“Forbidden” chemistry

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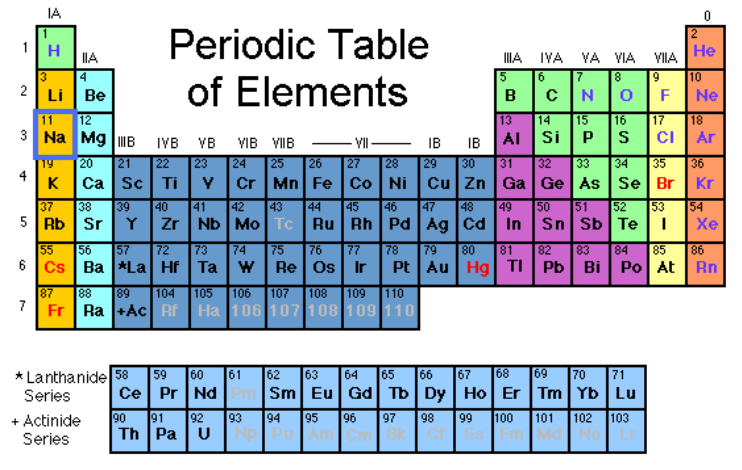
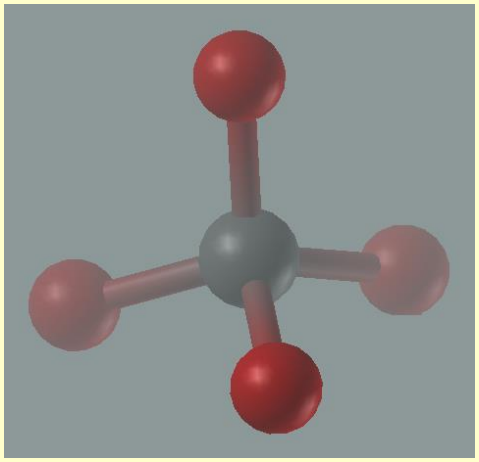
The basics

Periodic Law and Periodic Table

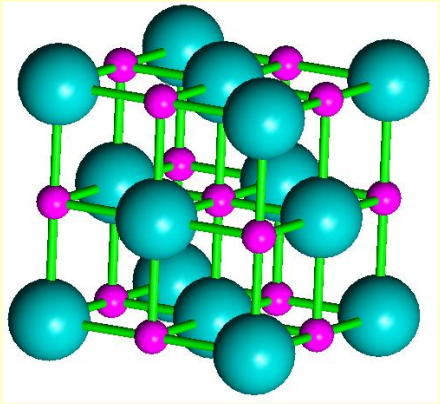


Valence

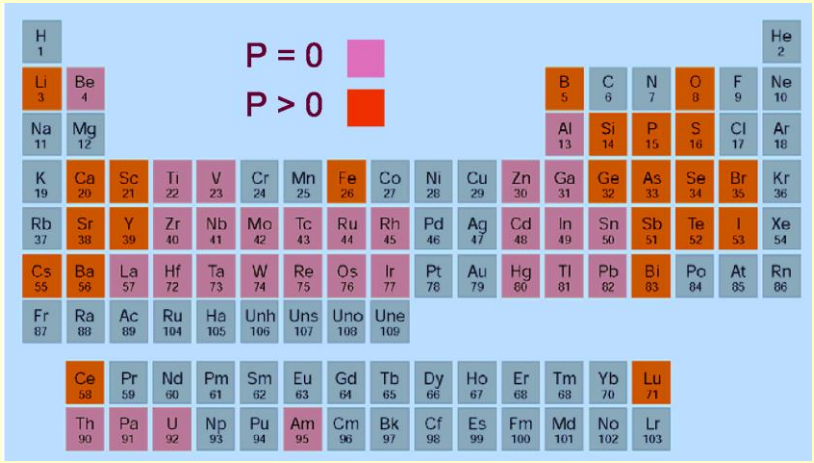
(«how many atoms can be bonded?»)
(“why sodium chloride is NaCl and silicon oxide is SiO_2?”)



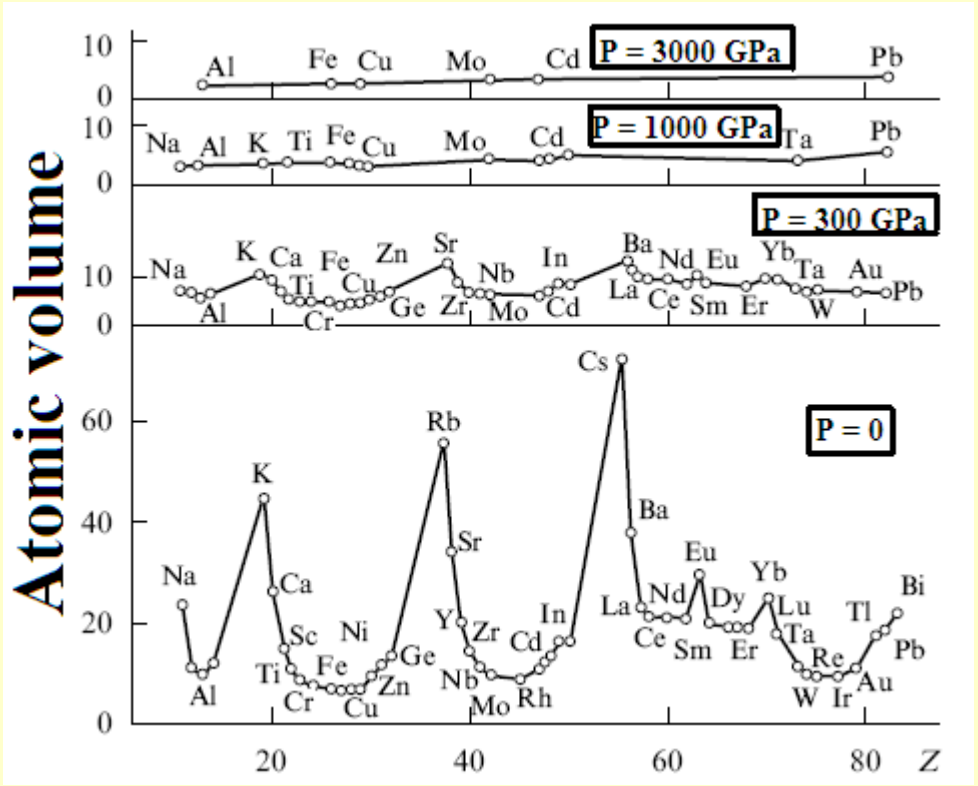
Structure of molecules and crystals and chemical bonding



Chemistry fundamentally changes under pressure

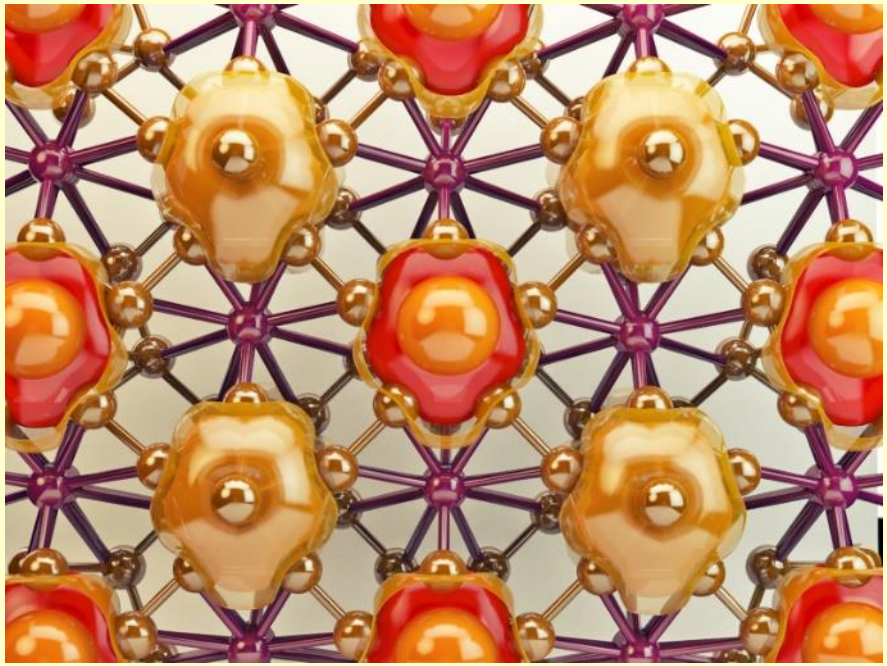


At 100 GPa oxygen becomes a superconductor!



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

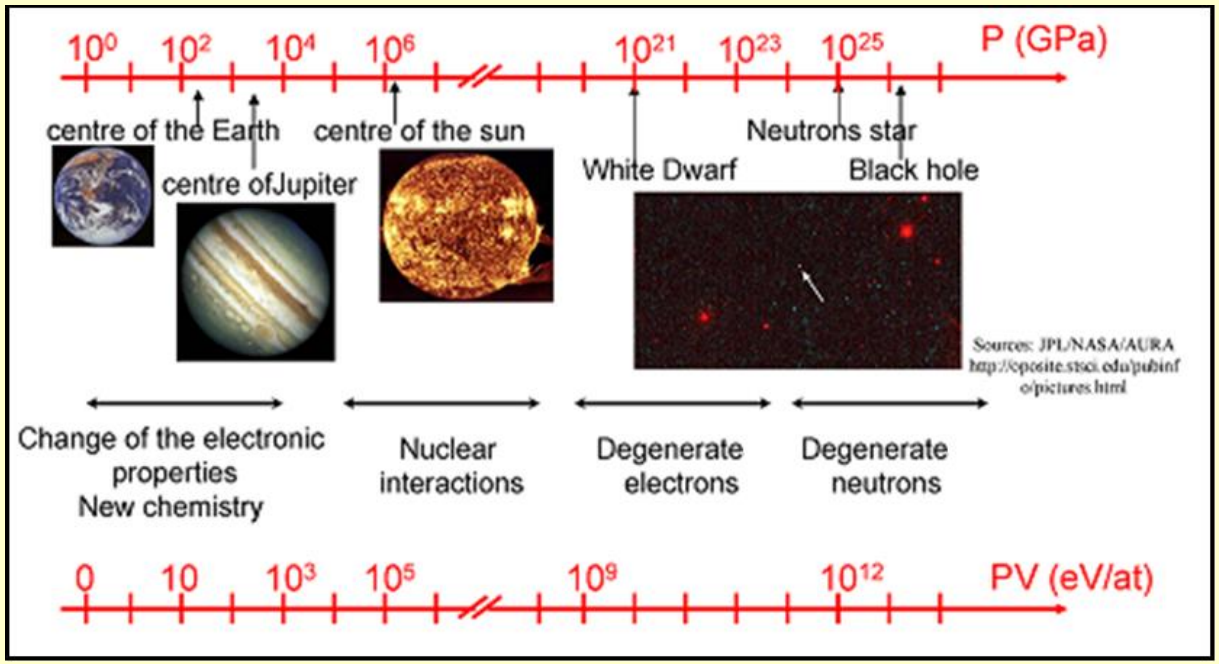
Novel chemistry of the elements under pressure



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

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

Most matter of the Universe is under pressure

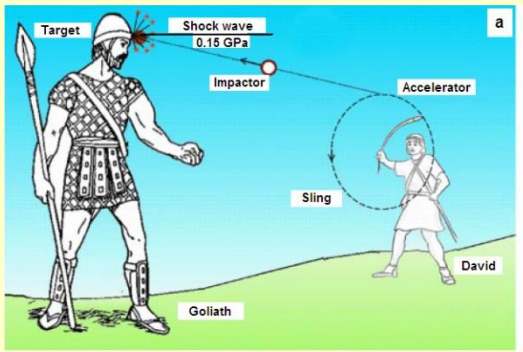


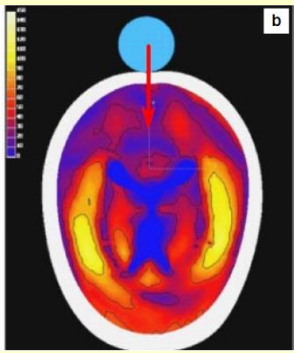
P.W. Bridgman

1946 Nobel laureate (Physics)

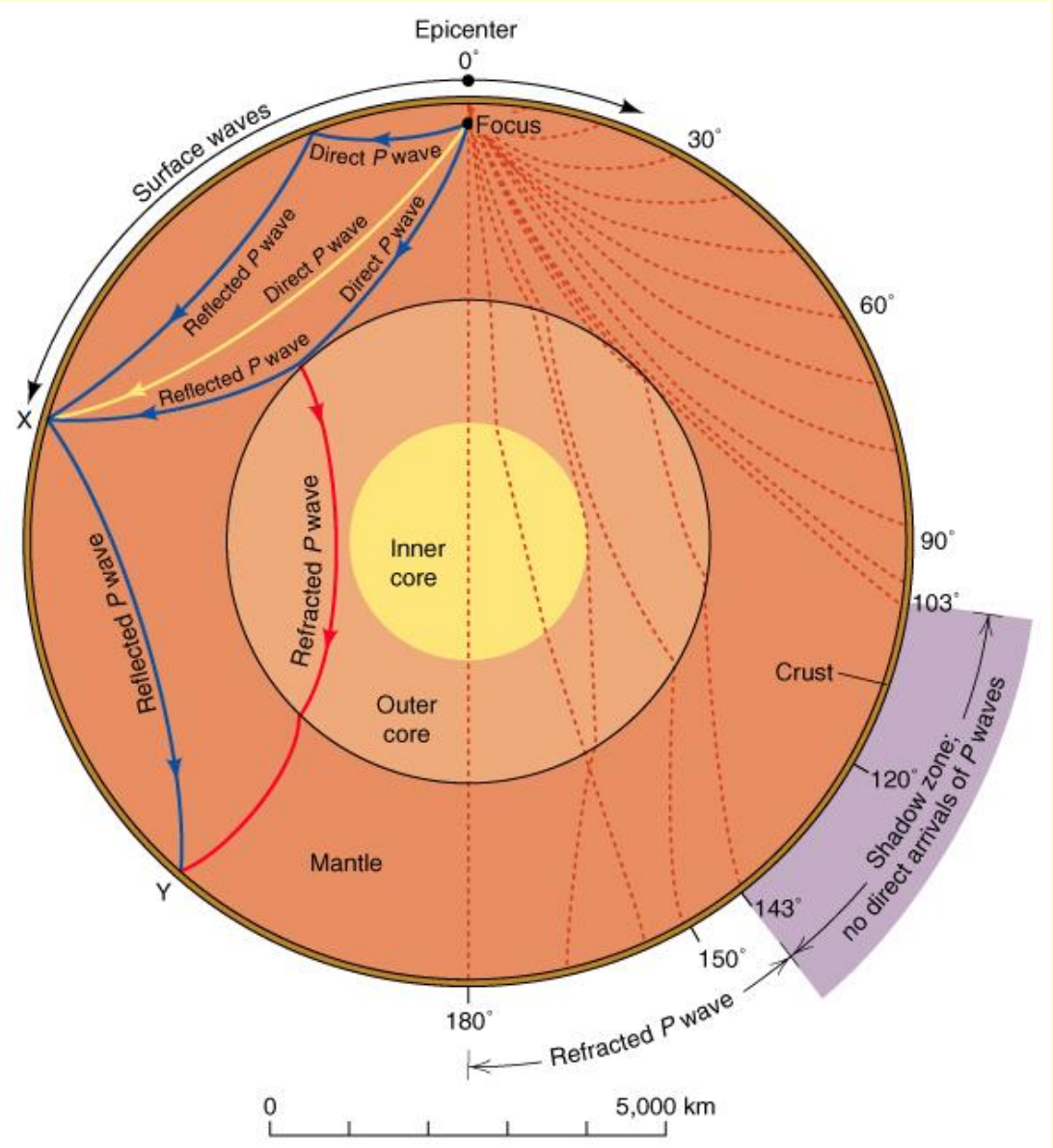
<u>Units:</u> 100 GPa = 1 Mbar =

200x





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

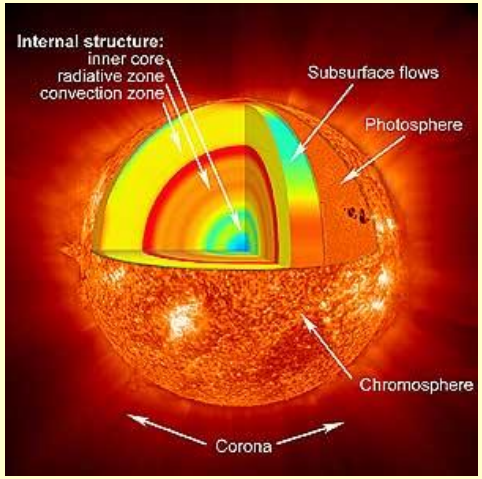
2002-2003: Discovery of the innermost core (Ishii, Beghein)

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

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

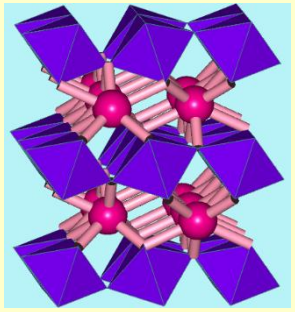


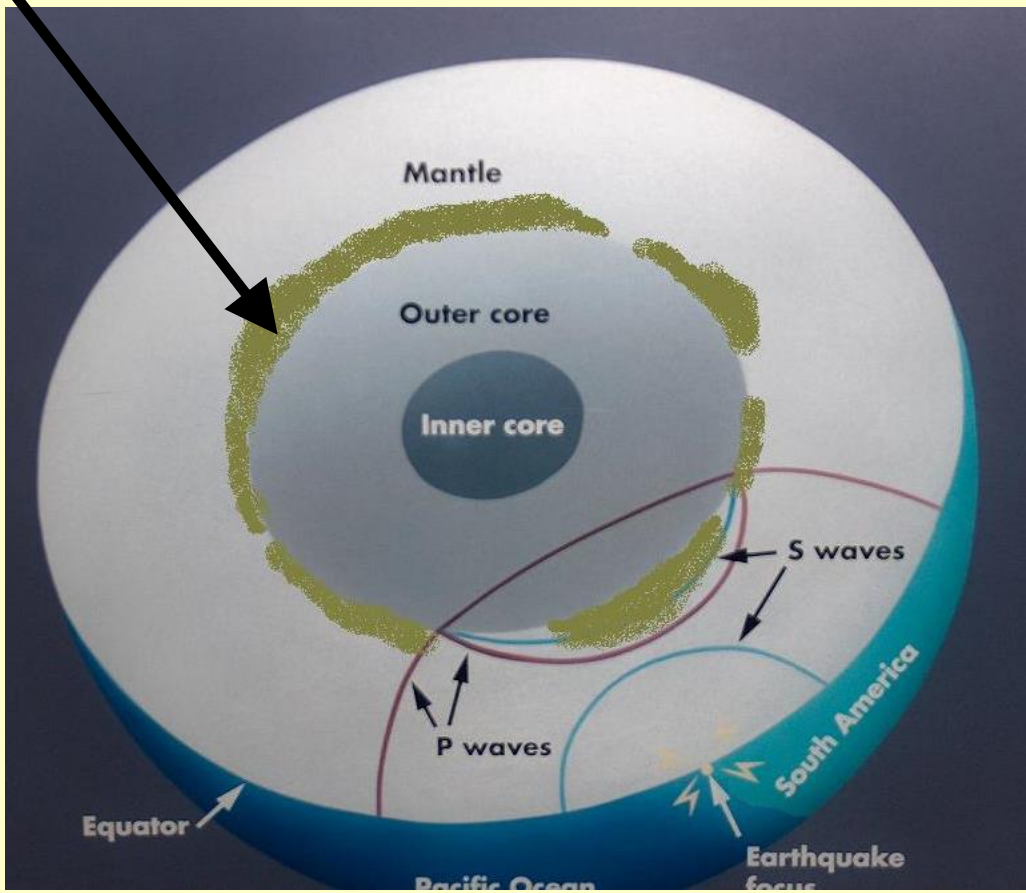
Properties of D” layer (2700-2890 km) were explained by $MgSiO_3$ post-perovskite

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[2]

22 January 2004; accepted 26 March 2004

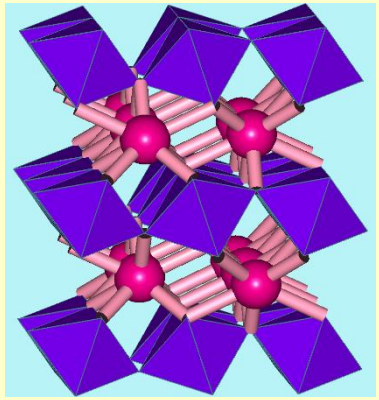
www.sciencemag.org SCIENCE VOL 304 7 MAY 2004 855

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

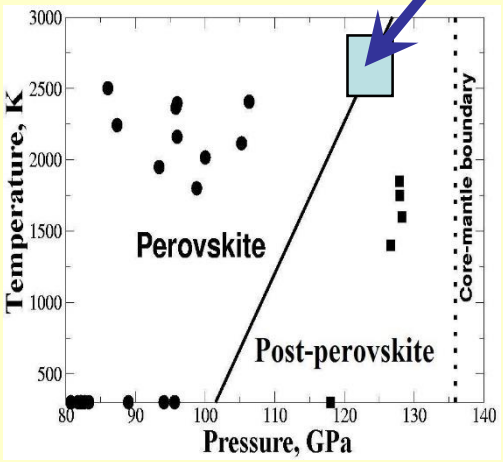
Received 24 March; accepted 27 May 2004; doi:10.1038/nature02701. 445



$MgSiO_3$ пост-перовскит

Phase diagram of $MgSiO_3$

D" discontinuity

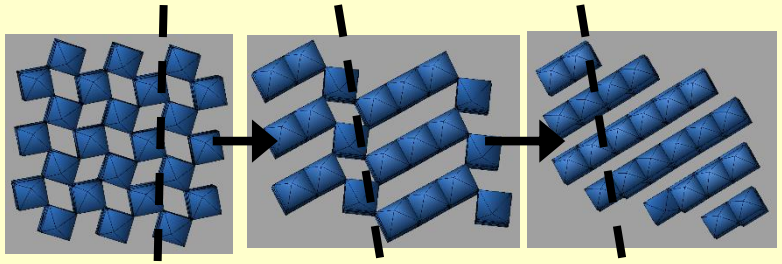


Explains existence of D", allows to determine its temperature. Explains variations of its thickness. Explains variations of the length of day. Predicts that D" grows with time as Earth cools down.

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

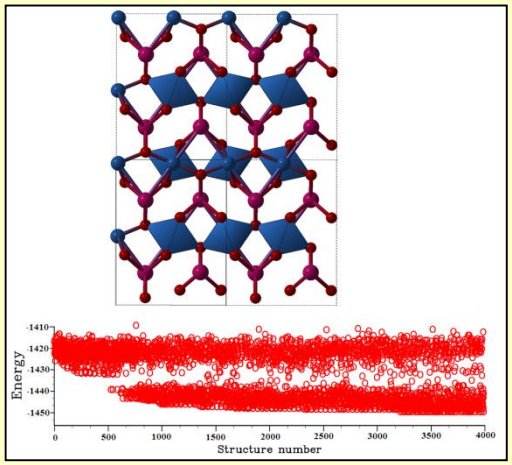
Artem R. Oganov[1], Roman Martoňák[2], Alessandro Laio[2], Paolo Raiteri[2] & Michele Parrinello[2]



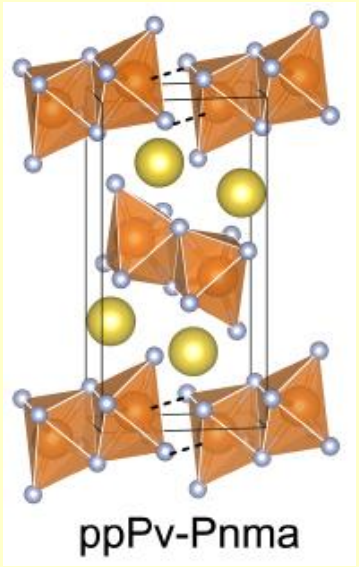
Predicted a new family of minerals.

Confirmation – Tschauner (2008)

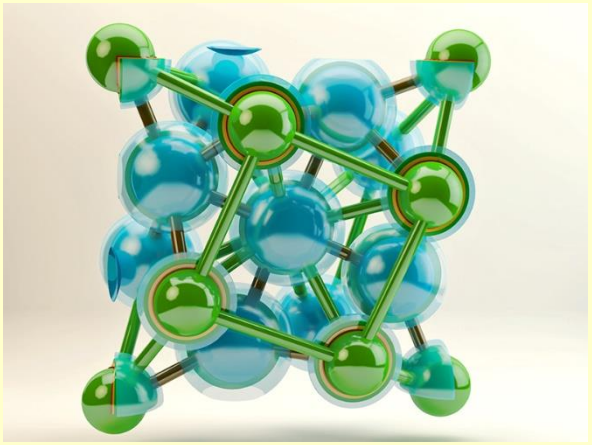
With novel predictive methods, we get a powerful tool to look inside the planets



1. Predicting crystal structures by evolution



2. Predicting planetary mineralogy



3. Discovering novel chemistry

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

Are Crystal Structures Predictable?

ANGELO GAVEZZOTTI*

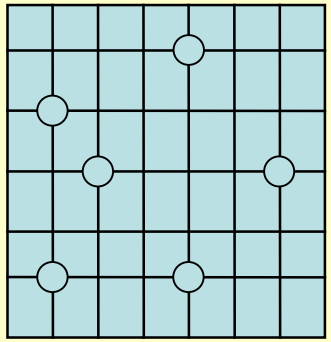
"No": by just writing down this concise statement, in what would be the first one-word paper in the chemical literature, one could safely summarize the present state of affairs

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

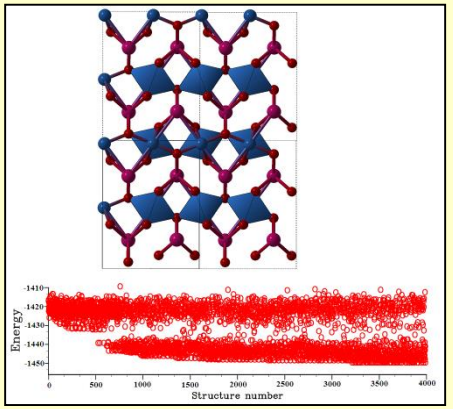
Crystal structure prediction – evolutionary or revolutionary crystallography?

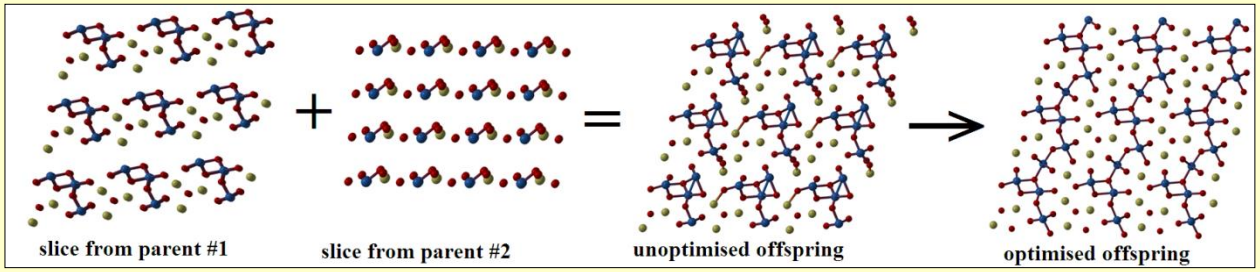
S. L. Chaplot and K. R. Rao CURRENT SCIENCE, VOL. 91, NO. 11, 10 DECEMBER 2006

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

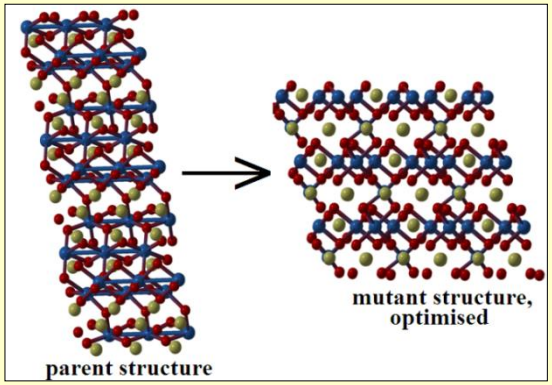
USPEX
(Universal Structure Predictor: Evolutionary Xtallography)

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

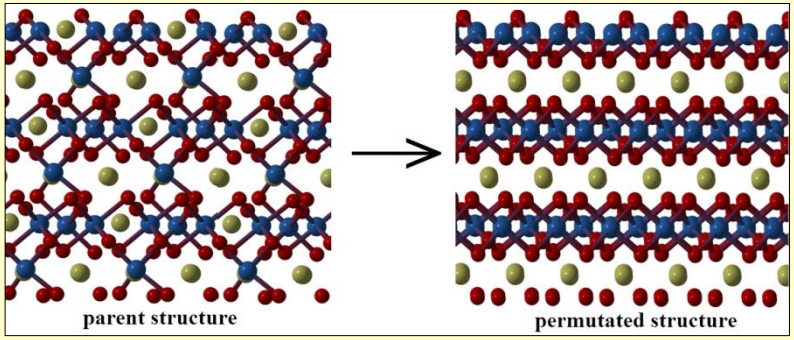




(1) Heredity (crossover)

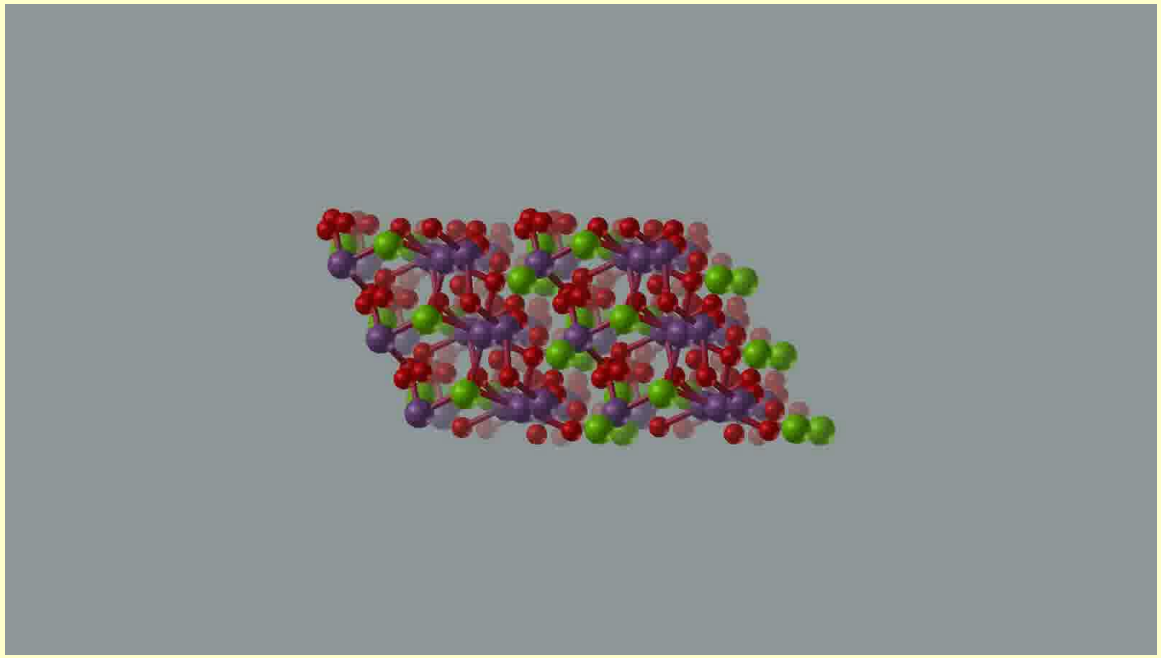


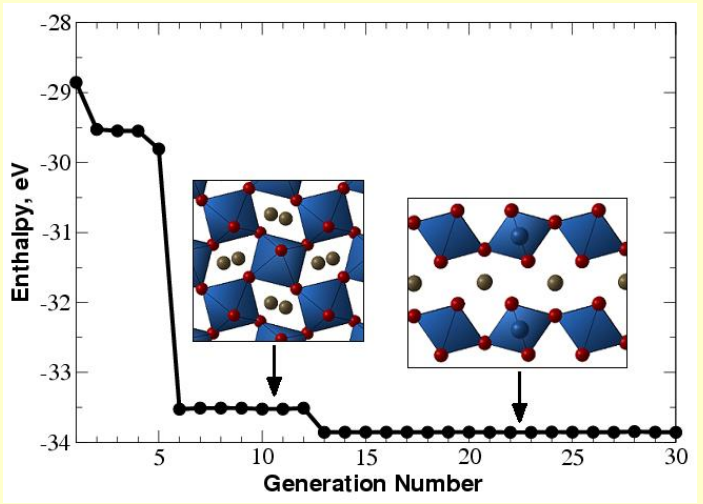
(2) Lattice mutation



(3) Permutation

Test: $MgSiO_3$ at 120 GPa





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

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

The USPEX project
(Universal Structure Prediction: Evolutionary Xtallography)

http://uspex-team.org

[Oganov A.R., Glass C.W., *J.Chem.Phys.* 124, 244704 (2006)]

- Combination of evolutionary algorithm and quantum-mechanical calculations.
- >3500 users.

- Solves «intractable» problem of structure prediction
-3D, 2D, 1D, 0D –systems,
-prediction of phase transition mechanisms.

Quantun-mechanical calculations (density functional theory):

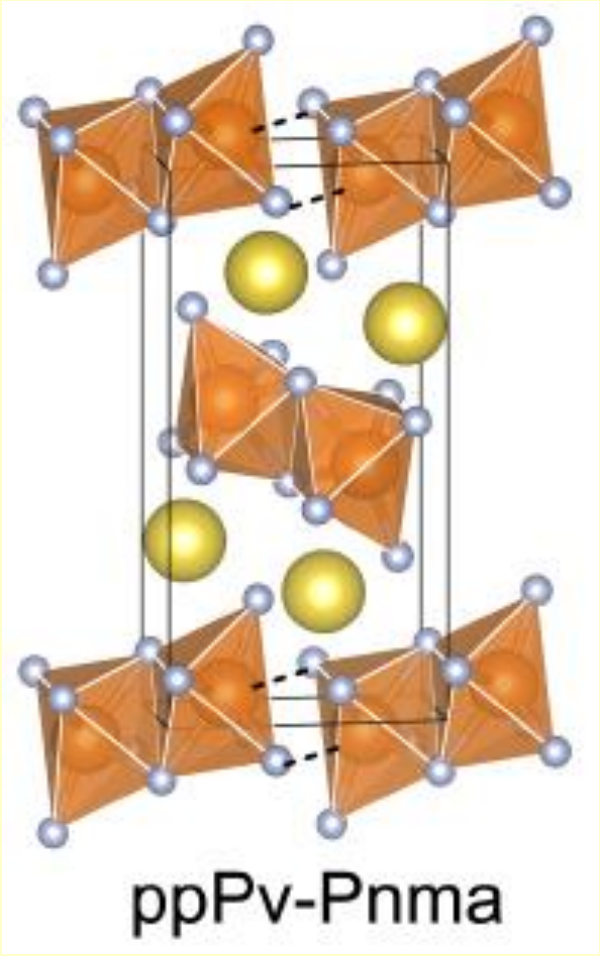
$$(-\frac{\nabla^2}{2}+v_{e-n}[\rho(\mathbf{r})]+v_H[\rho(\mathbf{r})]+v_{xc}[\rho(\mathbf{r})])\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r})$$

$$E_{GGA,\mathrm{xc}}=\int \mathrm{d}\mathbf{r}\, F_{\mathrm{xc}}(\rho,\frac{|\nabla\rho|}{2k_{\mathrm{F}}\rho(\mathbf{r})})\rho(\mathbf{r})e_{\mathrm{x}}[\rho(\mathbf{r})]$$

E.Schroedinger

W. Kohn

2. Predicting planetary mineralogy



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

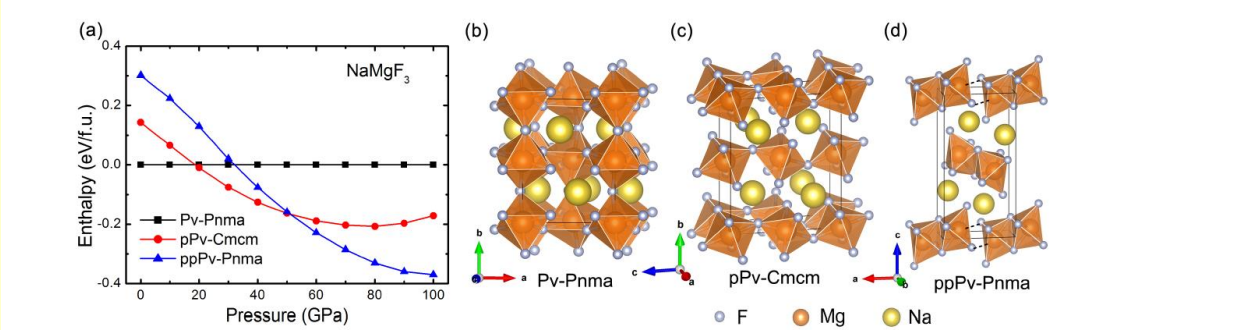
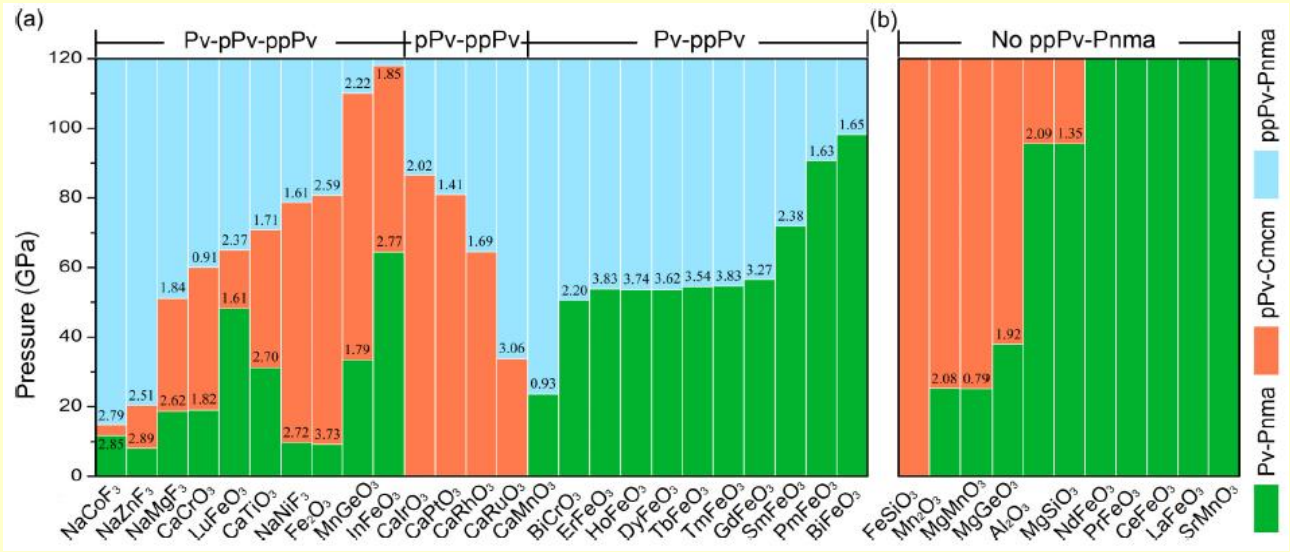


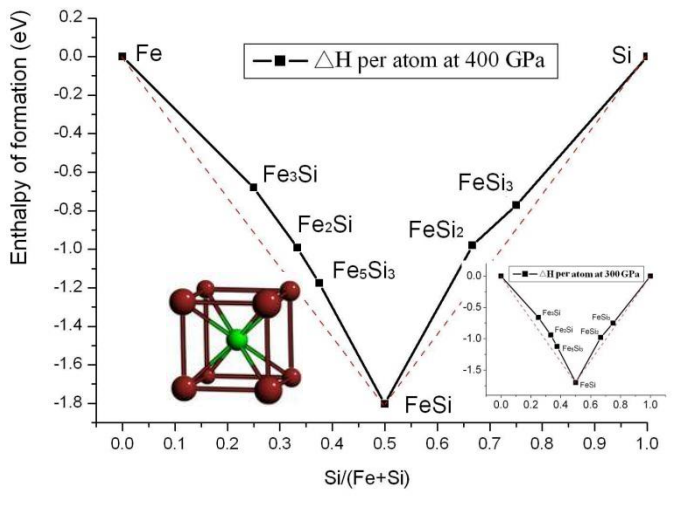
FIG. 2: (Color online). Pressure dependence of the enthalpy of the Pv-*Pnma*, pPv-*Cmcm* and ppPv-*Pnma* phases of $NaMgF_3$ (Panel (a)), along with the schematization of (b) the Pv-*Pnma*, (c) pPv-*Cmcm* and (c) and (d) ppPv-*Pnma* crystallographic structures. Note that the enthalpy of the Pv-*Pnma*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

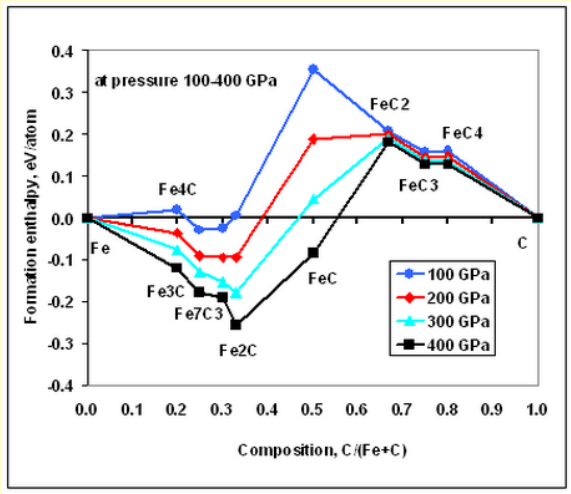
$NaMgF_3$ post-post-perovskite and its stability for $NaMgF_3$. Independently discovered by Crichton (2015) using experiment

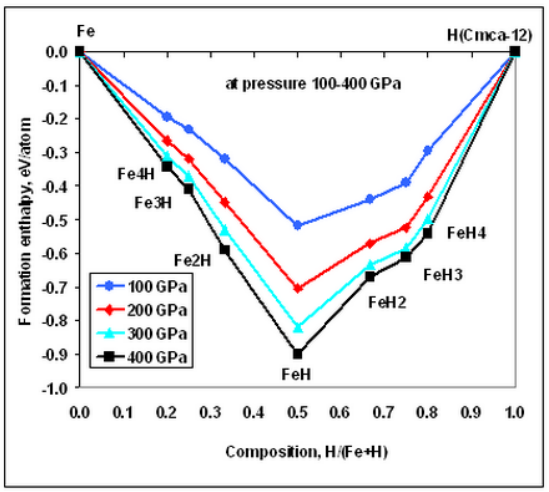


Pressure ranges of stability of perovskite, post-perovskite and post-post-perovskite

What is the chemistry of the Earth's core?

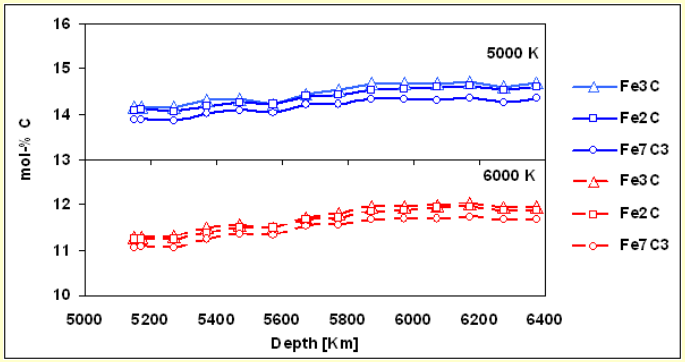






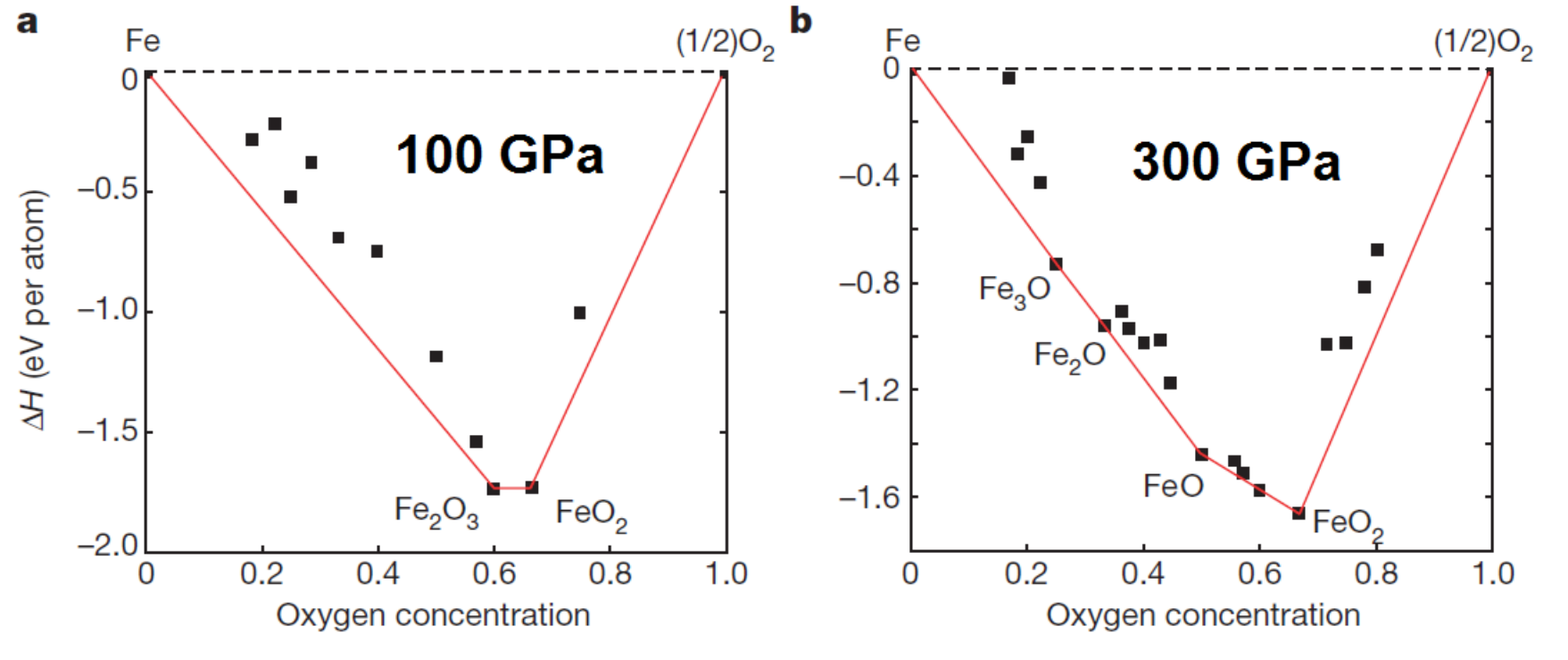
- **The core is less dense than pure iron.**
- **It must contain lighter elemens, e.g. S, Si, O, C, H.**
- **In Fe-C and Fe-H systems, new compounds are predicted (FeH_4!).**
- **Carbon can exist in the core in large concentrations**

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



Carbon content needed to reproduce the density of the inner core

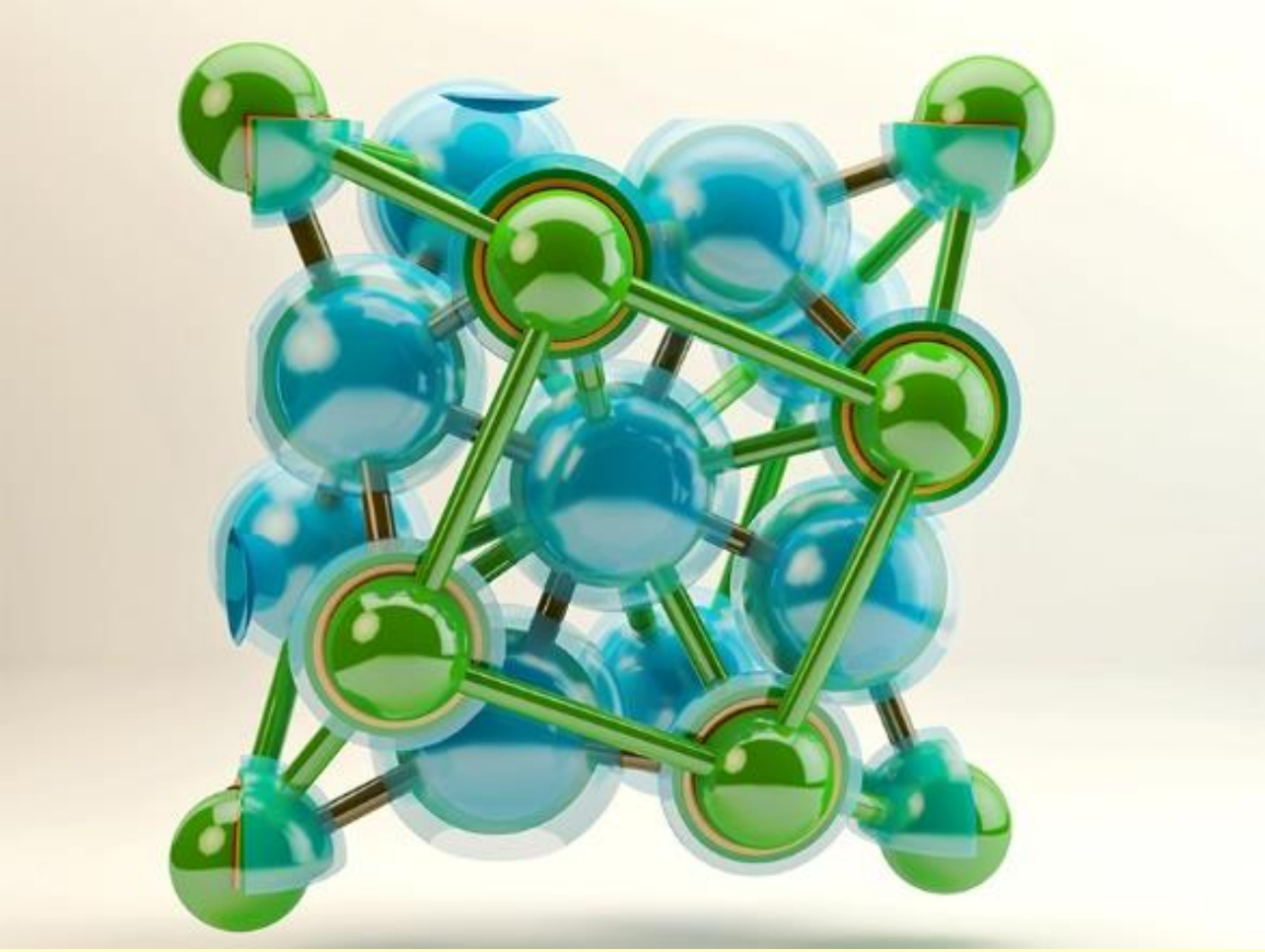
A very recent discovery: stable compound FeO_2 (Hu et al., Nature 2016)



Calculations show thermodynamic stability of FeO_2 both at 100 and 300 GPa

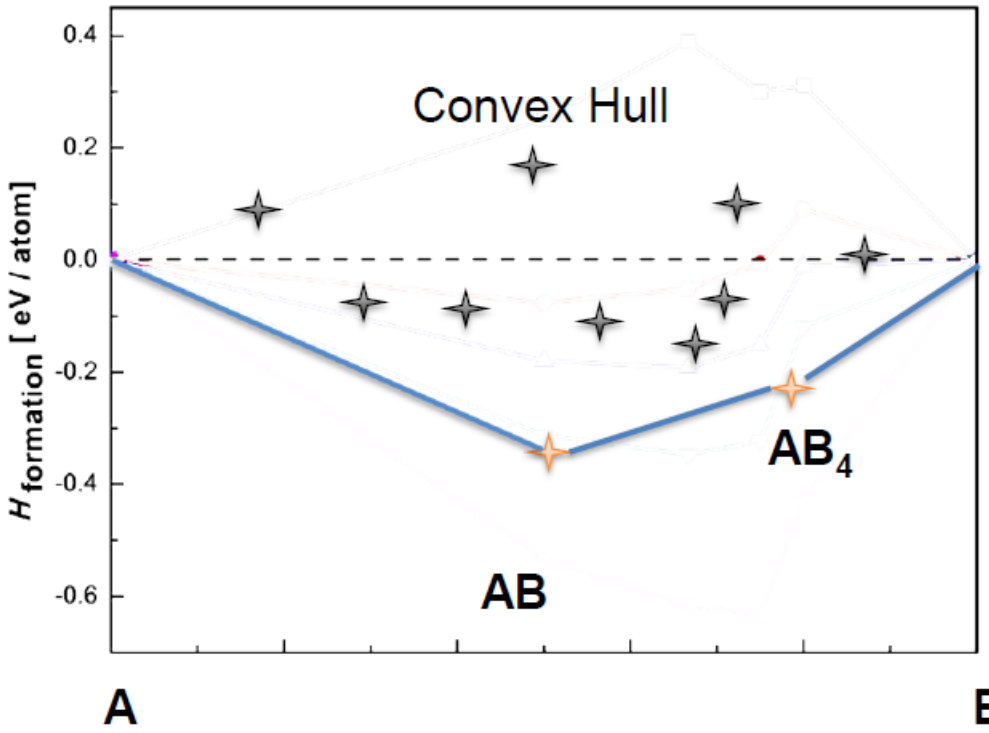
- **FeO_2 is a new stable compound, in the pyrite-like structure, both from experiment and theory.**
- **Surprising reaction: $2FeOOH = 2FeO_2 + H_2$**

3. Discovering novel chemistry



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

How to evaluate the thermodynamic stability



$$A + B \longrightarrow AB$$

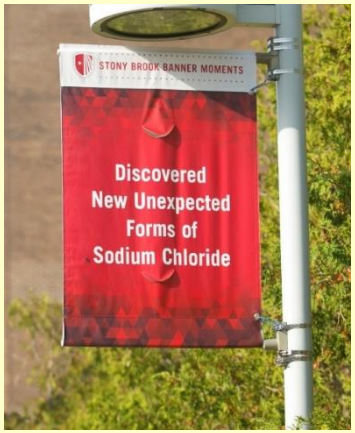
$E_A + E_B > E_{AB}$; AB decompose

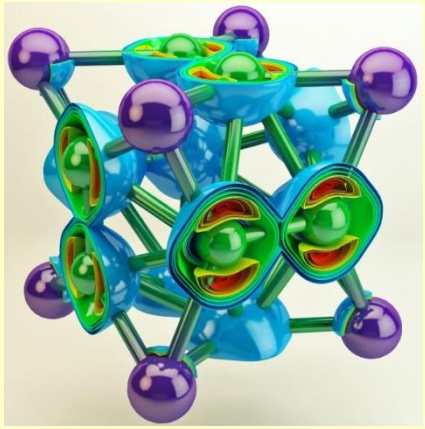
$E_A + E_B < E_{AB}$; AB is stable

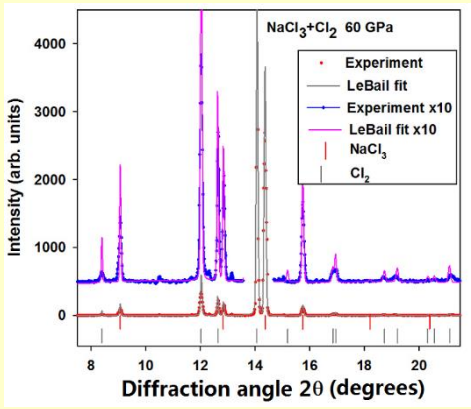
Stable structure must be below all the possible decomposition lines !!

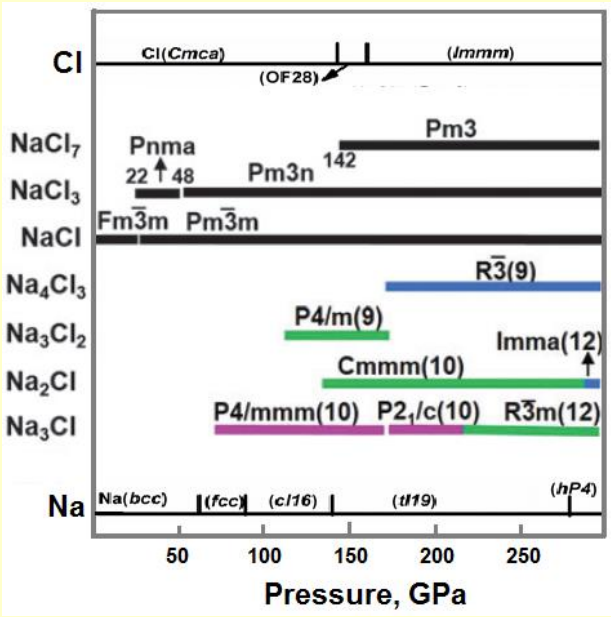
Na-Cl

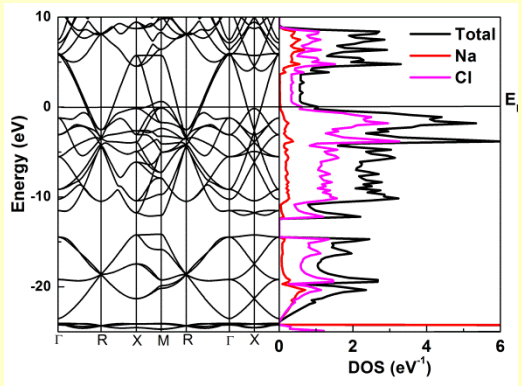
"Forbidden" Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$, $NaCl_7$ are stable under pressure (Zhang, Oganov, et al. *Science*, 2013).











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

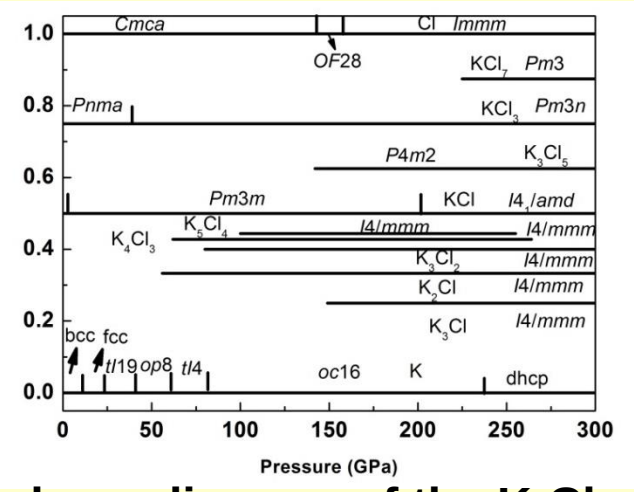
[Zhang, Oganov, et al., *Science* (2013)]
[Saleh & Oganov, *PCCP* (2016)]

Stability fields of sodium chlorides

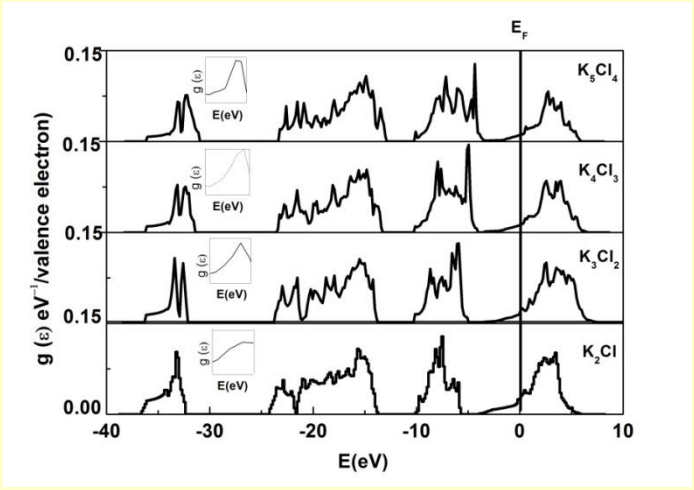
K-Cl: extreme richness of the phase diagram

K-Cl

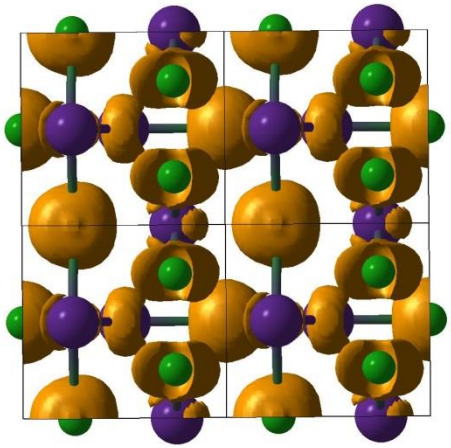
(Zhang, Oganov, Goncharov, 2016). Predictions confirmed by experiment!

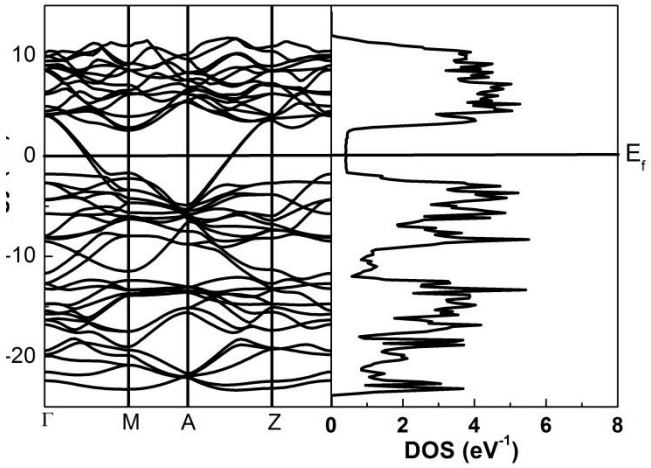


P-x phase diagram of the K-Cl system

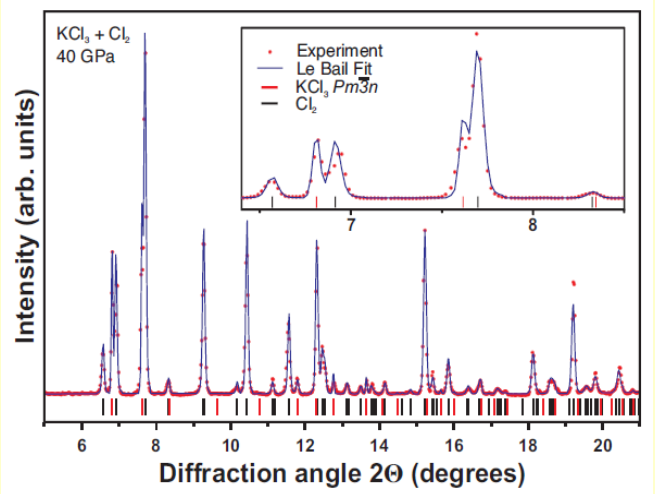


Electronic DOS of K-Cl compounds





Electronic structure of K_3Cl_5



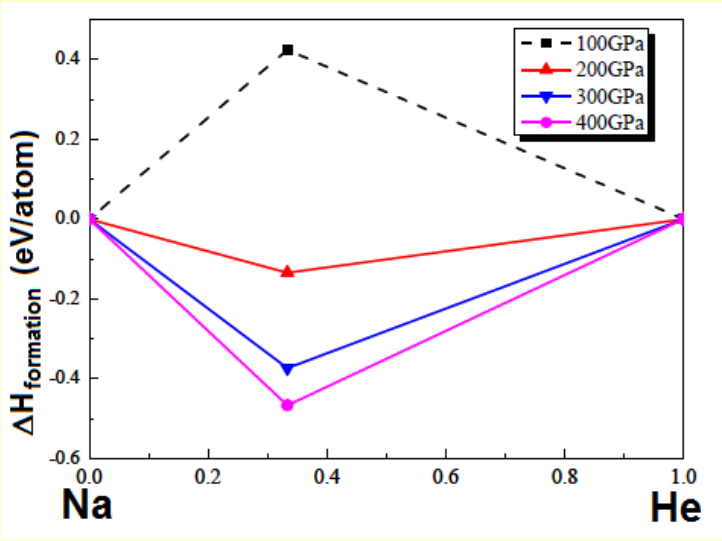
Experimental X-ray diffraction of KCl_3

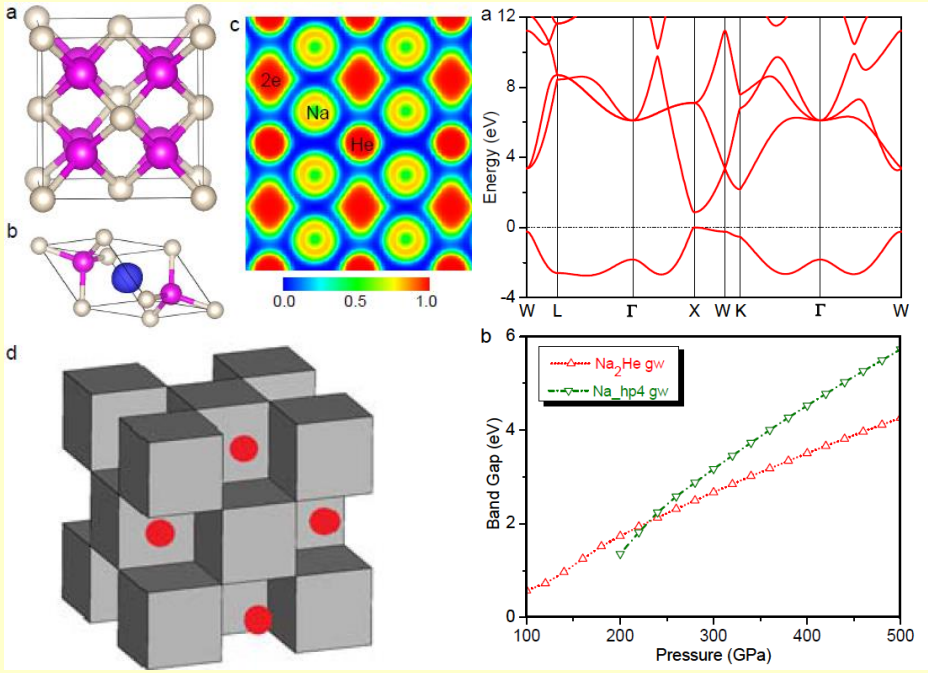
Helium chemistry? Yes!

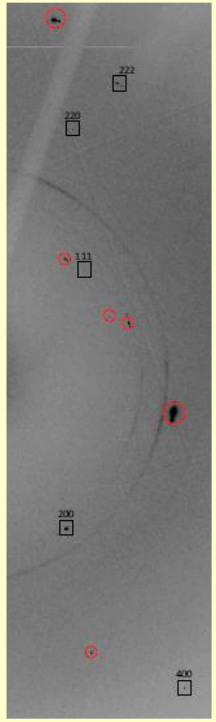
(Dong, Oganov, Goncharov, *Nature Chemistry*, in press)

Na-He

- **Helium is the 2nd most abundant element in the Universe (24 wt.%).**
- **Helium: ionization potential = 24.39 eV (record!)**
  electron affinity = 0.08 eV
- **No stable compounds are known at normal conditions. Under pressure: van der Waals compound $NeHe_2$ (Loubeyre et al., 1993).**







1. **Na_2He is stable at >120 GPa, at least up to 1000 GPa.**
2. **Stabilized by an acceptor of an electron pair on the "2e" site. Na_2HeO – stable already at 14 GPa.**

«Forbidden» compounds can exist in planetary interiors

(1) Rocky planets
(Mercury, Venus, Mars, Earth):

-Relatively small
-Solid
-Mantle – crudely, $MgSiO_3$
-Core – Fe with impurities (~20 мол.%)
-Earth's center – 364 GPa, 6000 K.

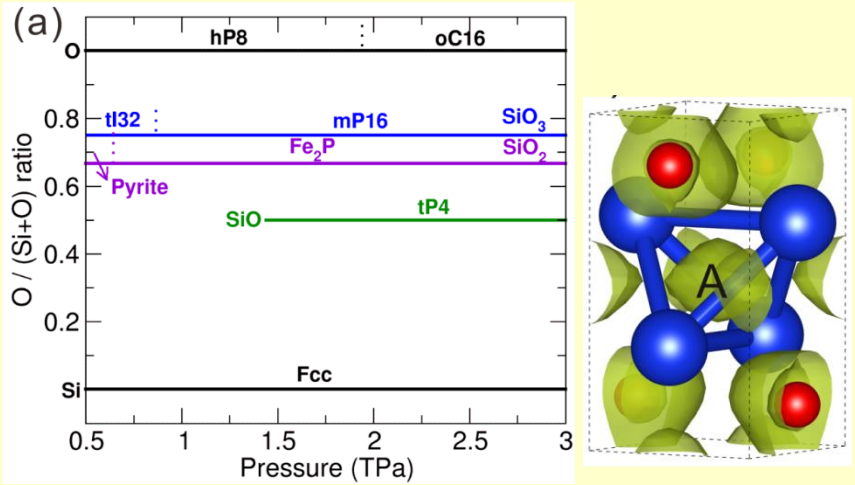
(2) Gas giants:

-Large
-Fluid
-Composition:
Jupiter, Saturn - H+He
Uranus, Neptune – H_2O+CH_4+NH_3
-Jovian center – 50000 GPa (?), 24000 K (?).

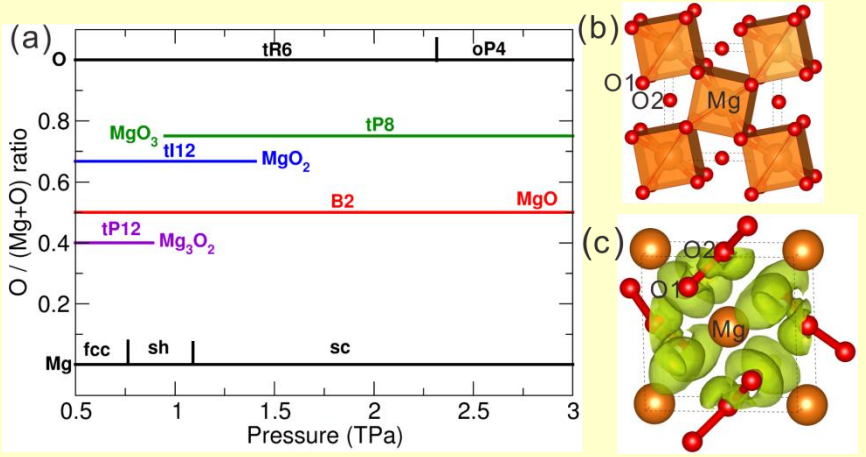
(3,4,...) Exoplanets: gas giants, superearths, diamond planets

Super-Earths

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



Phase diagram of Si-O system and structure of SiO (Niu & Oganov, 2015)



Phase diagram of Mg-O system and structure of MgO_3 (Niu & Oganov, 2015; Zhu & Oganov, 2013)

Experiment:
[Lobanov S. et al., *Sci. Rep.* 5, 13582 (2015)].

Niu H., Oganov A.R., Chen X., Li D., *Sci. Rep.* 5, 18347 (2015).
Zhu Q., Oganov A.R., Lyakhov A.O., *Phys. Chem. Chem. Phys.* 15, 7796-7700 (2013).

Super-Earths

At ultrahigh pressures $MgSiO_3$ post-perovskite decomposes

$$MgSiO_3 \rightarrow Mg_2SiO_4 + MgSi_2O_5 \rightarrow Mg_2SiO_4 + SiO_2 \rightarrow MgO + SiO_2 \ (T < 6500\ K)$$

$$MgSiO_3 \rightarrow Mg_2SiO_4 + MgSi_2O_5 \rightarrow MgSi_2O_5 + MgO \rightarrow MgO + SiO_2 \ (T > 6500\ K)$$

Multistage decomposition implies complex structure of super-Earths
[Niu H., Oganov A.R., Chen X., Li D., *Sci. Rep.* 5, 18347 (2015)].

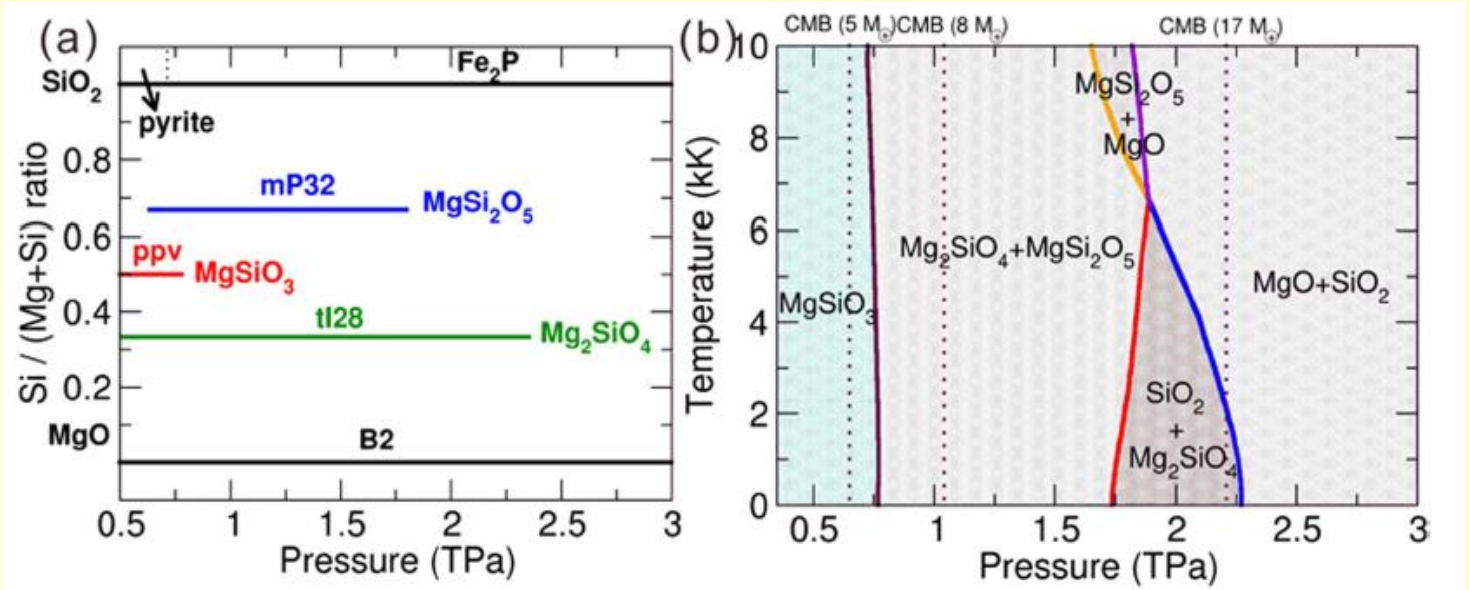
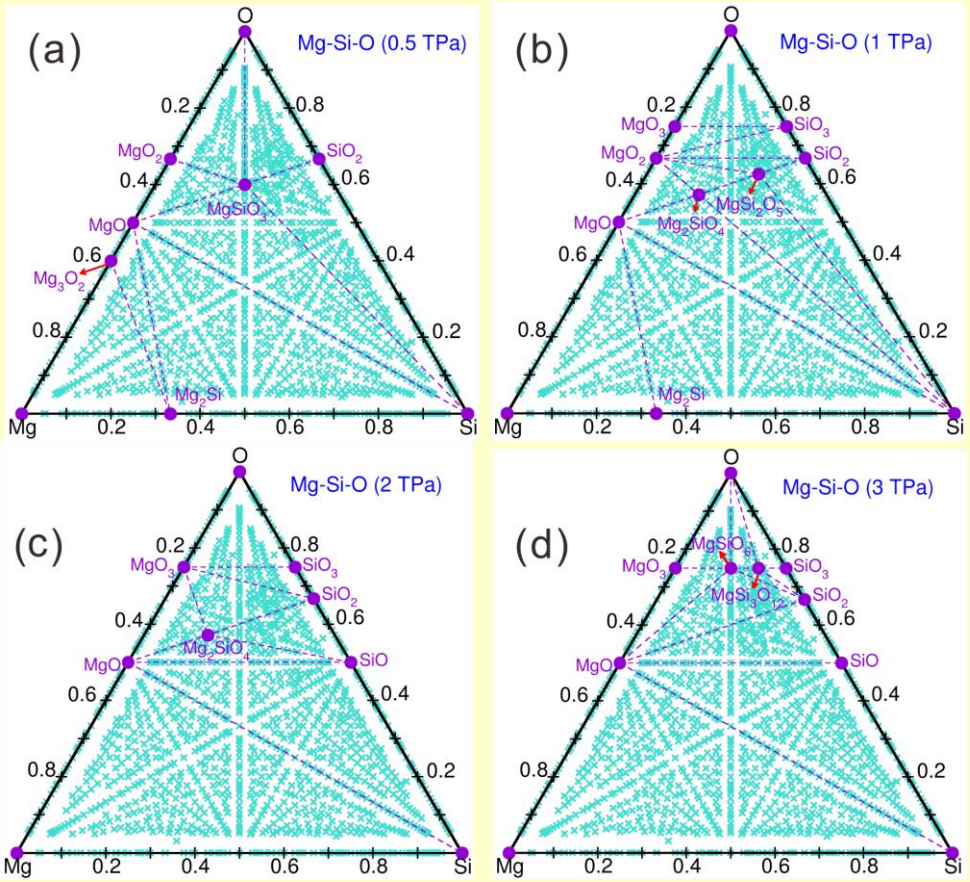


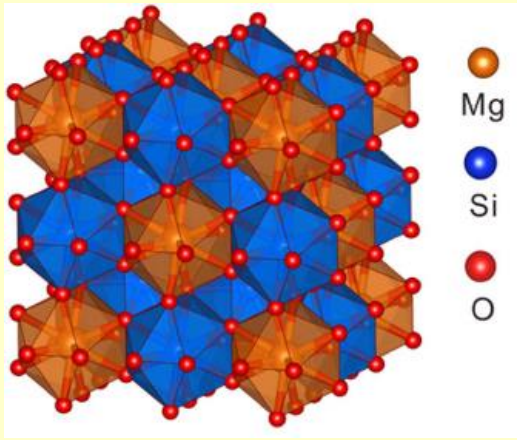
Figure 4. (a) Pressure-composition phase diagram of the pseudo-binary MgO-SiO_2 system. (b) *P-T* phase diagram of $MgSiO_3$. The core-mantle boundary (CMB) pressures of super-Earths and mega-Earths with 5, 8 and 17 $M_\oplus$ are also plotted by vertical dashed lines.

“Forbidden” $MgSi_3O_{12}$ and $MgSiO_6$ are stable at pressures of mantles of super-Earths

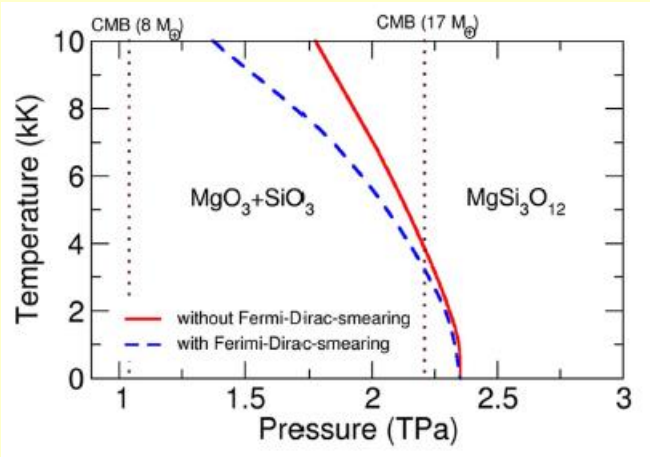
Super-Earths



Phase diagram of Mg-Si-O system [Niu H., Oganov A.R., Chen X., Li D., *Sci. Rep.* 5, 18347 (2015)].

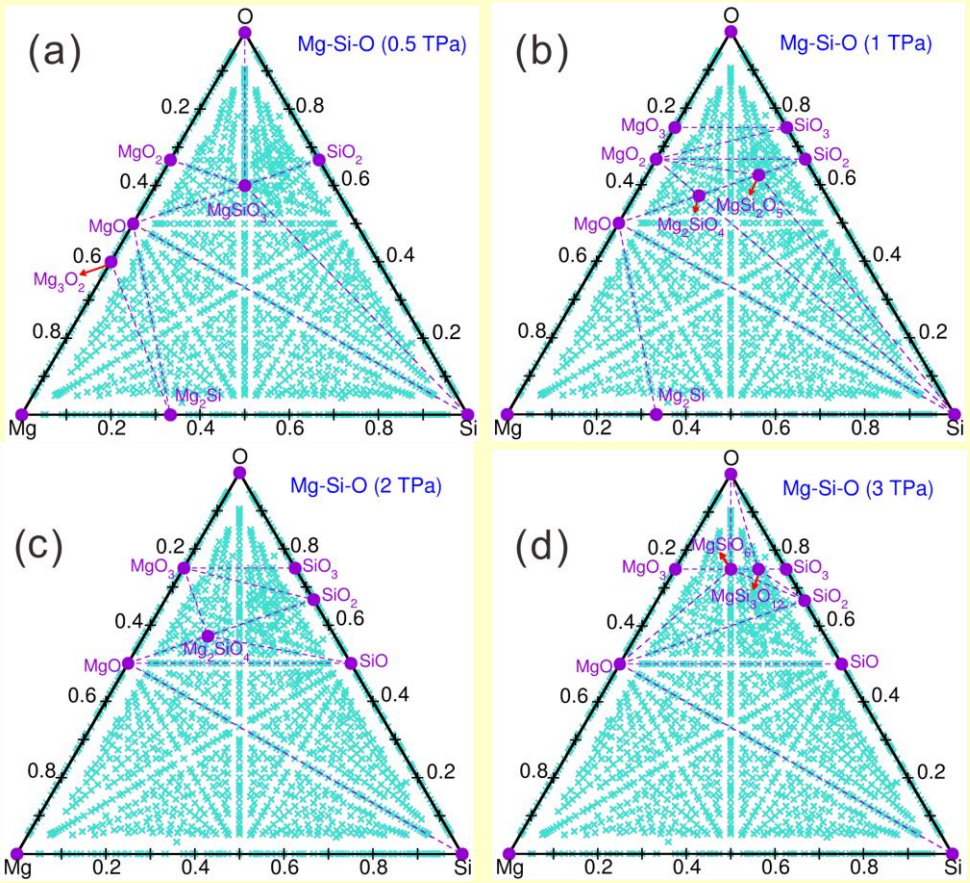


Structure of $MgSi_3O_{12}$

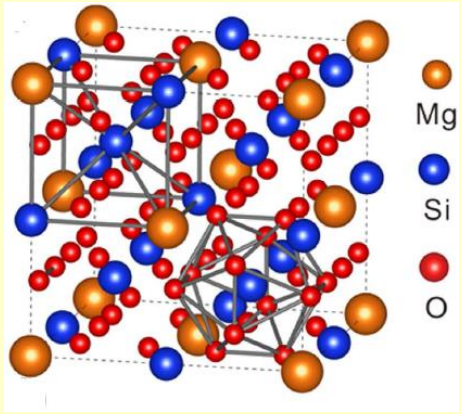


Phase diagram of $MgSi_3O_{12}$

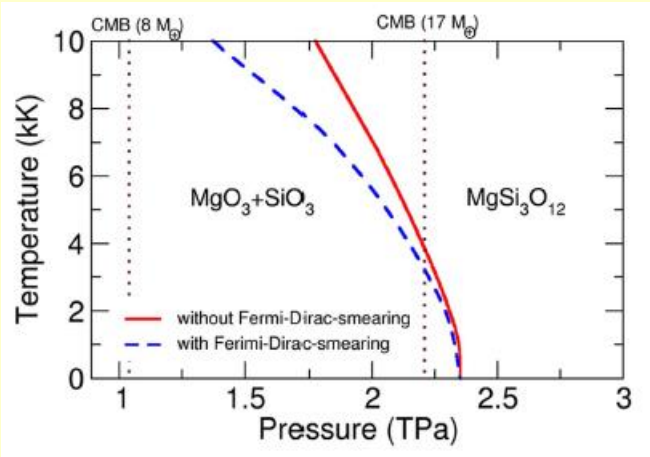
Mg-Si-O system: $MgSi_3O_{12}$ and $MgSiO_6$ in planetary mantles and cores?



Phase diagram of the Mg-Si-O system (Niu & Oganov, *Sci. Rep.* 2015)



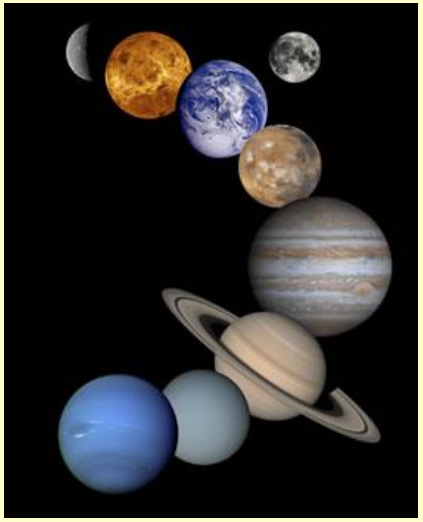
Structure of $MgSi_3O_{12}$



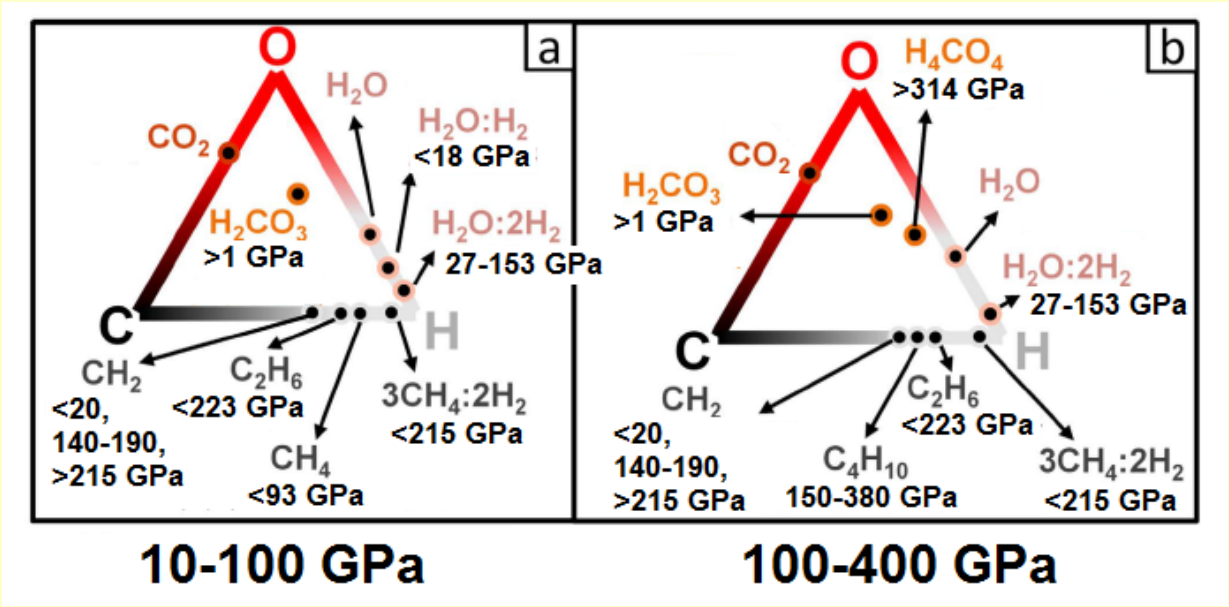
Stability of $MgSi_3O_{12}$

Uranus, Neptune

C-H-O system under pressure



- Uranus and Neptune: $H_2O:CH_4:NH_3$ = 59:33:8.
- Temperature in the center – 5500 K, pressure – 800 GPa.



- Ice H_2O and CO_2 are stable at all pressures.
- Methane CH_4: decomposes above 93 GPa. Ethane, butane, polyethylene stable.
- Carbonic acid H_2CO_3 stable at >1 GPa polymeric at >44 GPa.

Experimental confirmation: Wang H., et al., *Sci. Rep.* 6, 19902 (2016).

- Orthocarbonic acid H_4CO_4 is stable at >314 GPa.

[Saleh G., Oganov A.R, *Sci. Rep.* 6, 32486 (2016)]

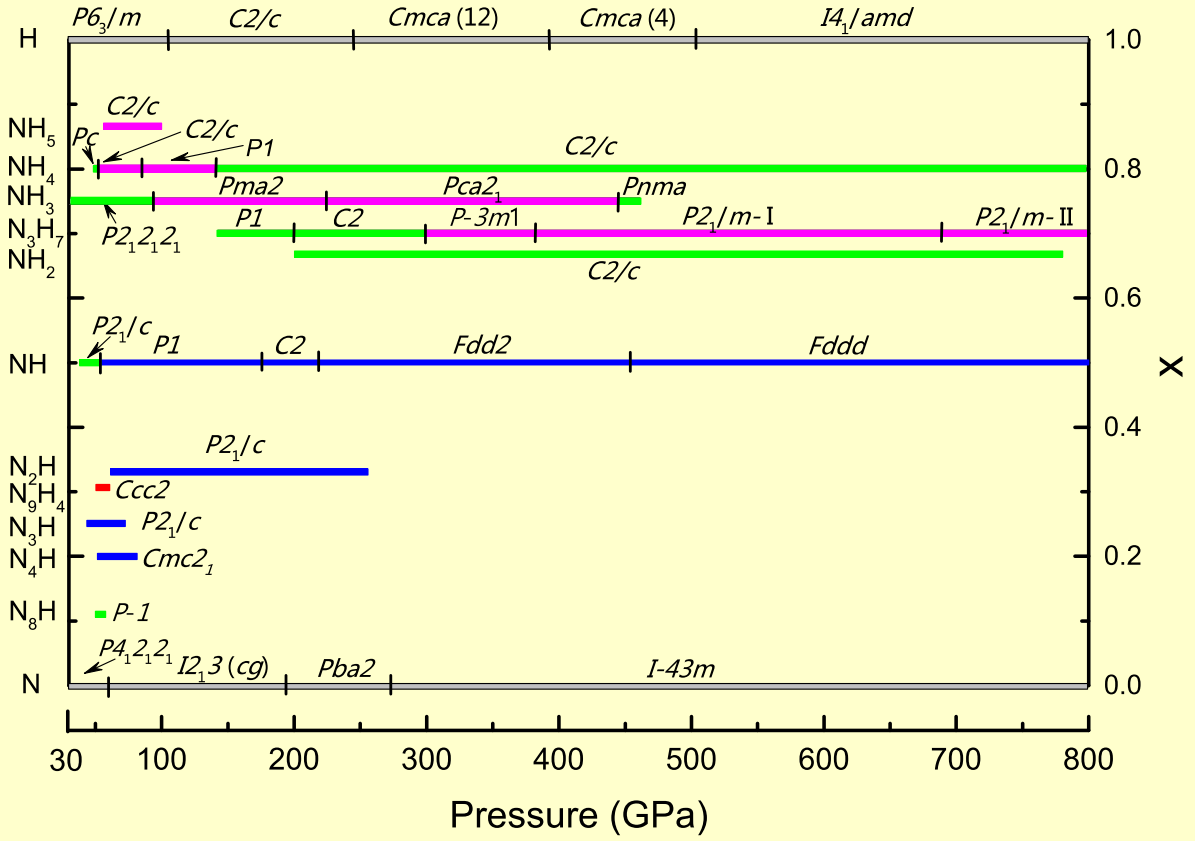
High-pressure hydronitrogens (Qian, Oganov, 2016)

Uranus, Neptune

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

Green: molecular

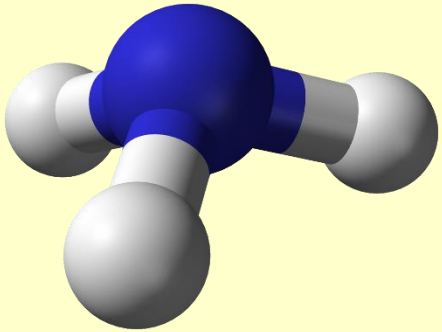
Purple: molecular ionic



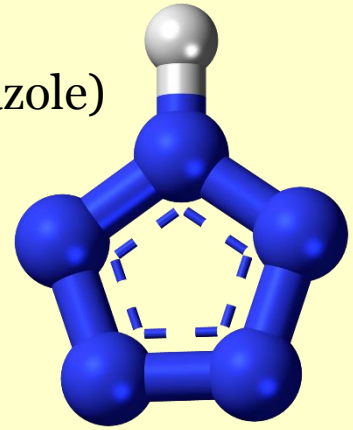
Uranus, Neptune

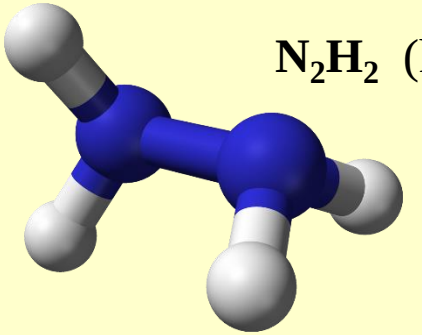
Hydronitrogen at ambient pressure

NH_3 (ammonia)

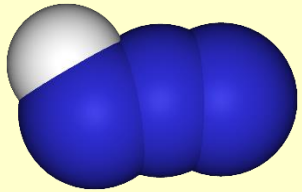


N_5H (pentazole)





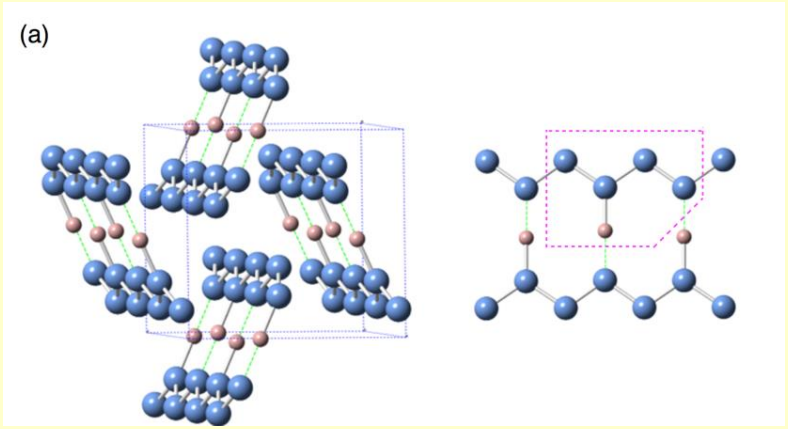
N_2H_2 (hydrazine)



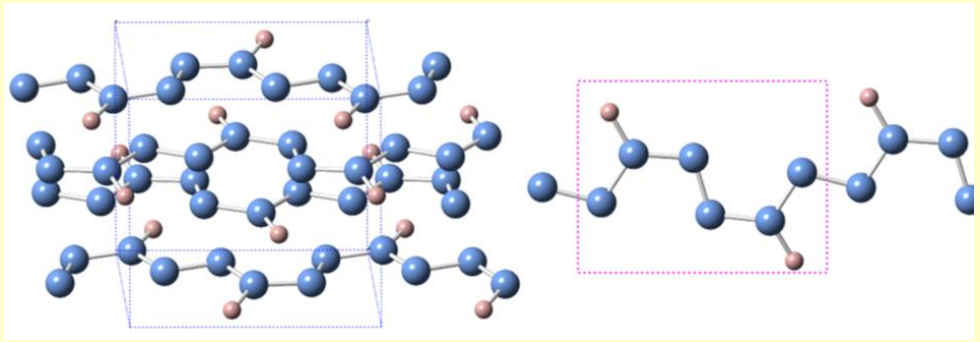
HN_3 (hydrazoic acid)

High-pressure hydronitrogens

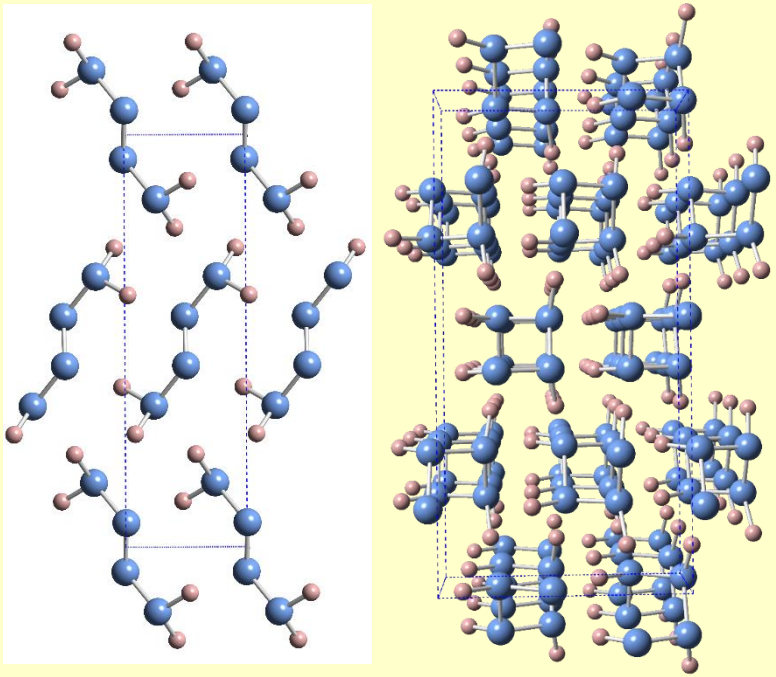
Uranus, Neptune



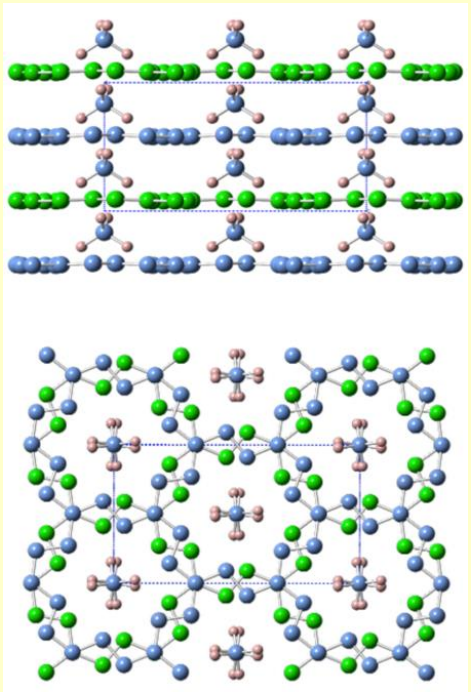
N_4H



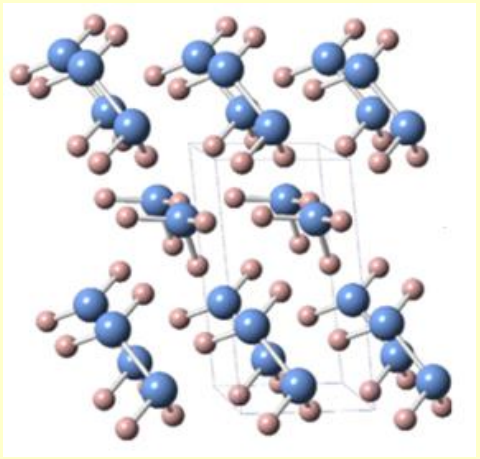
N_3H



NH



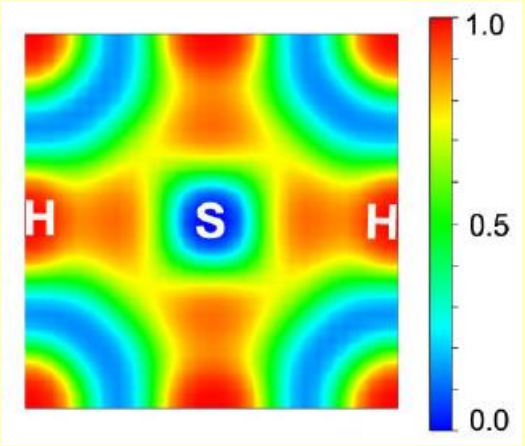
N_4H_9



N_3H_7

Highest-Tc superconductivity: new record, 203 Kelvin

H-S



OPEN

SUBJECT AREAS:
THEORY AND COMPUTATION
CONDENSED MATTER PHYSICS

Received
7 July 2014

Accepted
29 September 2014

Published
10 November 2014

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Pressure-induced metallization of dense $(H_2S)_2H_2$ with high-T_c superconductivity

Defang Duan[1,2], Yunxian Liu[1], Fubo Tian[1], Da Li[1], Xiaoli Huang[1], Zhonglong Zhao[1], Hongyu Yu[1], Bingbing Liu[1], Wenjing Tian[2] & Tian Cui[1]

[1]State Key Laboratory of Superhard Materials, College of physics, Jilin University, Changchun, 130012, P. R. China, [2]State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, 130012, P. R. China.

The high pressure structures, metallization, and superconductivity of recently synthesized H_2-containing compounds $(H_2S)_2H_2$ are elucidated by *ab initio* calculations. The ordered crystal structure with *P*1 symmetry is determined, supported by the good agreement between theoretical and experimental X-ray diffraction data, equation of states, and Raman spectra. The *Cccm* structure is favorable with partial hydrogen bond symmetrization above 37 GPa. Upon further compression, H_2 molecules disappear and two intriguing metallic structures with *R*3*m* and *Im*-3*m* symmetries are reconstructive above 111 and 180 GPa, respectively. The predicted metallization pressure is 111 GPa, which is approximately one-third of the currently suggested metallization pressure of bulk molecular hydrogen. Application of the Allen-Dynes-modified McMillan equation for the *Im*-3*m* structure yields high T_c values of 191 K to 204 K at 200 GPa, which is among the highest values reported for H_2-rich van der Waals compounds and MH_3 type hydride thus far.

Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin

Nature (2015) | doi:10.1038/nature14964
Received 25 June 2015 | Accepted 22 July 2015 | Published online 17 August 2015

A superconductor is a material that can conduct electricity without resistance below a superconducting transition temperature, T_c. The highest T_c that has been achieved to date is in the copper oxide system[1]: 133 kelvin at ambient pressure[2] and 164 kelvin at high pressures[3]. As the nature of superconductivity in these materials is still not fully understood (they are not conventional superconductors), the prospects for achieving still higher transition temperatures by this route are not clear. In contrast, the Bardeen–Cooper–Schrieffer theory of conventional superconductivity gives a guide for achieving high T_c with no theoretical upper bound—all that is needed is a favourable combination of high-frequency phonons, strong electron–phonon coupling, and a high density of states[4]. These conditions can in principle be fulfilled for metallic hydrogen and covalent compounds dominated by hydrogen[5, 6], as hydrogen atoms provide the necessary high-frequency phonon modes as well as the strong electron–phonon coupling. Numerous calculations support this idea and have predicted transition temperatures in the range 50–235 kelvin for many hydrides[7], but only a moderate T_c of 17 kelvin has been observed experimentally[8]. Here we investigate sulfur hydride[9], where a T_c of 80 kelvin has been predicted[10]. We find that this system transforms to a metal at a pressure of approximately 90 gigapascals. On cooling, we see signatures of superconductivity: a sharp drop of the resistivity to zero and a decrease of the transition temperature with magnetic field, with magnetic susceptibility measurements confirming a T_c of 203 kelvin. Moreover, a pronounced isotope shift of T_c in sulfur deuteride is suggestive of an electron–phonon mechanism of superconductivity that is consistent with the Bardeen–Cooper–Schrieffer scenario. We argue that the phase responsible for high-T_c superconductivity in this system is likely to be H_3S, formed from H_2S by decomposition under pressure. These findings raise hope for the prospects for achieving room-temperature superconductivity in other hydrogen-based materials.

Prior record Tc=135 K (Putilin, Antipov, 1993) is broken: theorists (T. Cui, 2014) predicted new compound H_3S with Tc~200 K. Confirmed by A.Drozdov (Nature, 2015).

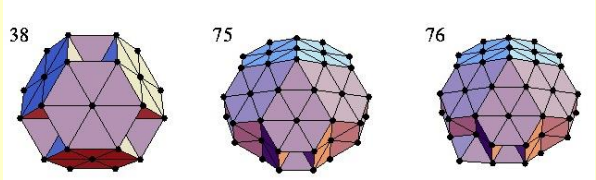
0D-materials (nanoparticles) also display unexpected chemistry

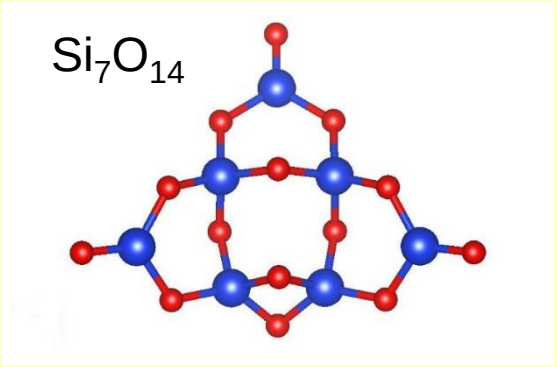
Performance of USPEX and other methods for Lennard-Jones clusters (Lyakhov & Oganov, *Comp.Phys.Comm.* 2013)

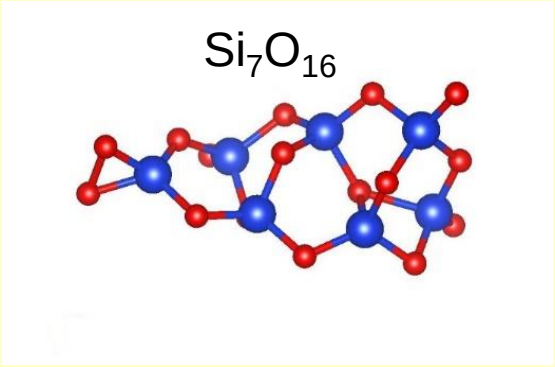
Statistics for Lennard-Jones clusters with different algorithms. Best algorithms are highlighted in bold.

	Success rate (%)	Average number of structures until global minimum is found	Dispersion	Number of calculations
LJ_{38} (PSO [48])	100	605	N/a	100
LJ_{38}(USPEX)	**100**	**35**	**58**	**183**
LJ_{38} (EA [46])[b]	N/a	1265	N/a	100
LJ_{38} (MH [46])[b]	100	1190	N/a	100
LJ_{38} (EA [47])[b]	N/a	~2000[a]	N/a	N/a
LJ_{38} (PSO [48])	100	1649	N/a	20
LJ_{55} (PSO [48])	100	159	N/a	100
LJ_{55}(USPEX)	**100**	**11**	**30**	**60**
LJ_{55} (EA [46])[b]	100	100	N/a	100
LJ_{55} (MH [46])[b]	100	190	N/a	100
LJ_{75} (PSO [48])	98	2858	N/a	50
LJ_{75}(USPEX)	**100**	**2145**	**2024**	**53**

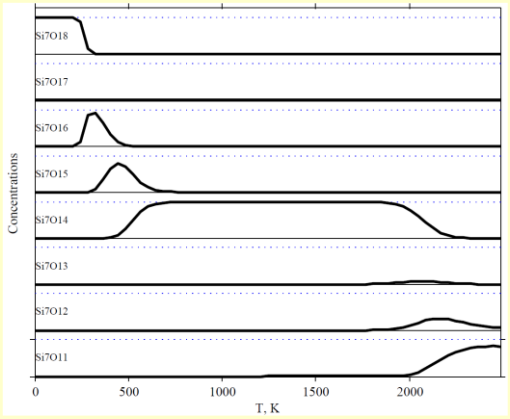
PSO = Particle Swarm Optimization
MH = Minima Hopping
EA = Evolutionary Algorithm







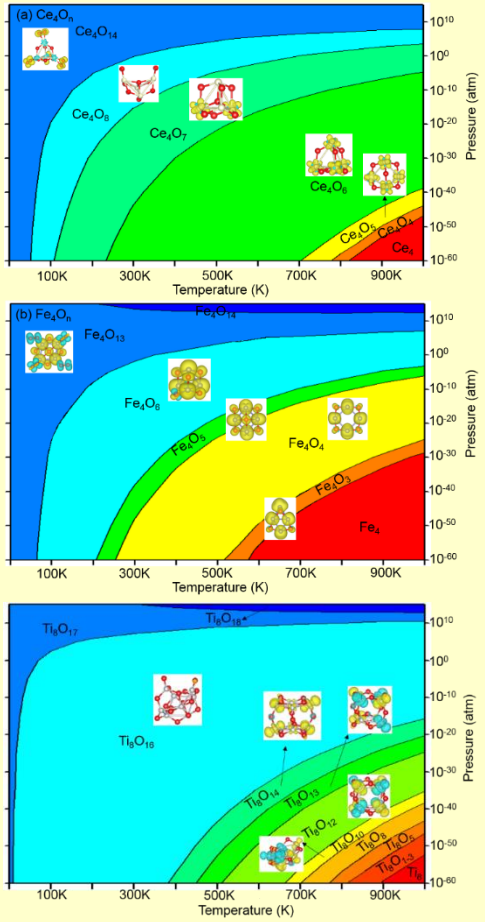
Peroxo-group!
Dominant at T=300 K, $P(O_2)$=1 atm



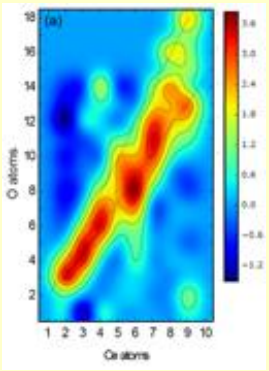
Predicted abundances of nanoparticles

Aromaticity of “magic” clusters

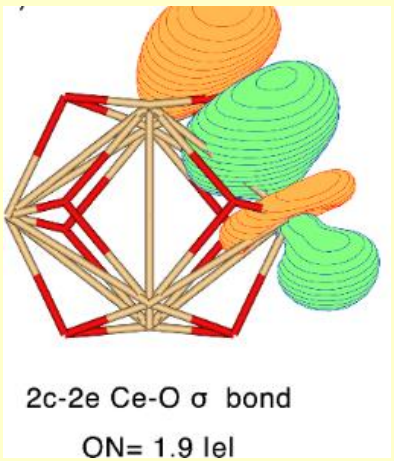
(Yu & Oganov, *J. Comp. Chem.* 2015; *Angew. Chem.* 2016)



Phase diagrams of Ce_6O_n, Fe_4O_n, Ti_8O_n clusters.



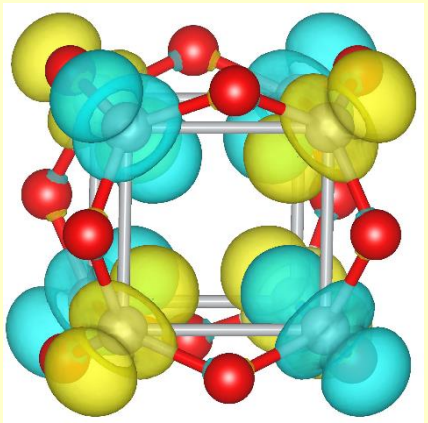
Magic clusters = islands of stability



Natural bond orbitals in Ce_6O_8:

a) 2-center σ-bond Ce-O;

b) 6-center d-orbital bond.

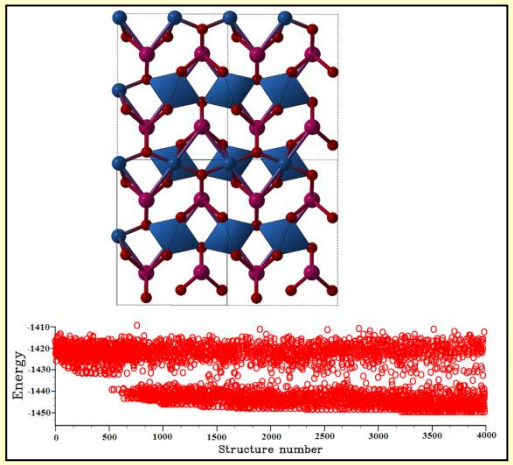


Spin density in Ti_8O_{12}

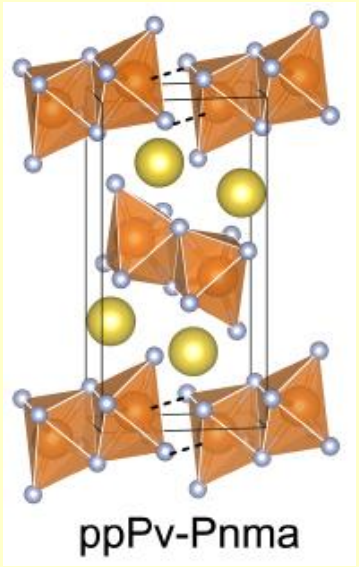
Ce_6O_8 – first example of spherical d-aromaticity

Ti_8O_{12} – first example of small antiferromagnetic cluster

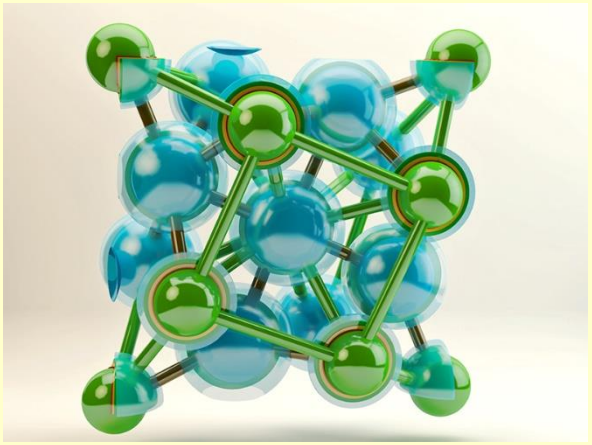
With novel predictive methods, we get a powerful tool to look inside the planets – and there is much to explore!



1. Predicting crystal structures by evolution



2. Predicting planetary mineralogy



3. Discovering novel chemistry

The team.

Where great minds do NOT think alike

USPEX Computational Materials Discovery

Experimental confirmation:

A. Goncharov

M. Eremets