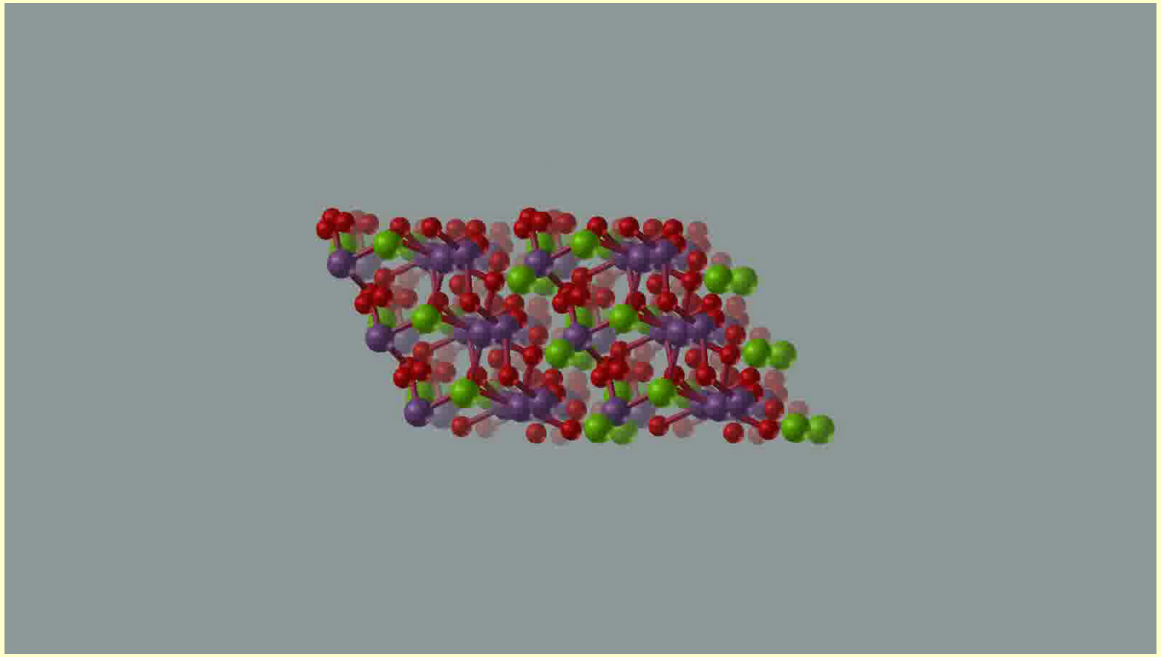


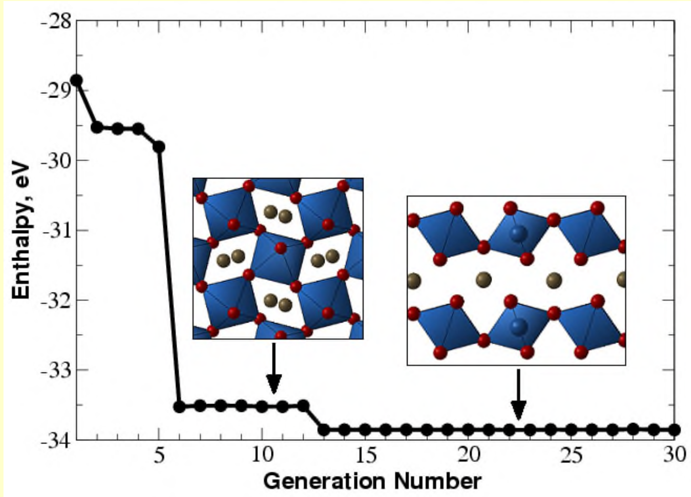
(2) Lattice mutation



(3) Permutation

Test: $MgSiO_3$ at 120 GPa



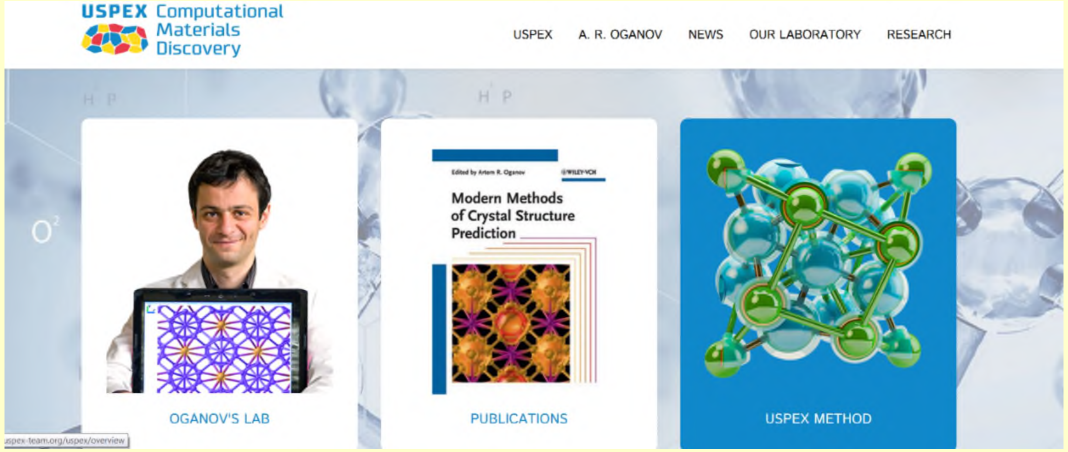


<u>120 GPa:</u> post-perovskite is stable

[Oganov & Glass, J.Chem.Phys. 2006]

The USPEX
(Universal Structure Prediction: Evolutionary Xtallography) project

http://uspex.stonybrook.edu

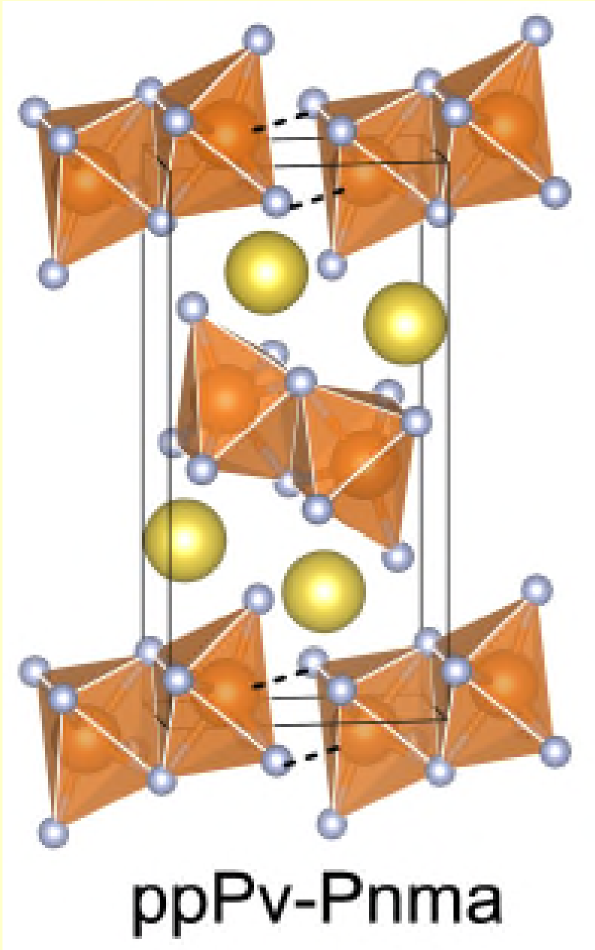


- The most popular code for computational materials design in the world (>2700 users from 77 countries).
- Effort of ~60 man-years.
- >300 publications, 5 patents.
- Licenses bought by Sony, Toyota, Intel, Fujutsu.

- Universal:

-prediction of stable structure AND composition, 3D, 2D, 1D, 0D – systems.
-optimization of physical properties,
-prediction of phase transition mechanisms

2. Predicting planetary mineralogy



With USPEX, discovered a universal *Pnma* post-post-perovskite structure (Xu et al., PRB 2015)

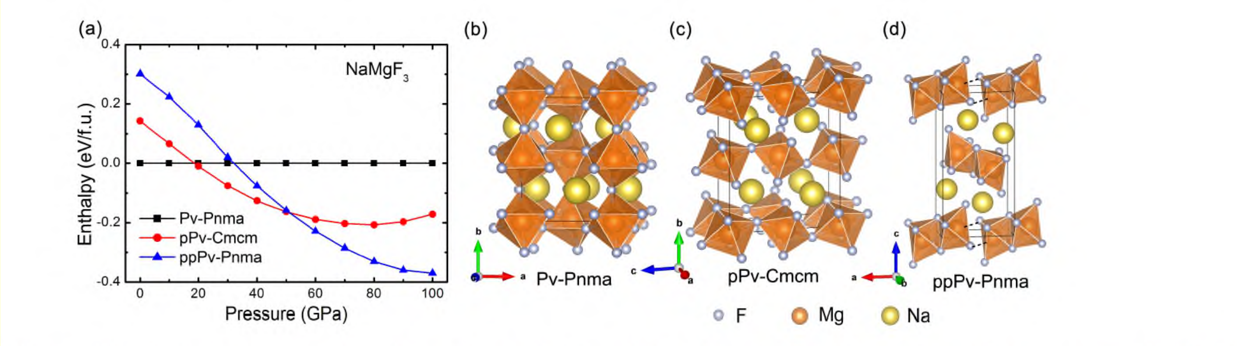
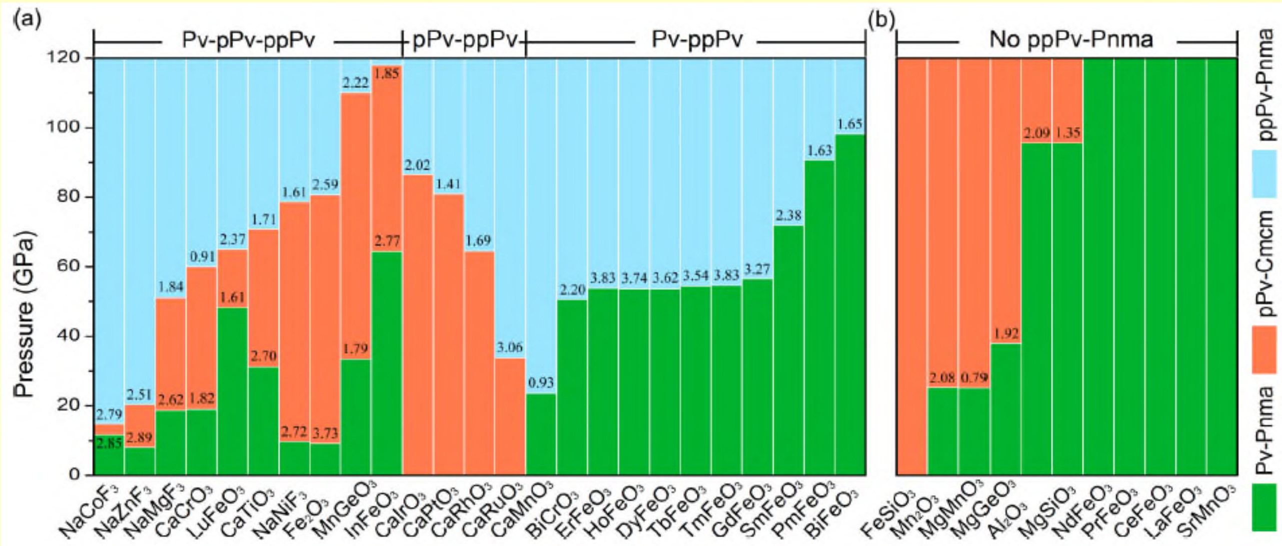


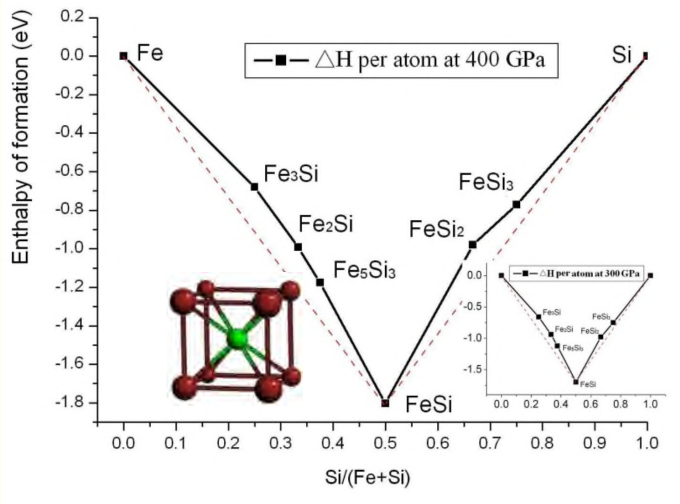
FIG. 2: (Color online). Pressure dependence of the enthalpy of the Pv-$Pnma$, pPv-$Cmcm$ and ppPv-$Pnma$ phases of $NaMgF_3$ (Panel (a)), along with the schematization of (b) the Pv-$Pnma$, (c) pPv-$Cmcm$ and (c) and (d) ppPv-$Pnma$ crystallographic structures. Note that the enthalpy of the Pv-$Pnma$ phase has been set to be zero for any pressure in Panel (a).

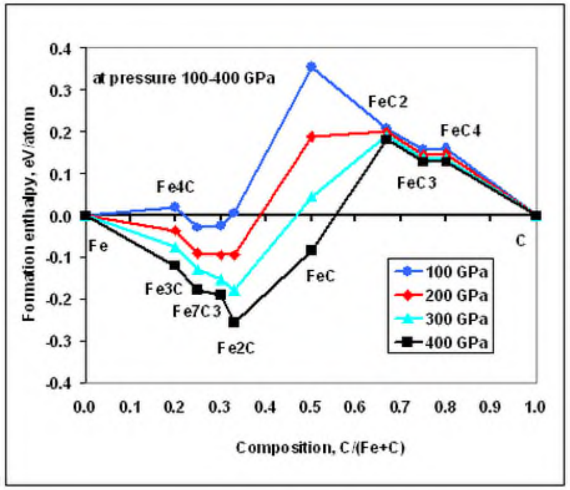
$NaMgF_3$ post-post-perovskite and its stability for $NaMgF_3$. Independently discovered by Crichton (2015) using experiment

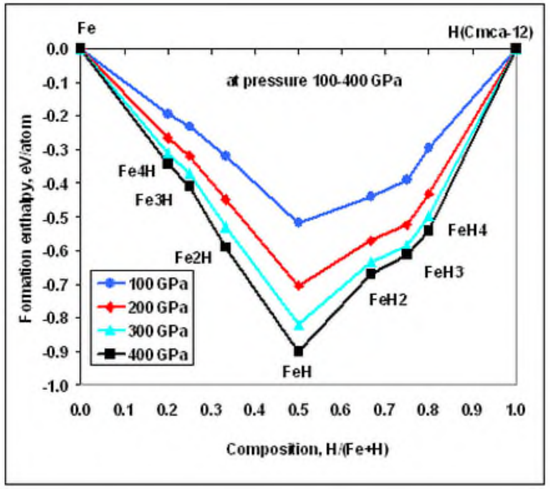


Pressure ranges of stability of perovskite, post-perovskite and post-post-perovskite

What is the chemistry of the Earth's core?

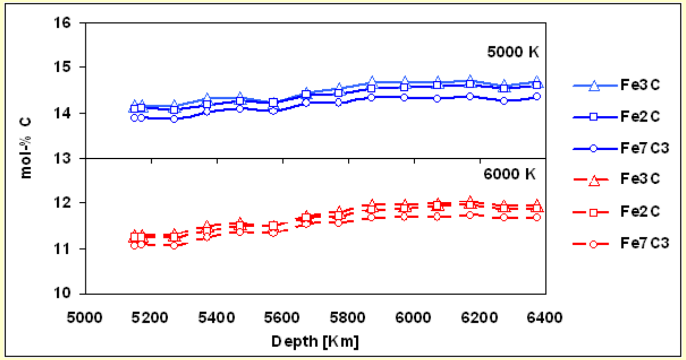






- **The core is less dense than pure iron.**
- **It must contain lighter elemens, e.g. S, Si, O, C, H.**
- **In Fe-C and Fe-H systems, new compounds are predicted (FeH_4!).**
- **Carbon can exist in the core in large concentrations**

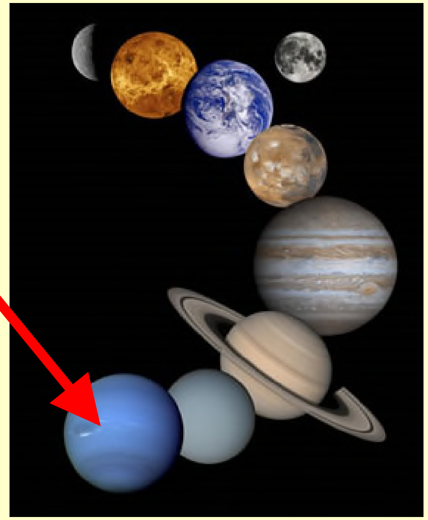
[Bazhanova, ARO, Gianola, Physics-Uskekhi 2012].



Carbon content needed to reproduce the density of the inner core

Neptune generates heat through falling diamond

CH_4

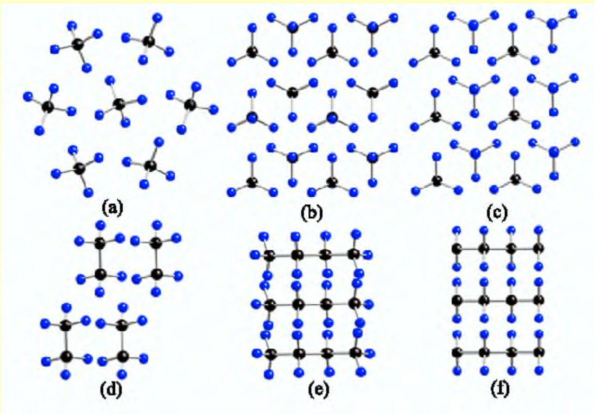


- **Uranus and Neptune: $H_2O:CH_4:NH_3$ = 59:33:8.**
- **Temperature of the core – 8000 K, pressure - 800 GPa.**
- **Neptune produces heat (Hubbard'99).**

- **Ross'81 (and Benedetti'99):**

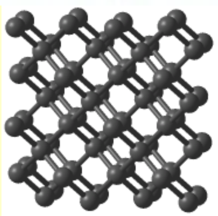
CH_4=C(diamond) + $2H_2$. <u>Fall of diamond as the source of Neptune's heat?</u>

- **Theory (Ancilotto'97; Gao & ARO'2010) confirms this.**

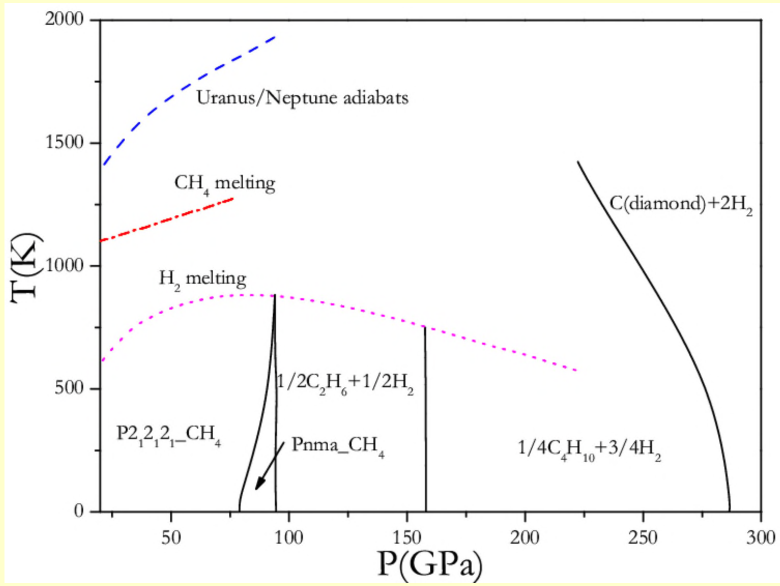


methane

hydrocarbons



diamond



[Gao & Oganov, *J. Chem. Phys.* 133, 144508 (2010)]

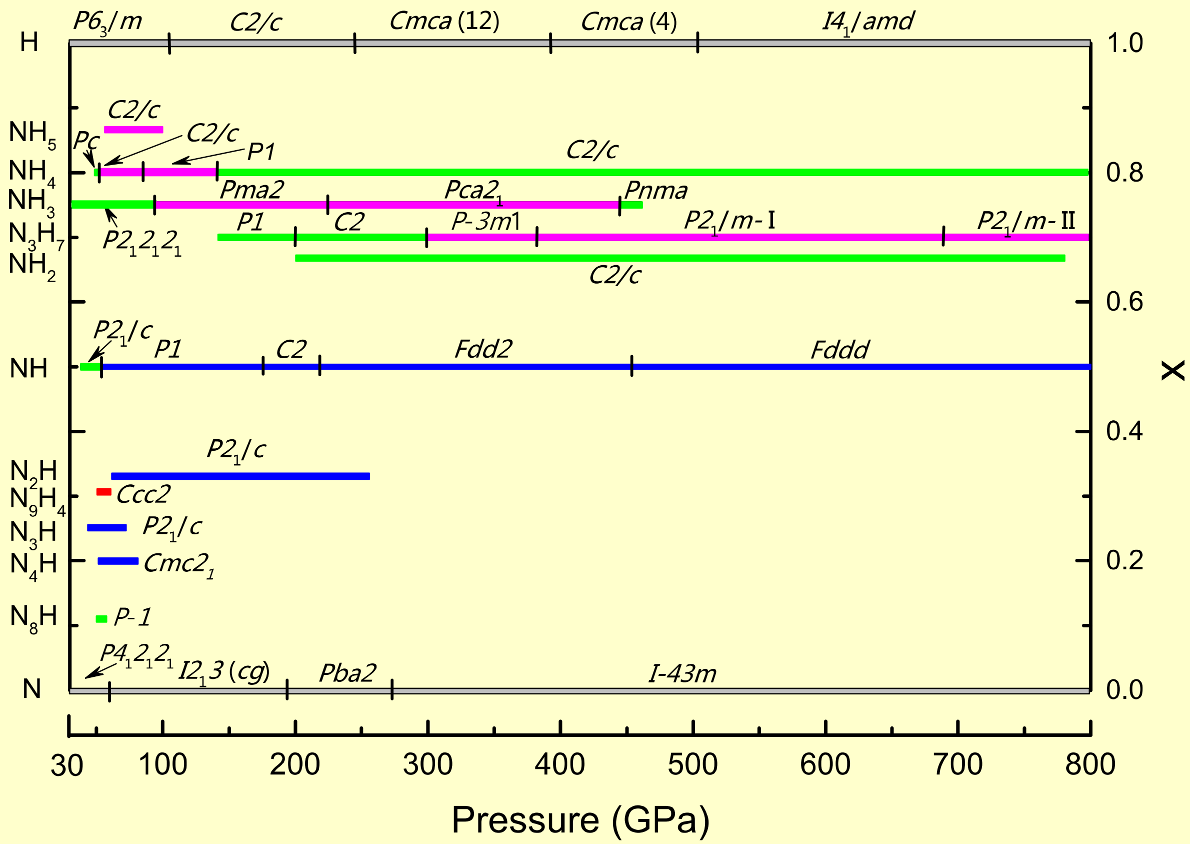
N-H

High-pressure hydronitrogens

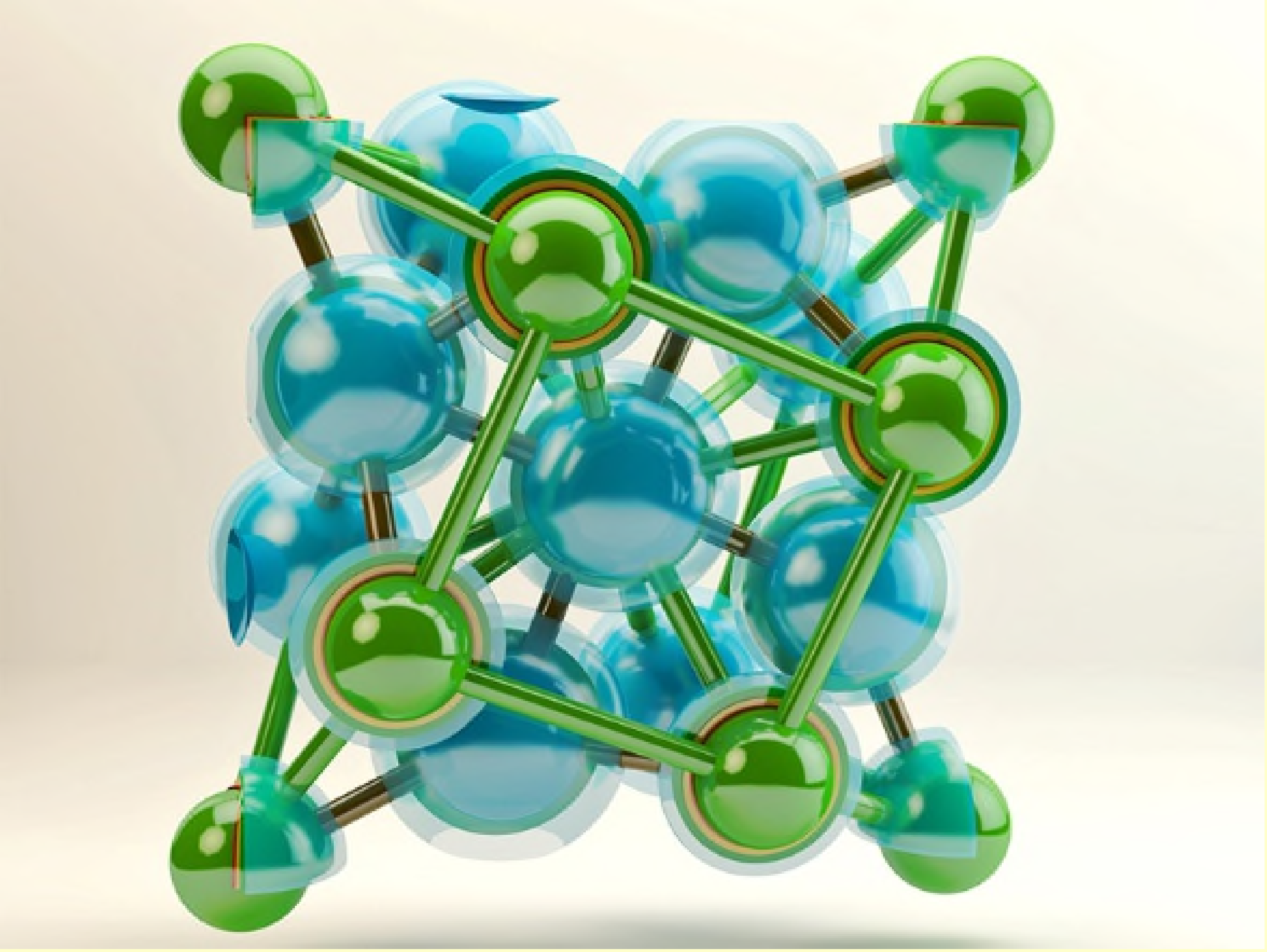
- Polymeric hydronitrogens
  - N_xH (x ≥1)
- 2D-polymeric phase
  - N_9H_4
- Molecular hydronitrogens
  - NH_5, NH_4, NH_3, NH_2, N_3H_7
  - N_8H

Green: molecular

Purple: molecular ionic

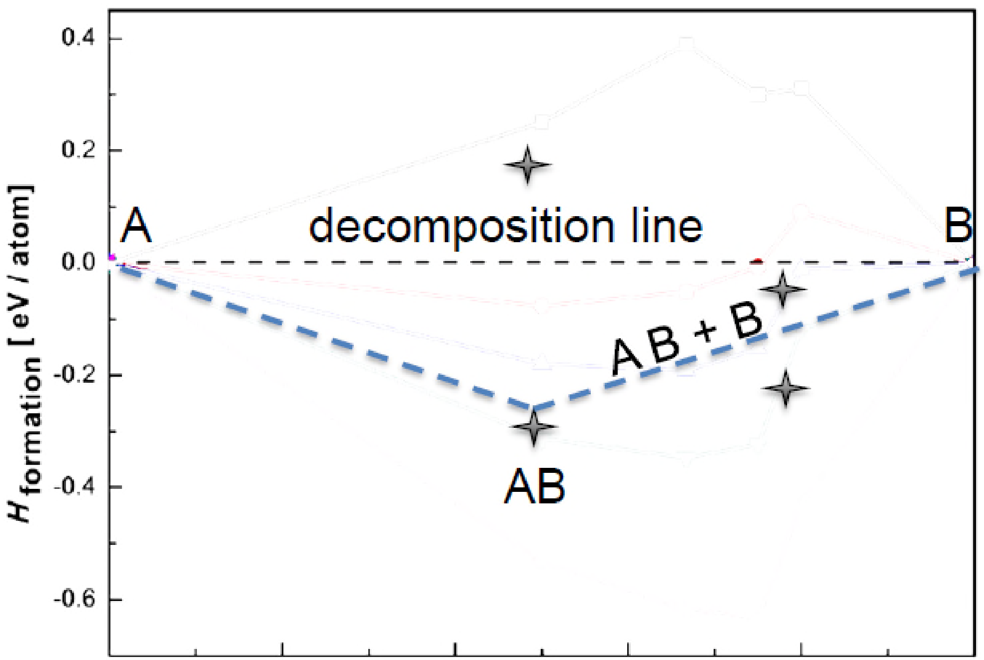


3. Predicting planetary chemistry



With minor (but carefully made) modifications, USPEX can be made to predict stable compositions

How to evaluate the thermodynamic stability



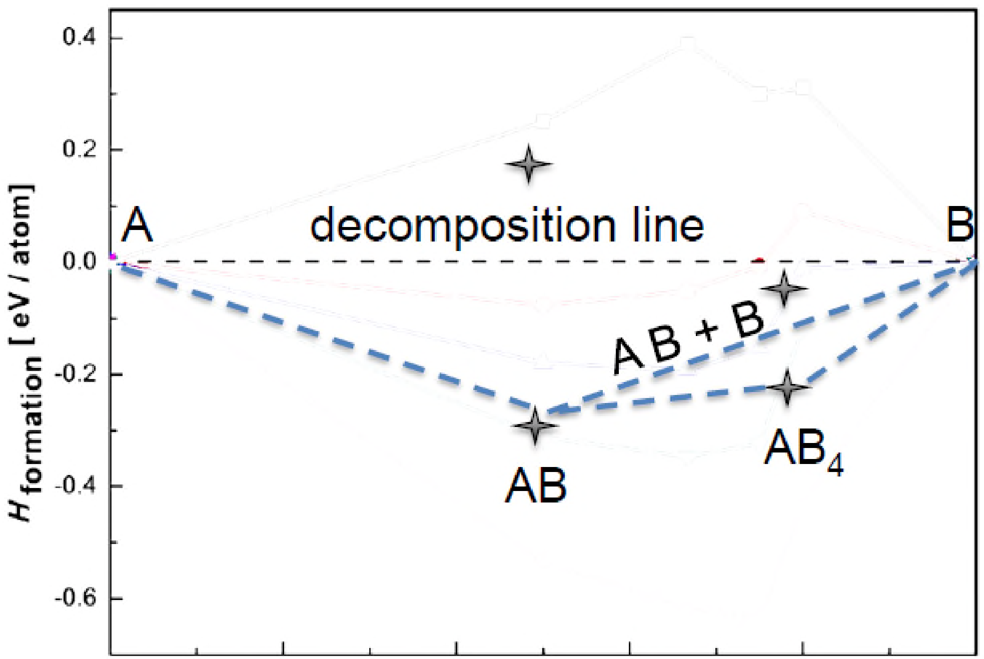
$$A + B \longrightarrow AB$$

$E_{AB} > E_A + E_B$; AB decompose

$E_{AB} < E_A + E_B$; AB is stable

With minor (but carefully made) modifications, USPEX can be made to predict stable compositions

How to evaluate the thermodynamic stability



$$A + B \longrightarrow AB$$

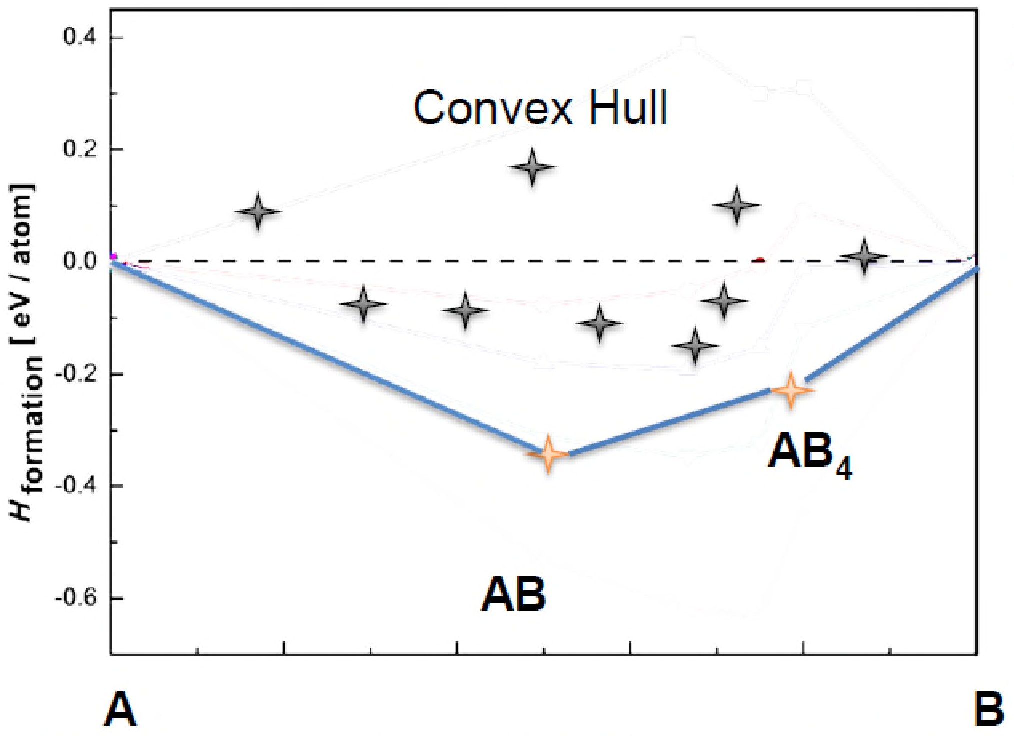
$E_A + E_B > E_{AB}$; AB decompose

$E_A + E_B < E_{AB}$; AB is stable

Stable structure must be below all the possible decomposition lines !!

With minor (but carefully made) modifications, USPEX can be made to predict stable compositions

How to evaluate the thermodynamic stability



$$A + B \longrightarrow AB$$

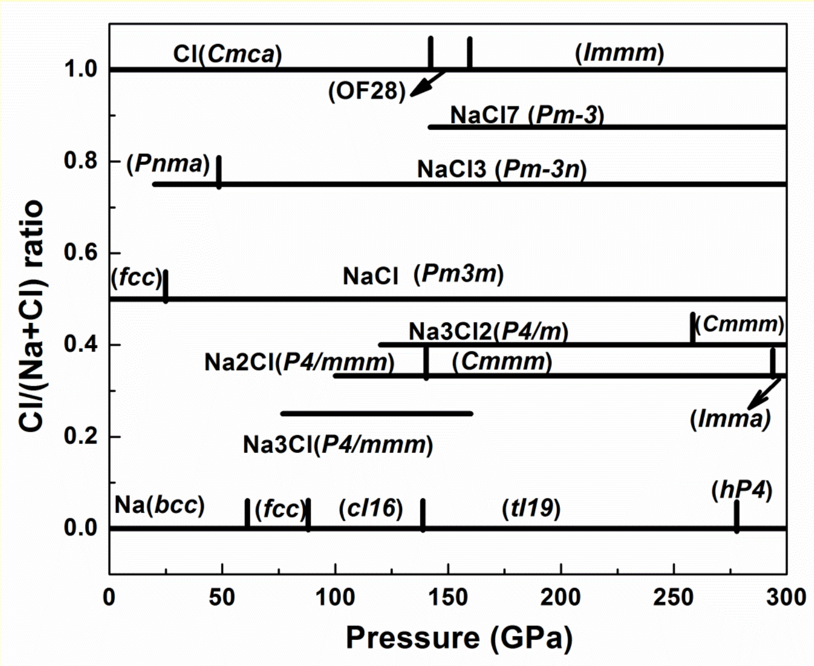
$E_A + E_B > E_{AB}$; AB decompose

$E_A + E_B < E_{AB}$; AB is stable

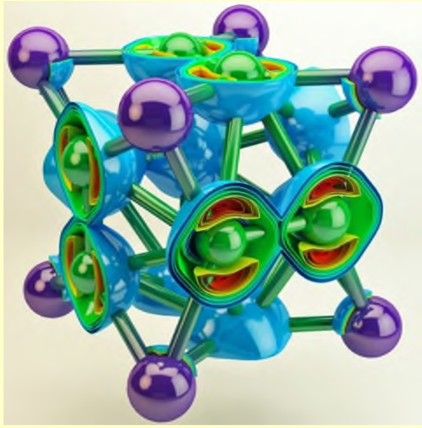
Stable structure must be below all the possible decomposition lines !!

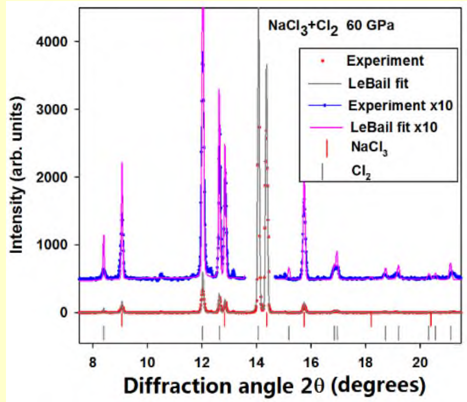
Na-Cl

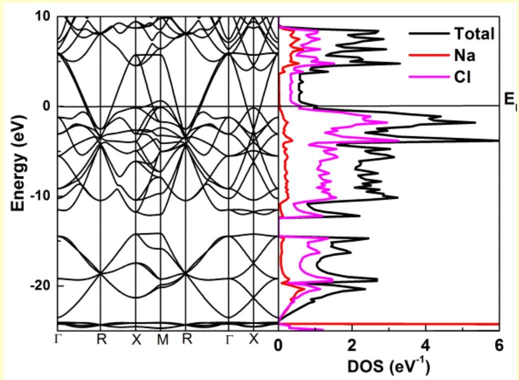
"Forbidden" Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$, $NaCl_7$ are stable under pressure (Zhang, Oganov, et al. *Science*, 2013).



Stability fields of sodium chlorides





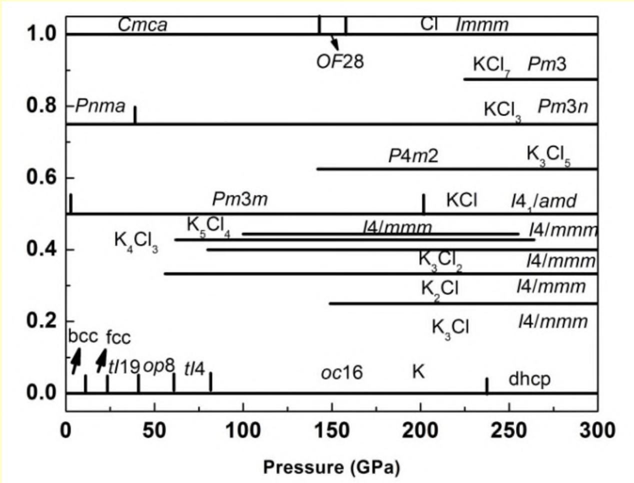


$NaCl_3$: atomic and electronic structure, and X-ray diffraction pattern

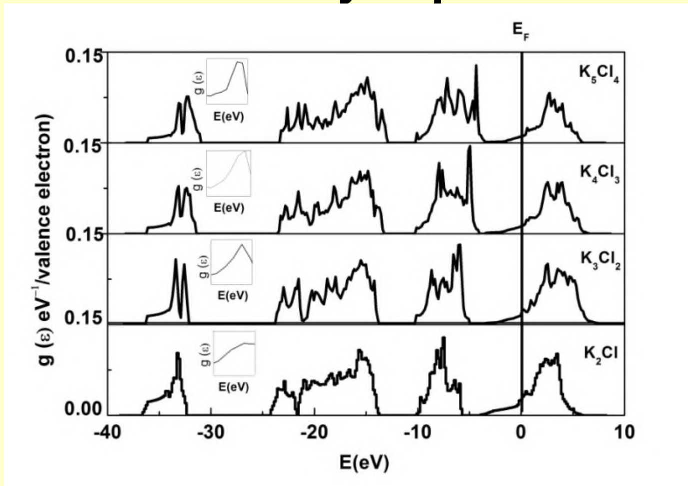
[Zhang, Oganov, et al., *Science* (2013)]

K-Cl: extreme richness of the phase diagram

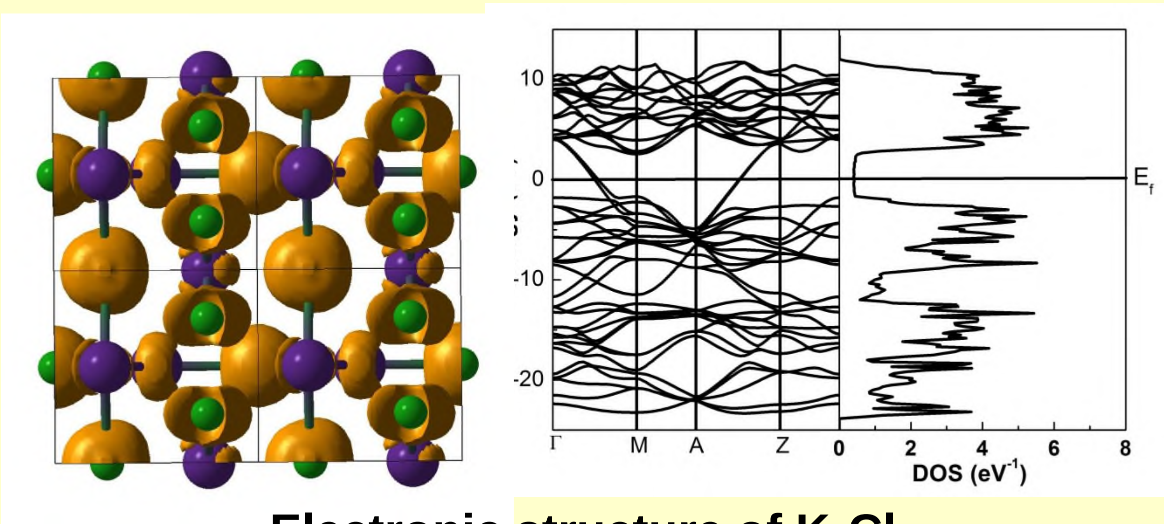
(Zhang, Oganov, Goncharov, 2015). Predictions confirmed by experiment!



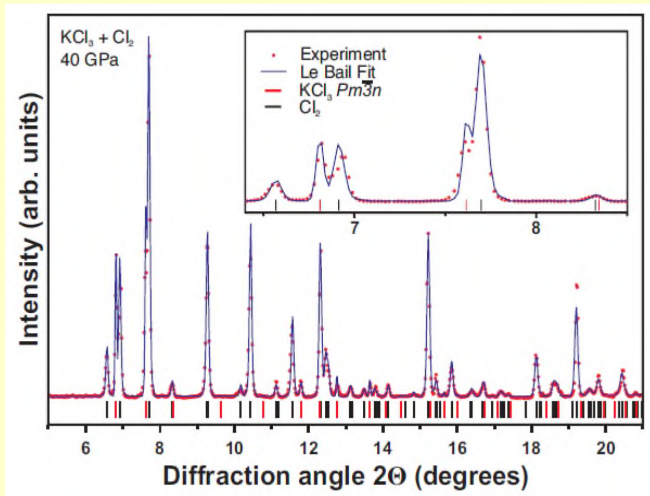
P-x phase diagram of the K-Cl system



Electronic DOS of K-Cl compounds



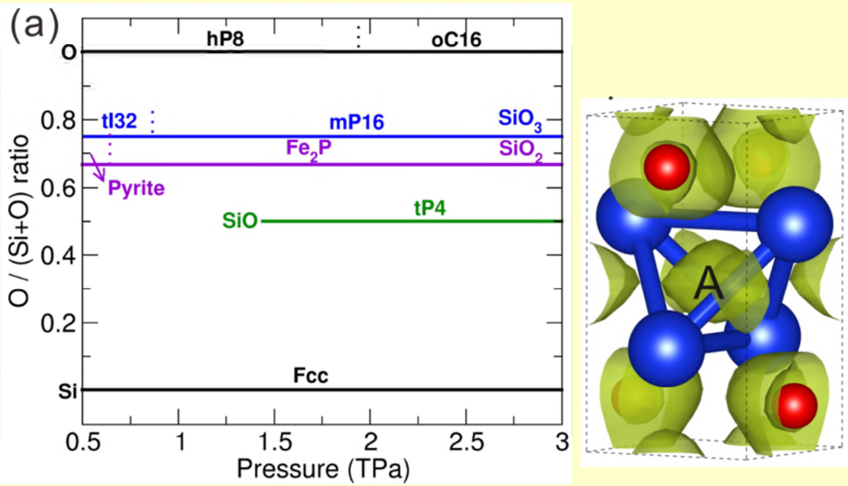
Electronic structure of K_3Cl_5



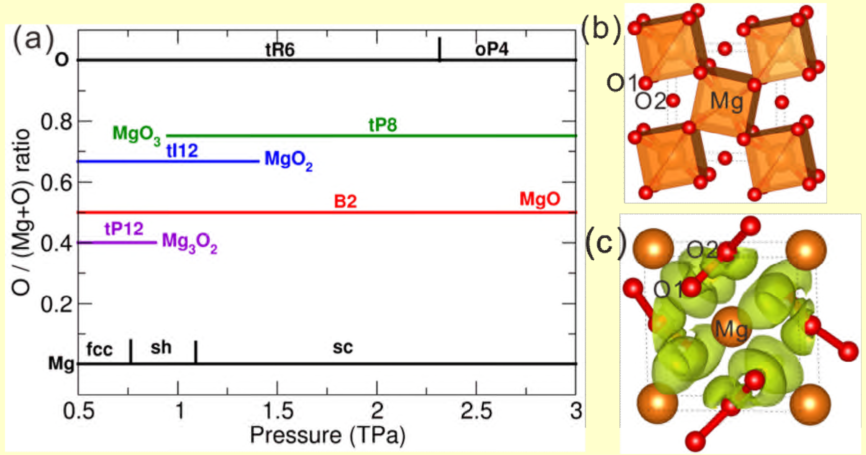
Experimental X-ray diffraction of KCl_3

"Forbidden" MgO_2, Mg_3O_2, SiO, SiO_3, Al_4O_7, AlO_2 are stable at planetary pressures

Giant planets



Phase diagram of Si-O system and structure of SiO (Niu & Oganov, submitted)



Phase diagram of Mg-O system and structure of MgO_3 (Niu & Oganov, submitted; Zhu & Oganov, 2013)

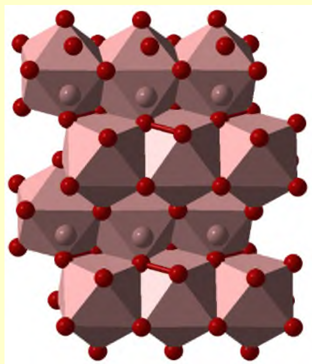
<u>**Al-O system:**</u>

Stable "oxide-peroxides":

$Al_4O_7 = Al_8O_{12}[O_2]$, stable at 330-443 GPa

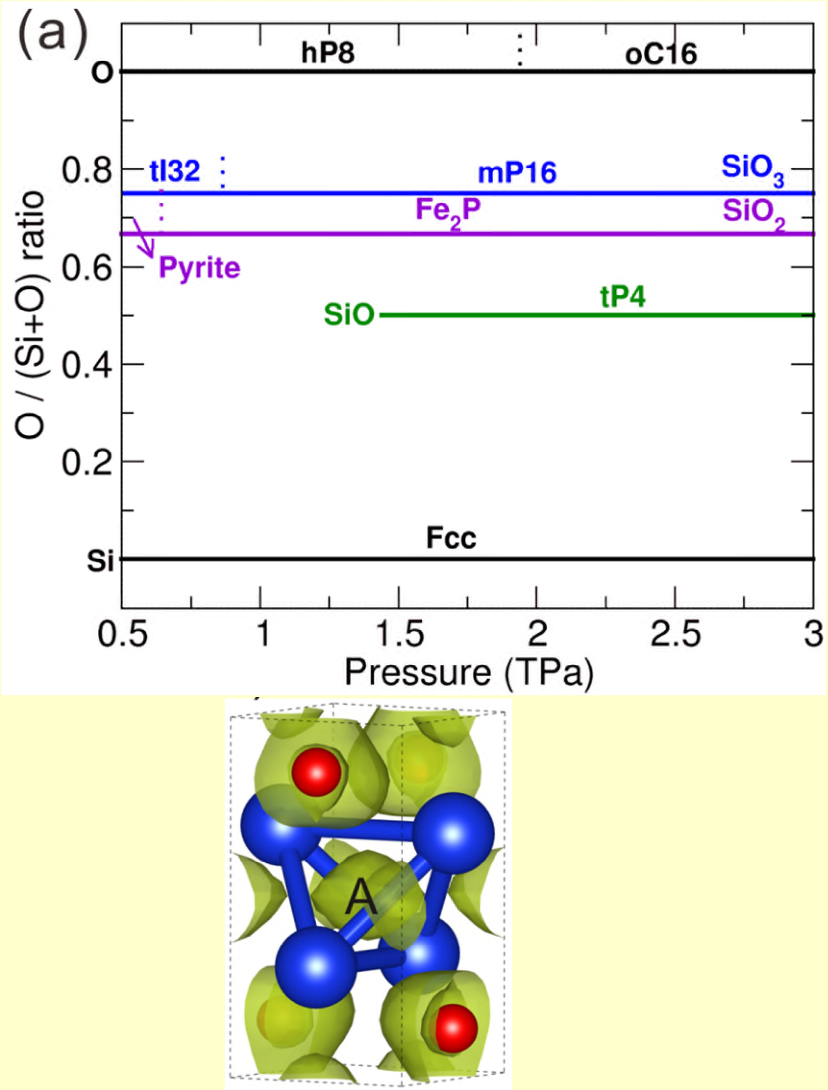
$AlO_2 = Al_4O_6[O_2]$, stable at >332 GPa

(Liu, Oganov, Kresse, *Sci. Rep.* 2015)

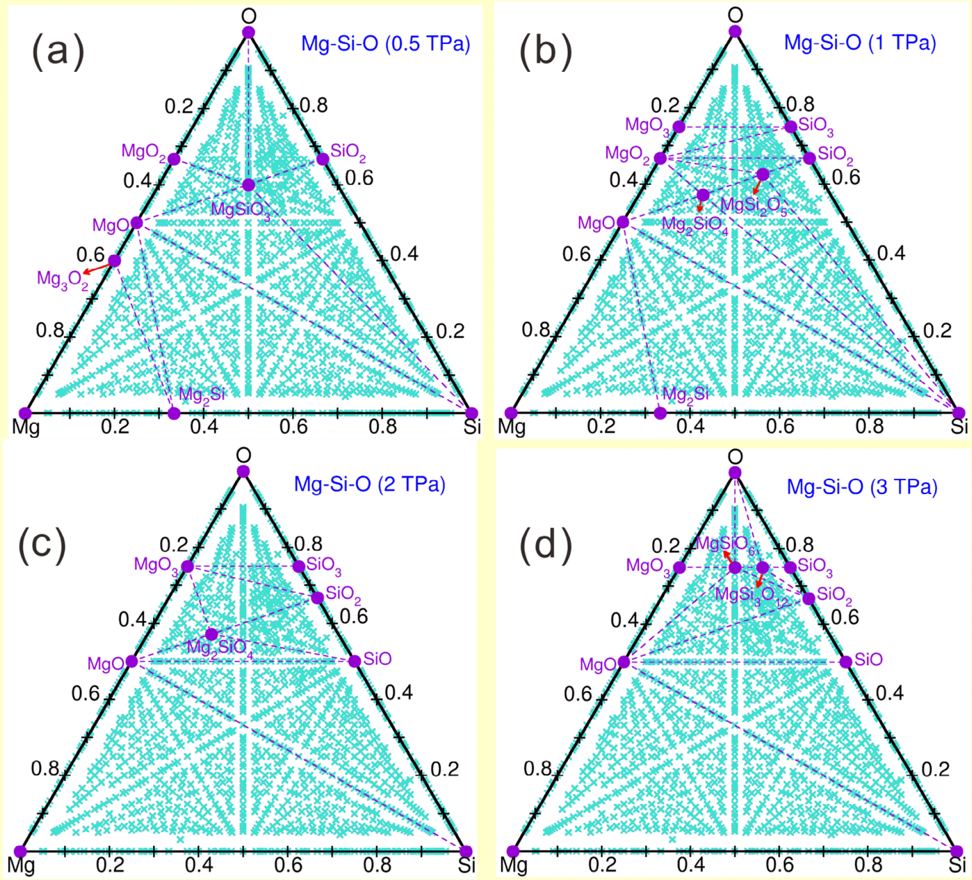


Структура AlO_2

New high-pressure silicates: materials of rocky exoplanets (Niu & Oganov, submitted to Scientific Reports)

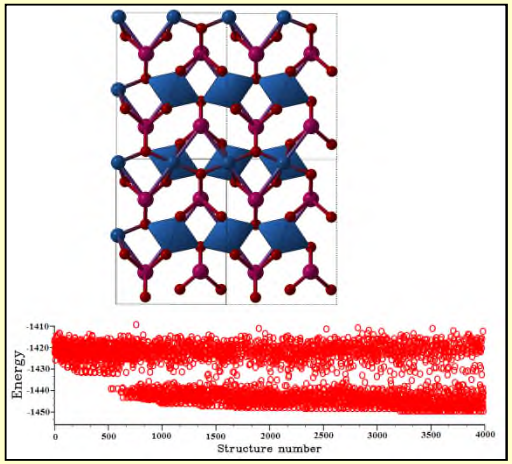


Phase diagram of Si-O system and structure of SiO.

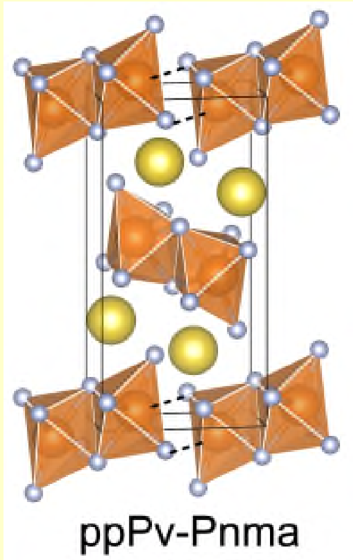


Phase diagram of Mg-Si-O system

With novel predictive methods, we get a powerful tool to look inside the planets – and there is much to explore!

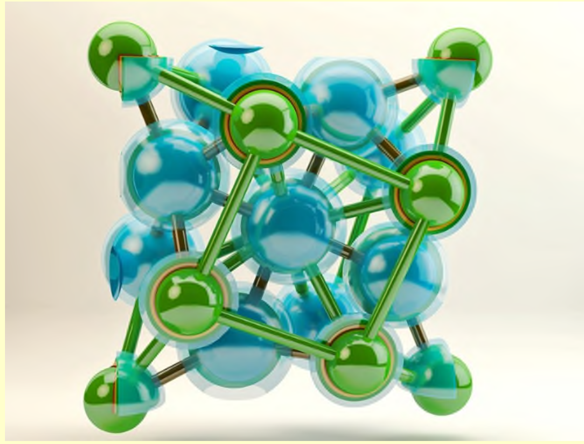


1. Predicting crystal structures by evolution



2. Predicting planetary mineralogy

Post-perovskite
Post-post-perovskite
C is likely in the core
Neptune's heat

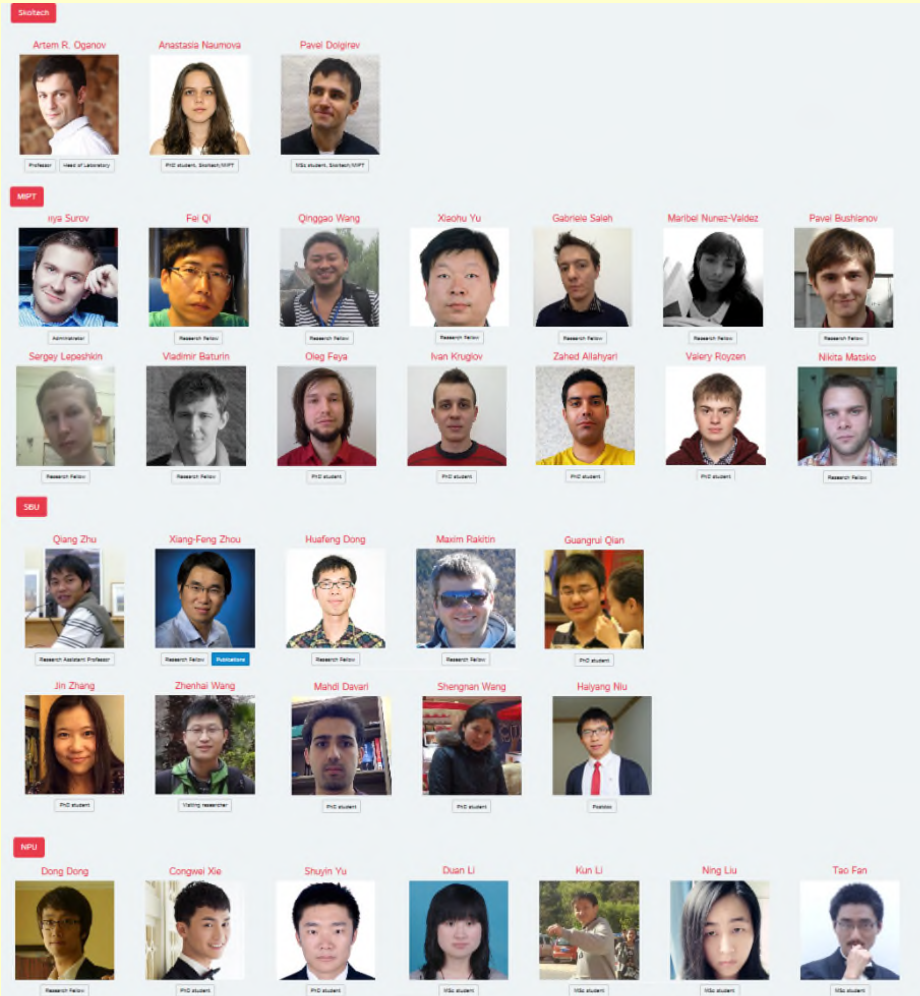


3. Predicting planetary chemistry

"Forbidden" chemistry
Extreme N-H chemistry
New oxides of Mg, Al, Si (SiO_3, etc)
New Mg silicates ($MgSiO_6$ etc)

The team.

Where great minds do NOT think alike



USPEX Computational Materials Discovery

ホンジツハ、アリガトウゴザイマス。