high-pressure

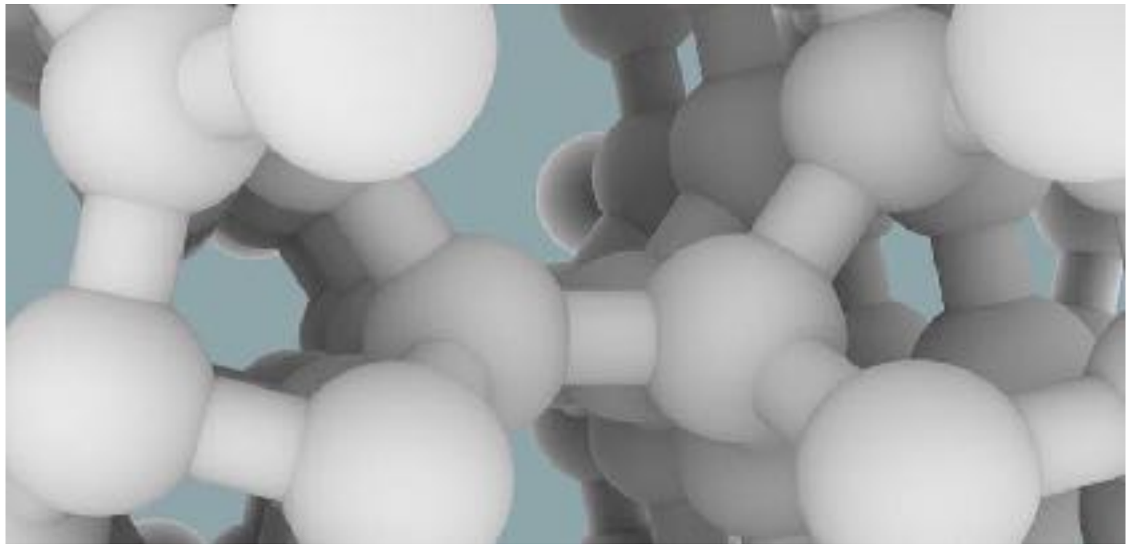
Computational condensed matter physics

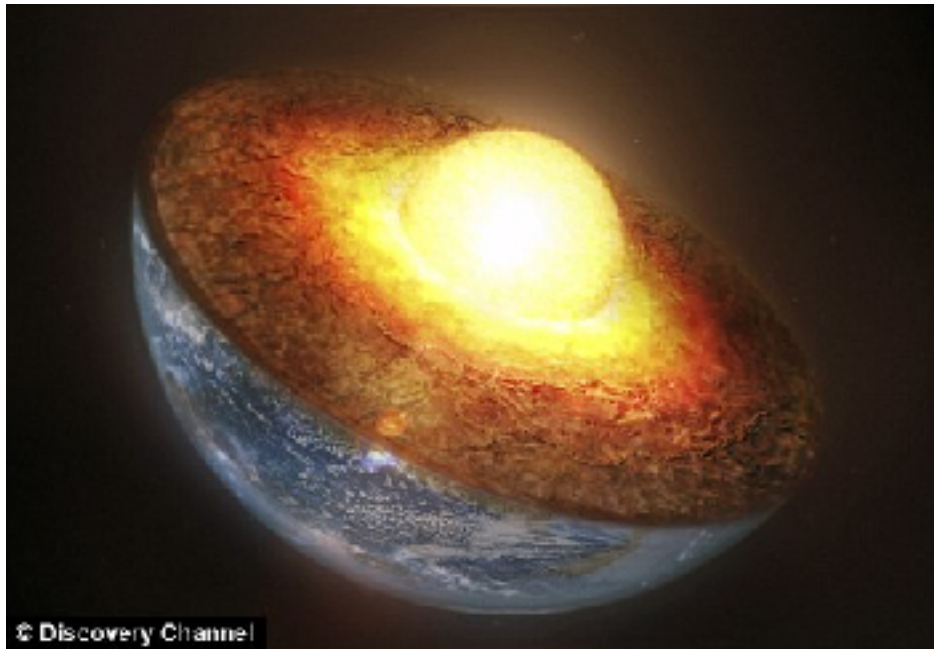
Novel oxidation state of iron, peroxide FeO_2: Understanding physical properties and implication to geoscience

crystal structure searching

Geoscience

Duck Young Kim





2018 Beijing univ.

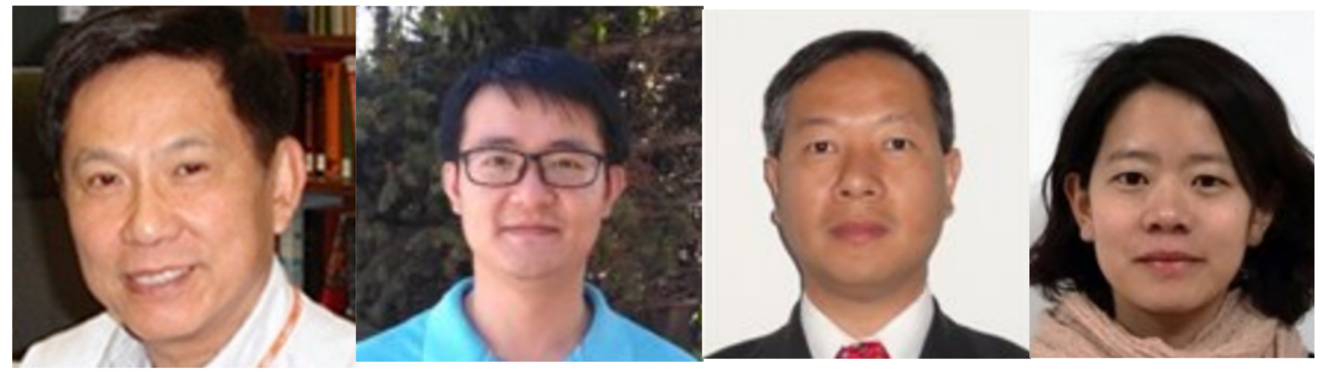
Collaborations

FeO_2H_x experimental synthesis

Center for High Pressure Science &Technology Advanced Research
HPSTAR

National Natural Science Foundation of China

Stanford University



Computational study of correlation effect of FeO_2

POSTECH

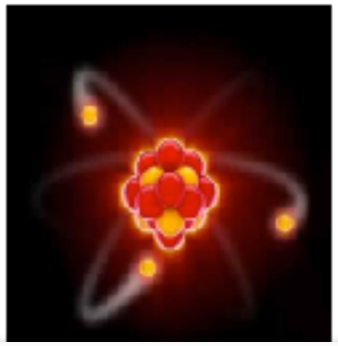
Material – plasma interaction experiment

Computational Crystal Structure Prediction

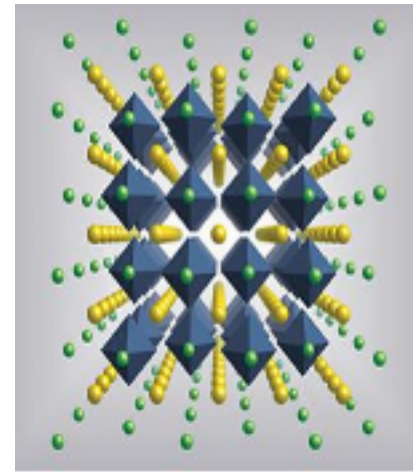
UNIVERSITY OF CAMBRIDGE

Center for High Pressure Science & Technology Advanced Research

HPSTAR



Top 1000-Talents Award



high pressure energy

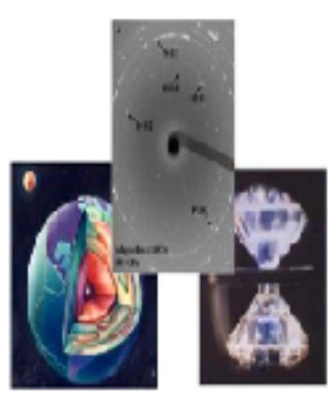
high pressure functional materials

The mission of HPSTAR is to become a world-leading research center in high-pressure research and to impact multidisciplinary physical sciences. HPSTAR provides ample research funding, advanced facilities, and open, liberal, collaborative research environment. Scientists of HPSTAR have the total freedom to define their research goals, paths, teams, and collaborations in China and abroad. They will be able to fully devote their time, efforts, and creativity to pursue individual scientific dreams.

high pressure chemistry

high pressure nano science

Superhard material

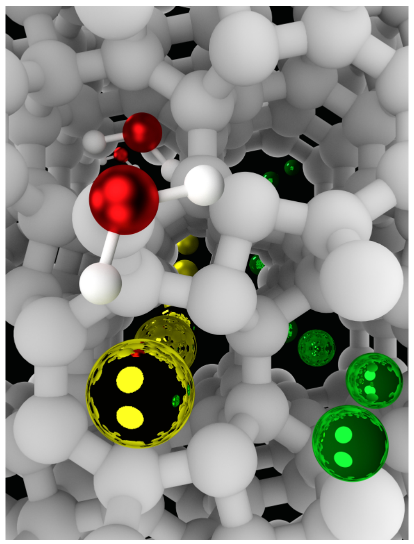


Earth & planetary sciences

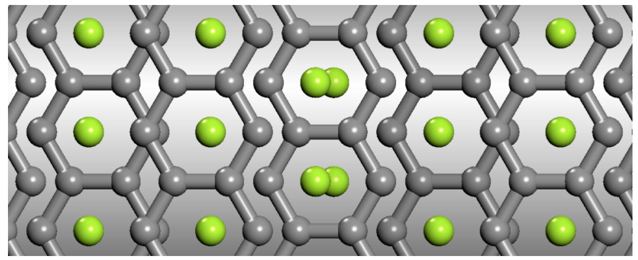
High Pressure Technology

High Pressure Synchrotron Sources

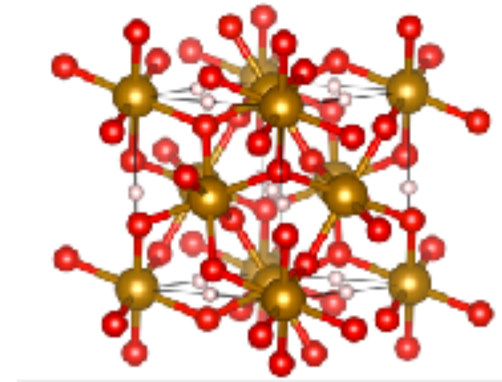
Computational theory group in HPSTAR



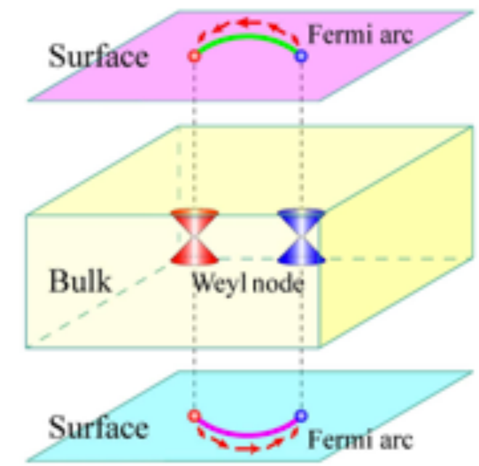
New silicon



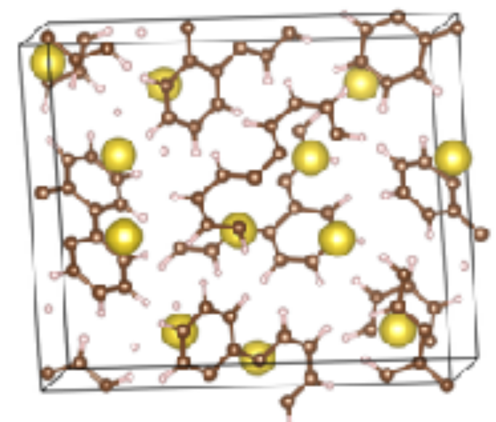
New Carbide



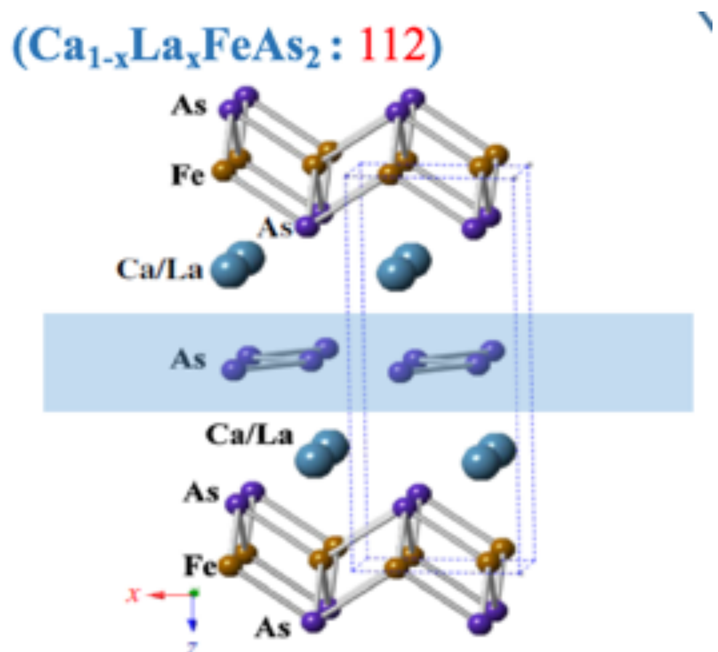
FeO_2



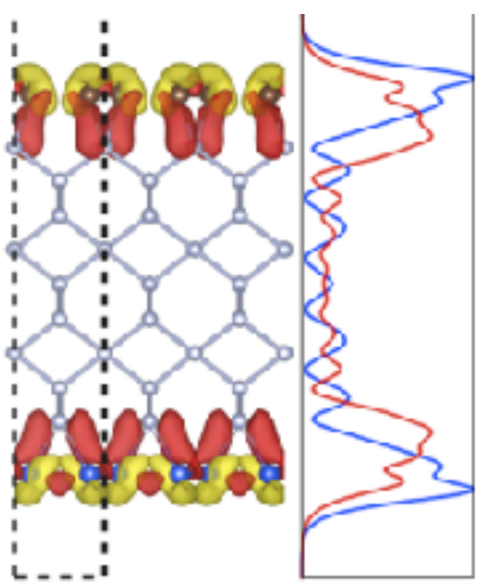
TI under pressure



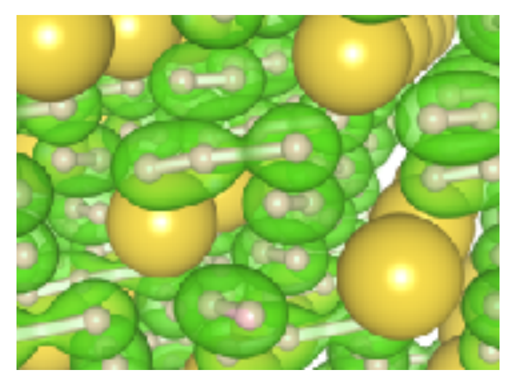
Organic superconductivity



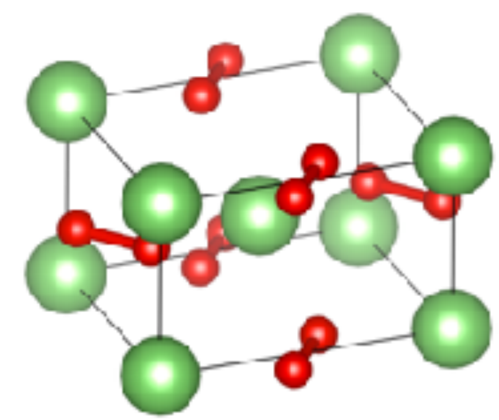
FeAs superconductivity



artificial low dim. materials



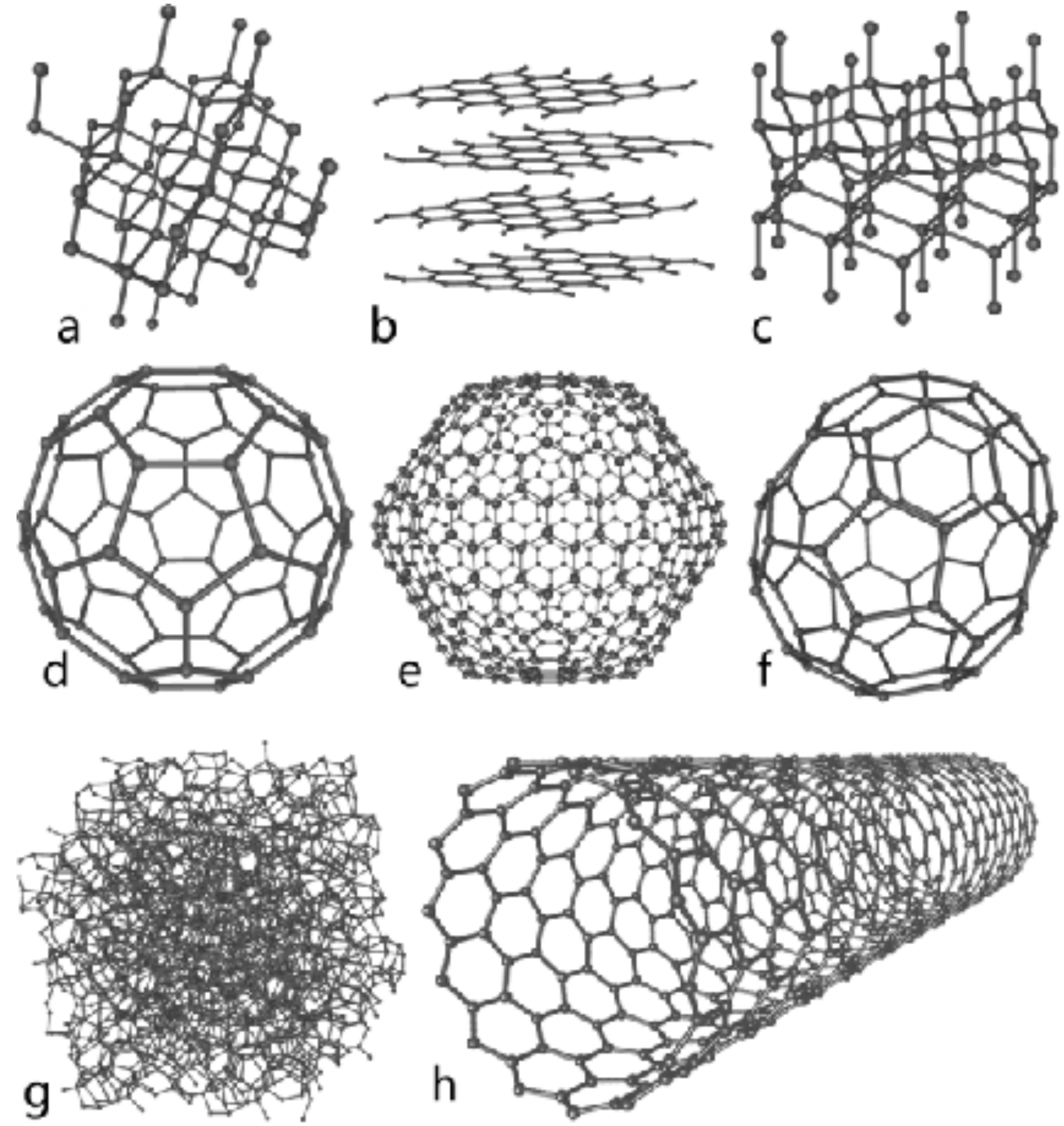
Hydrides under pressure



New superoxide

Under Pressure, graphite turns into diamond

sp^3 diamond *sp*^{2} graphite

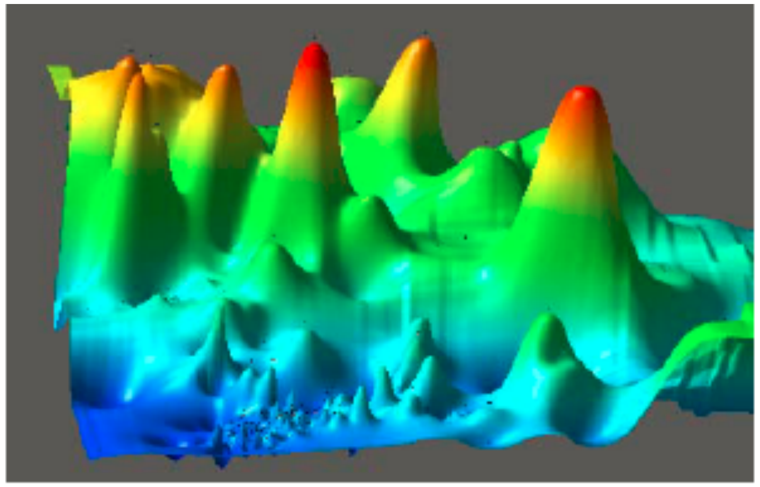


@ ambient conditions

1. Graphite is the ground state
2. Diamond is very stable
3. Many metastable phases coexist

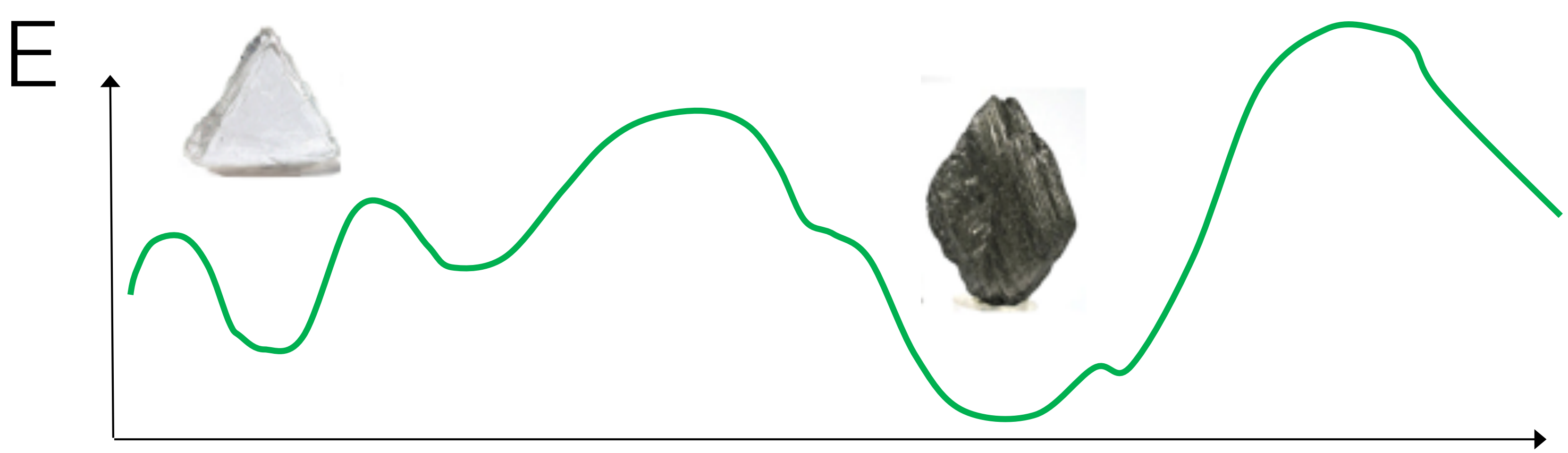
Energy Landscape changes with pressure

Enthalpy



Real landscape is multi-dimensional

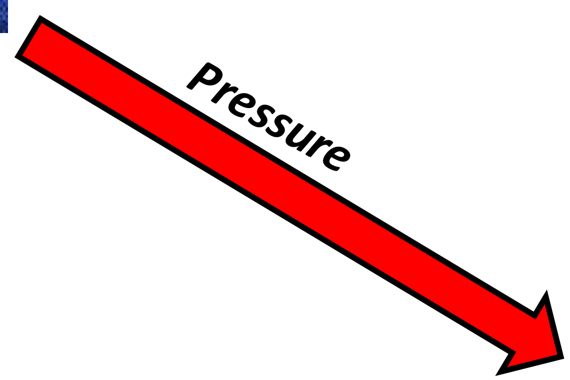
Low pressure



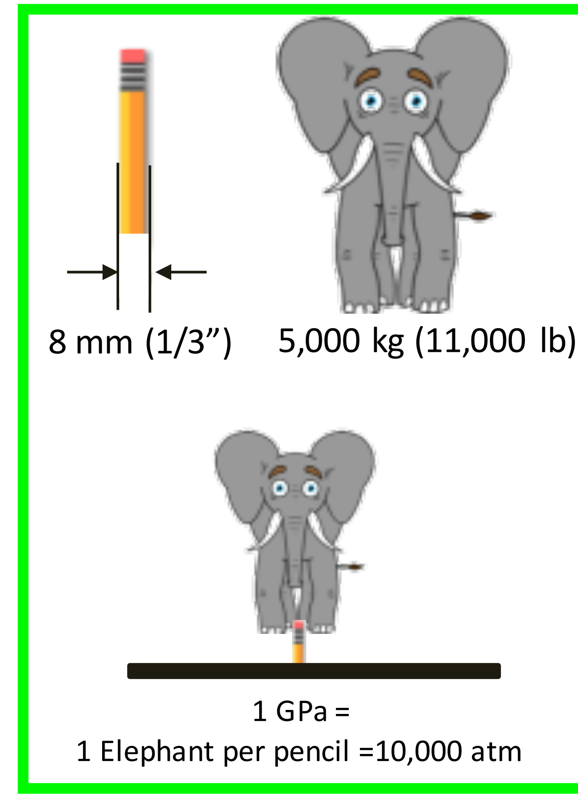
High pressure

Pressure induces structural transformation

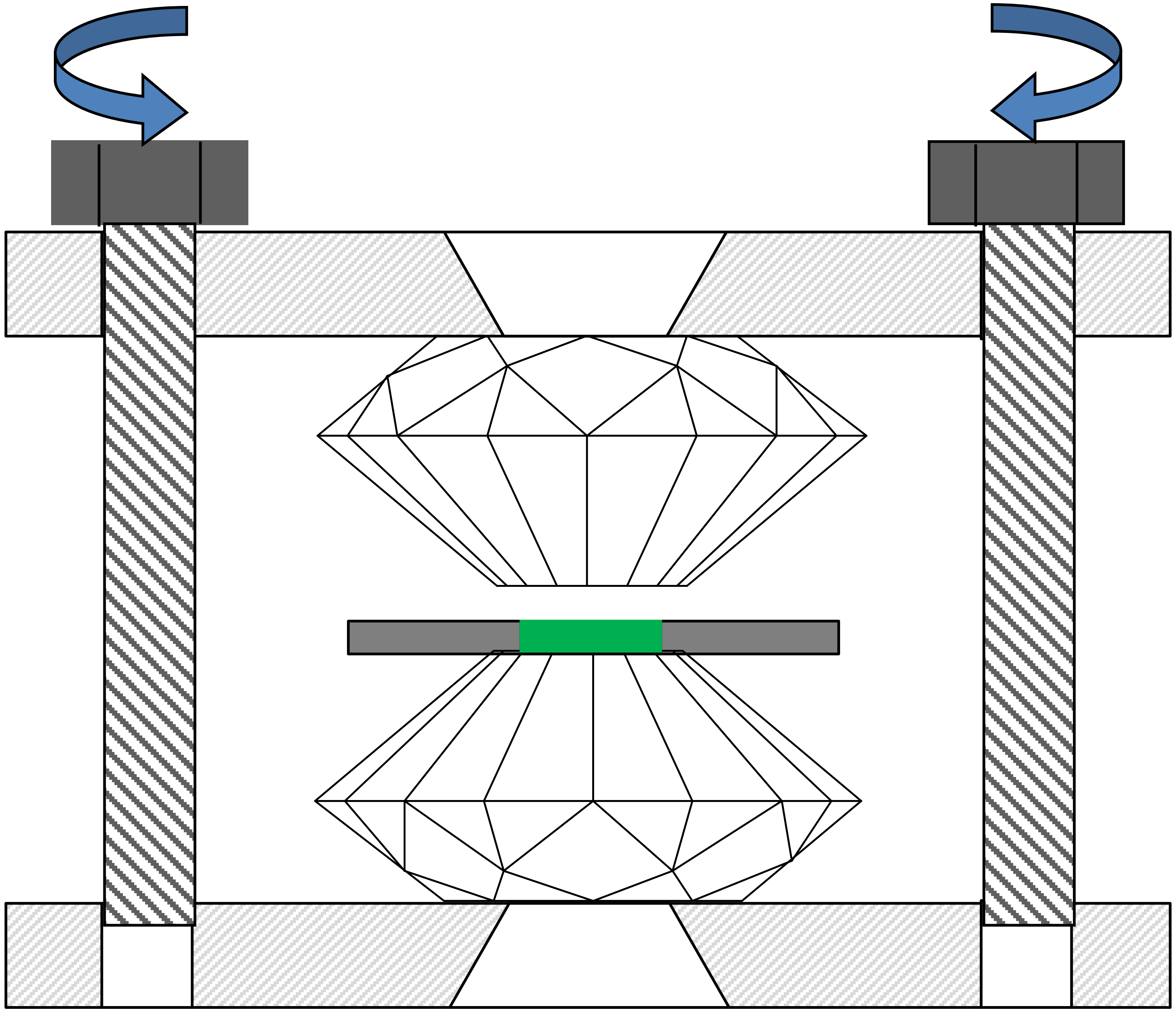
GRAPHITE
- *hexagonal crystal*
- *Black and opaque*
- *Very soft*
- *electrical conductor*
- *thermally insulating*

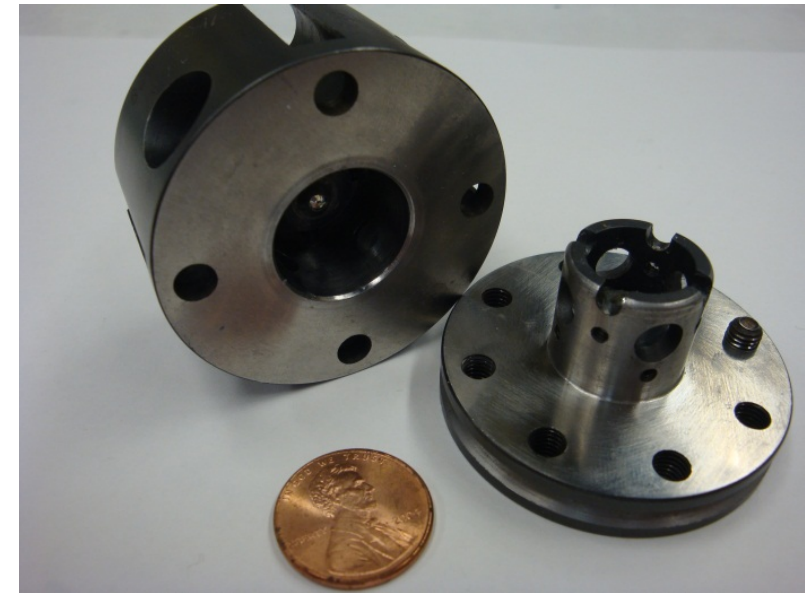


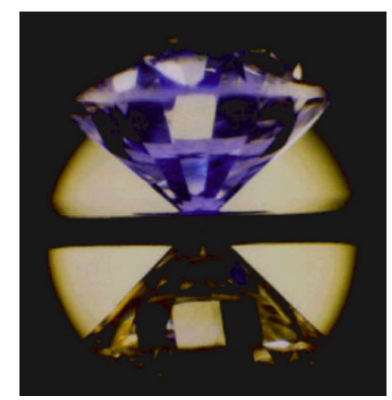
DIAMOND
- *Cubic crystal*
- *Clear and transparent*
- *Hardest mineral known*
- *electrical insulator*
- *Highest thermal conductivity*

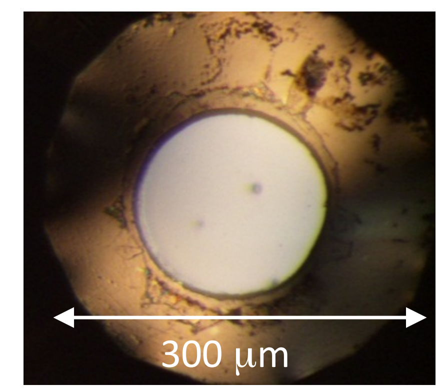


Diamond anvil cell (exp.)

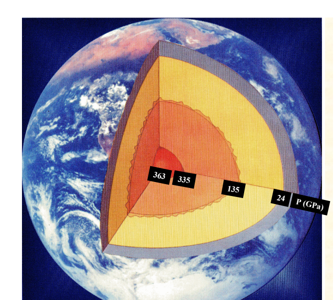








1×10^{-5} mm^3 @ 100 GPa
(very thin slice of hair)



Center of the earth = 360 GPa

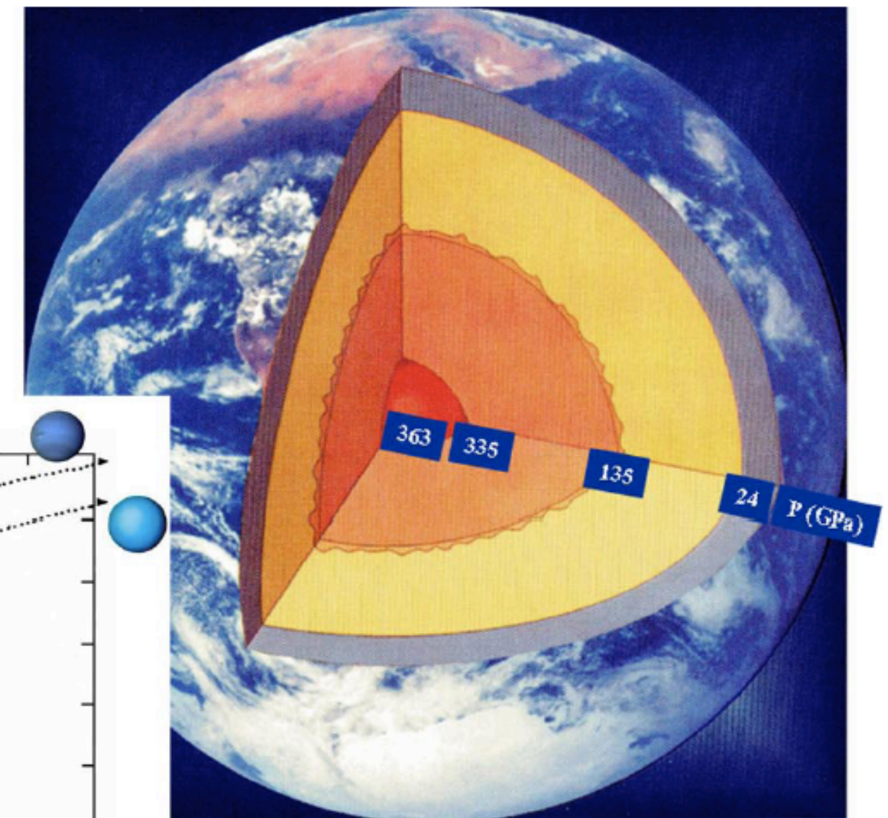
Pressure ranges

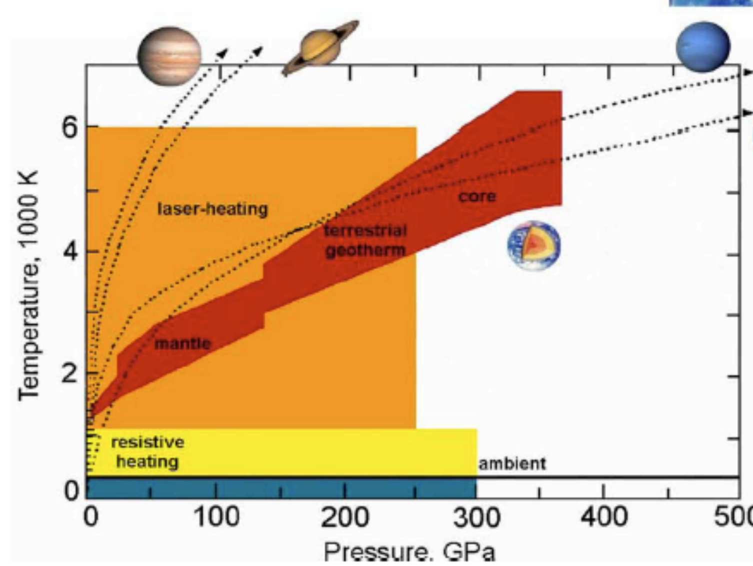
1 GPa = 10 kbar ≈10^4 atm

At the center of Earth ~ 350 GPa

At the center of Jupiter ~ 7 TPa

At the center of some exoplanet ~ 100 TPa





What is possible in the lab ?

Current maximum pressure in DAC ~ 350 GPa

Can achieve multi-TPa in shock-wave experiments

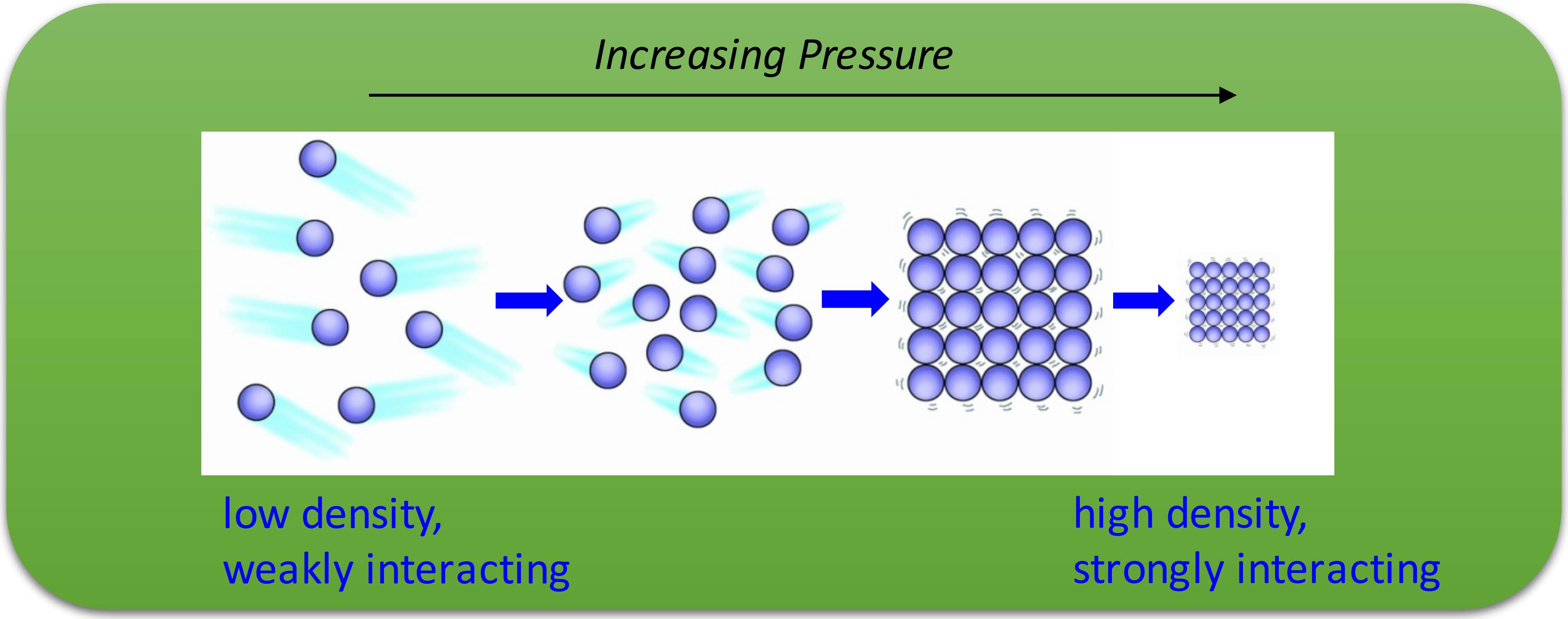
Aluminum subjected to 400 TPa in underground nuclear explosion

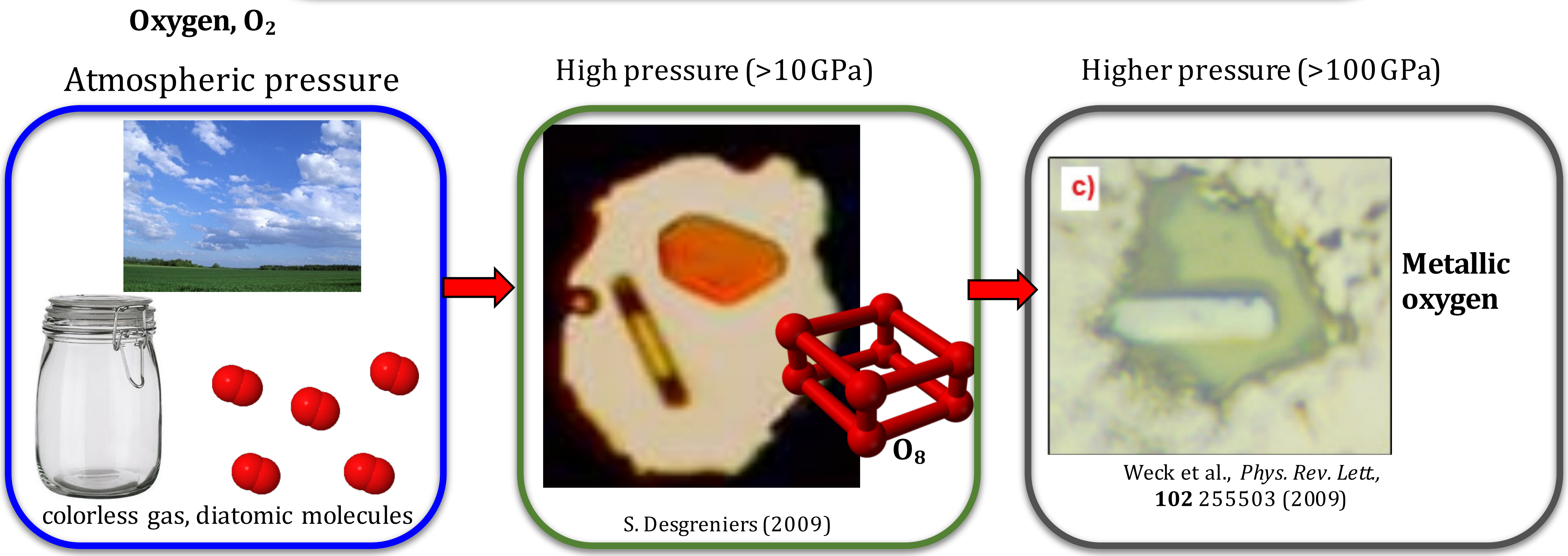
Development of apparatus for multi-TPa experiment, laser driven shock wave pre-compression, National Ignition Facility (NIF) etc

Conventional wisdom for elements is

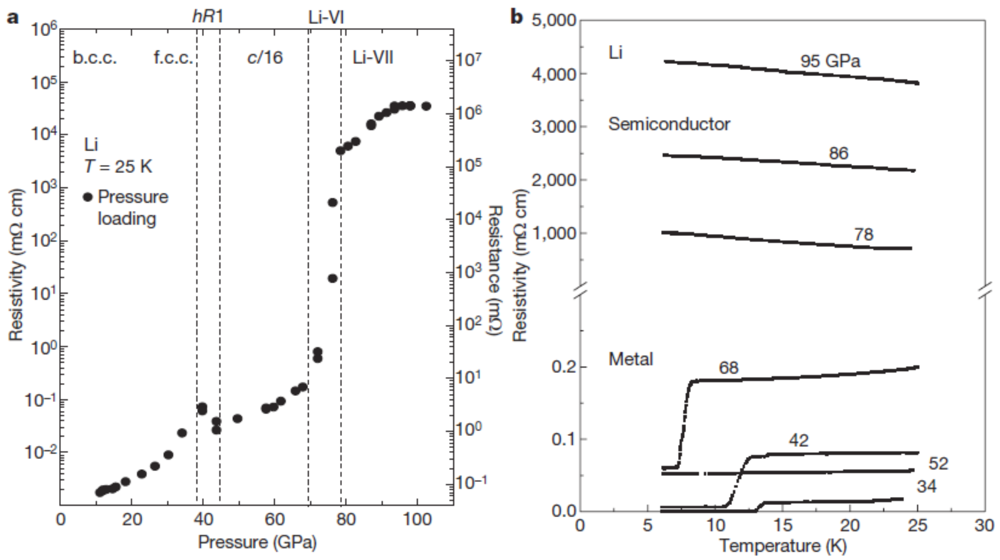
Group→ ↓Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Oxygen is a superconducting metal under compression

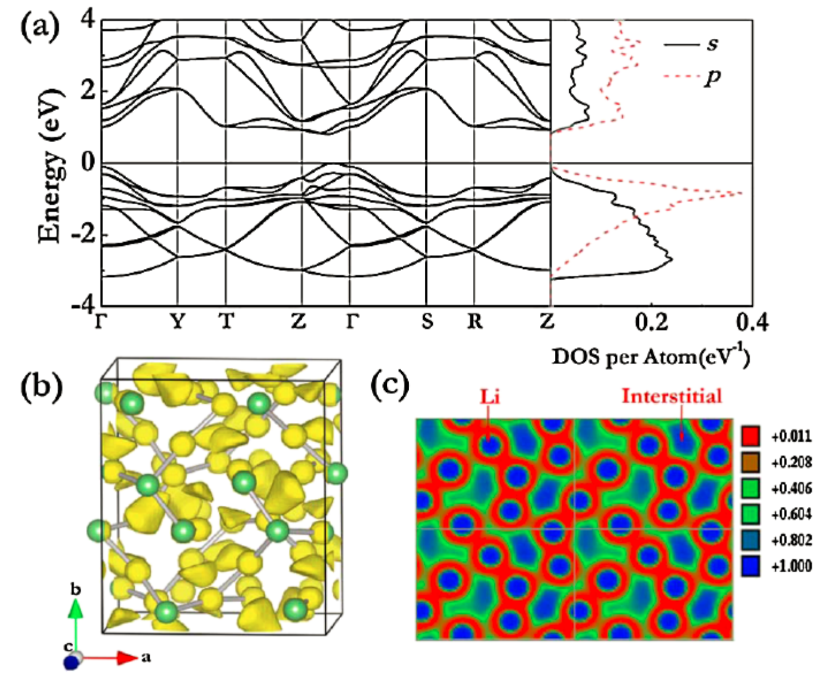




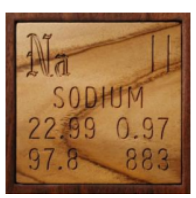
Alkali metals are insulators under compression

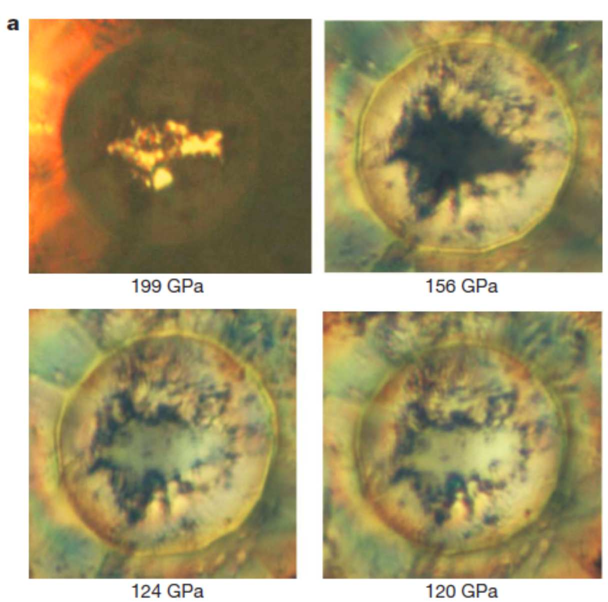


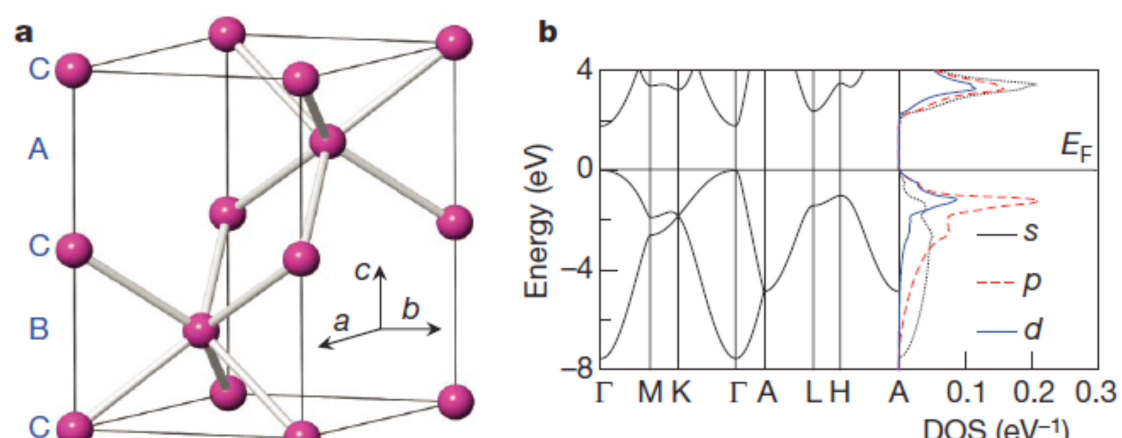
Nature **458** 186 (2009)



Phys. Rev. Lett. **106** 015503 (2011)







Nature **458** 182 (2009)

- Under pressure, it is common to find unexpected physical properties of most elements
- Atomic configuration determines materials property

Highest superconductivity Tc of elements under pressure

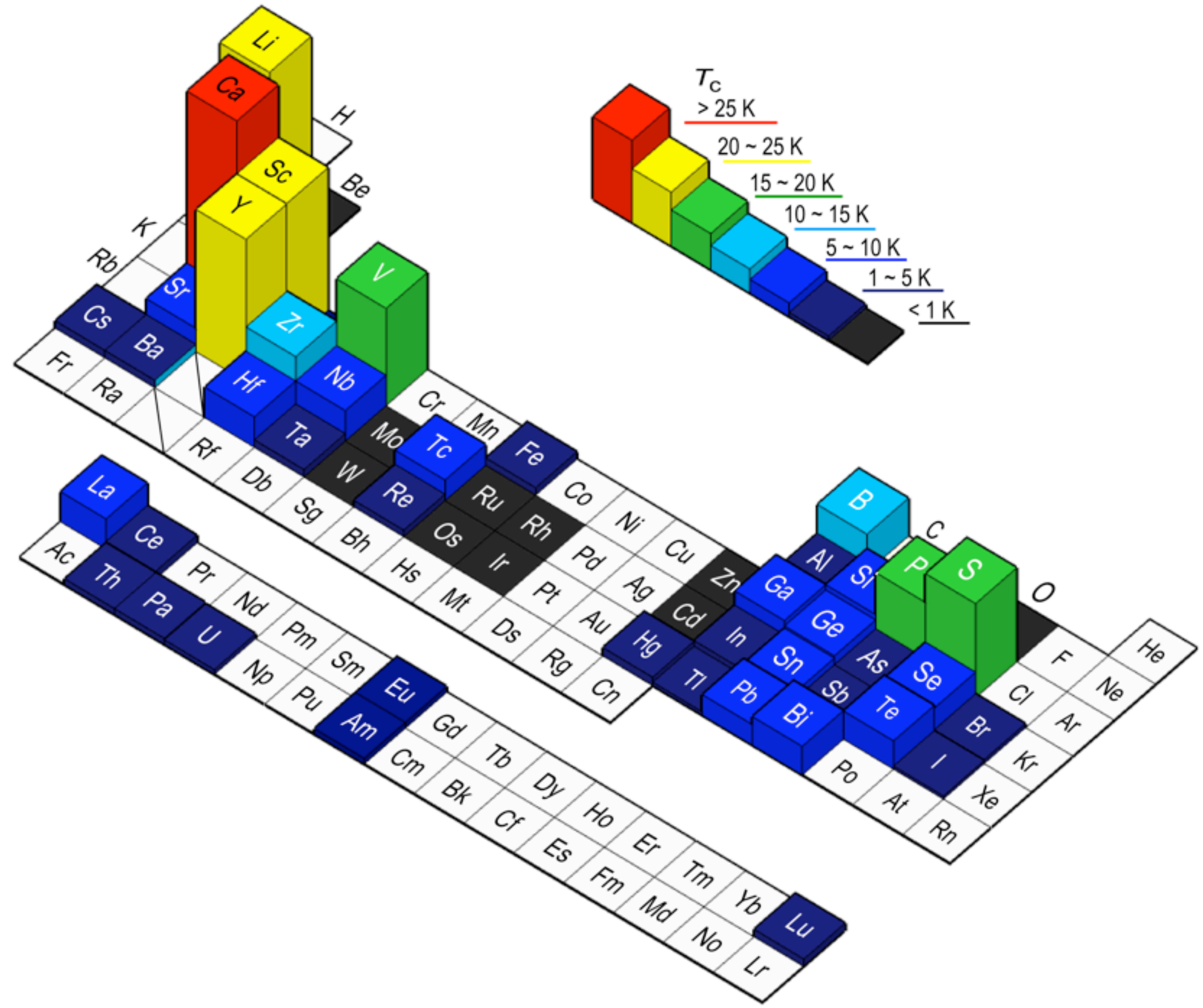


Image courtesy of Dr. Takahiro Matsuoka

30 elements are superconductors at ambient pressure
53 elements are superconductors under pressure

High–Pressure Chemistry:

What is the chemical formula for sodium chloride?

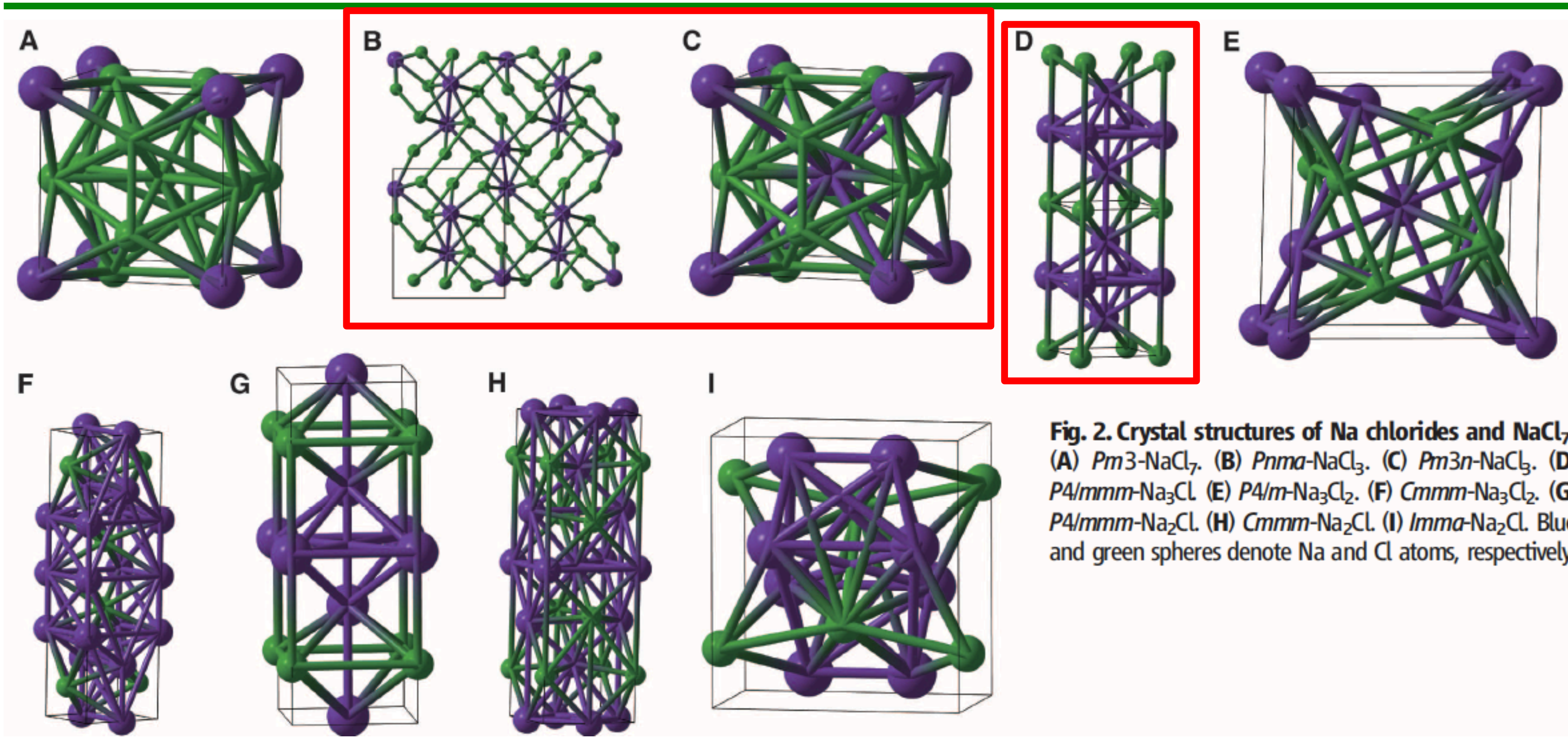


Fig. 2. Crystal structures of Na chlorides and $NaCl_7$. **(A)** *Pm*3-$NaCl_7$. **(B)** *Pnma*-$NaCl_3$. **(C)** *Pm*3*n*-$NaCl_3$. **(D)** *P4/mmm*-Na_3Cl. **(E)** *P4/m*-Na_3Cl_2. **(F)** *Cmmm*-Na_3Cl_2. **(G)** *P4/mmm*-Na_2Cl. **(H)** *Cmmm*-Na_2Cl. **(I)** *Imma*-Na_2Cl. Blue and green spheres denote Na and Cl atoms, respectively.

Unexpected Stable Stoichiometries of Sodium Chlorides

VOL 342 **SCIENCE**
20 DECEMBER 2013

Weiwei Zhang,[1,2]*† Artem R. Oganov,[2,3,4]*† Alexander F. Goncharov,[5,6] Qiang Zhu,[2] Salah Eddine Boulfelfel,[2] Andriy O. Lyakhov,[2] Elissaios Stavrou,[5] Maddury Somayazulu,[5] Vitali B. Prakapenka,[7] Zuzana Konôpková[8]

conventional superconductivity reaches 200 K

nature International weekly journal of science

NATURE | LETTER

日本語要約

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

Affiliations | Contributions | Corresponding author

Nature **525**, 73–76 (03 September 2015) | doi:10.1038/nature14964
Received 25 June 2015 | Accepted 22 July 2015 | Published online 17 August 2015

MgB_2 with T_c=39 K was highest

Science REPORTS

Cite as: R. P. Dias *et al.*, *Science* 10.1126/science.aal1579 (2017).

Observation of the Wigner-Huntington transition to metallic hydrogen

Ranga P. Dias and Isaac F. Silvera*
Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA.

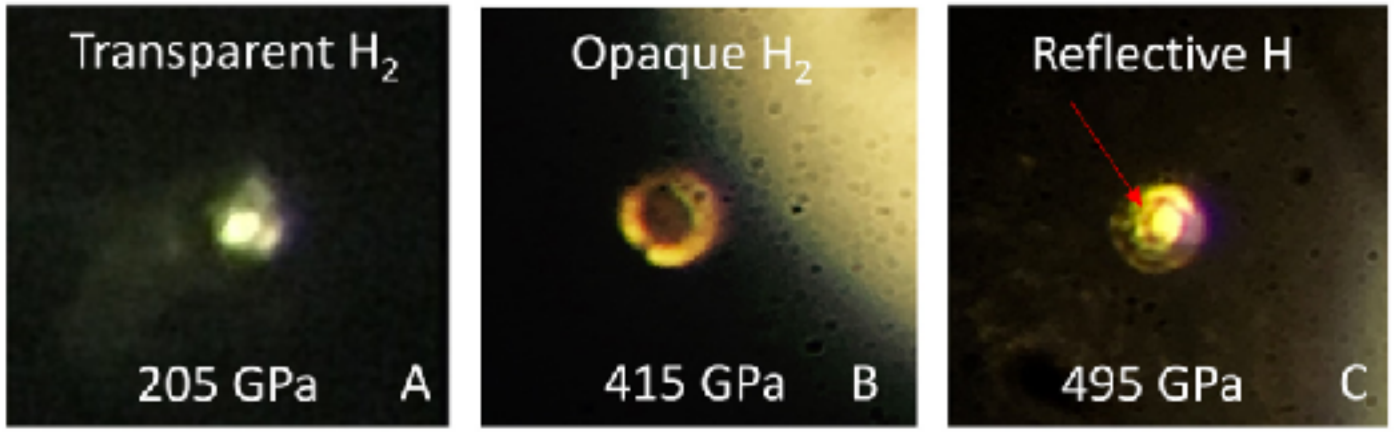
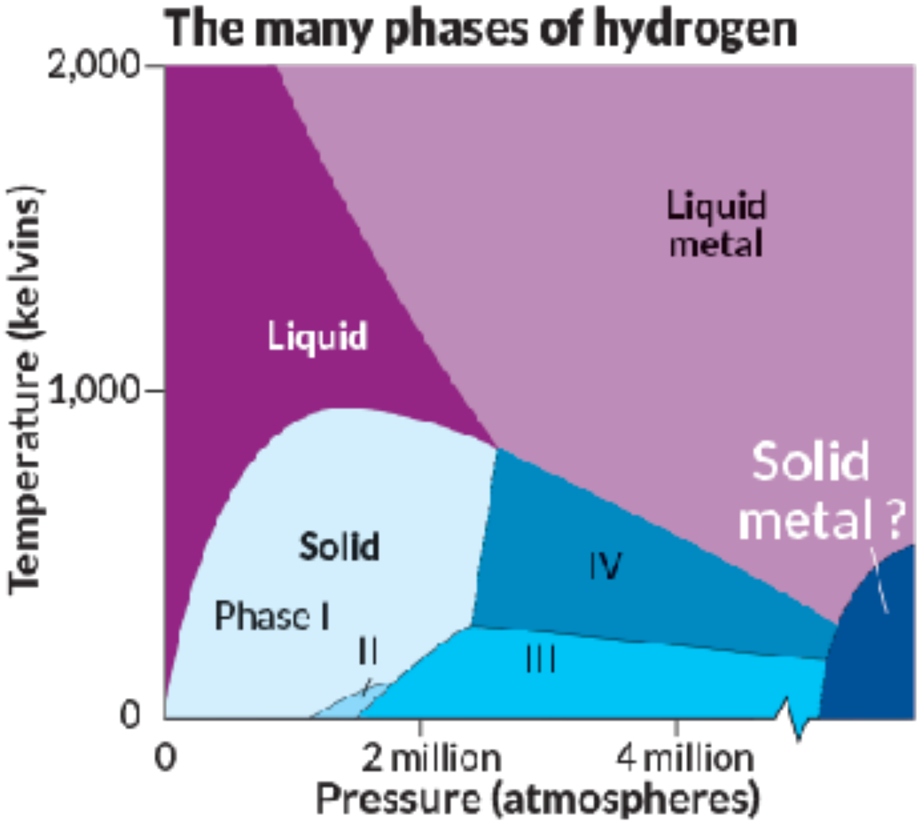
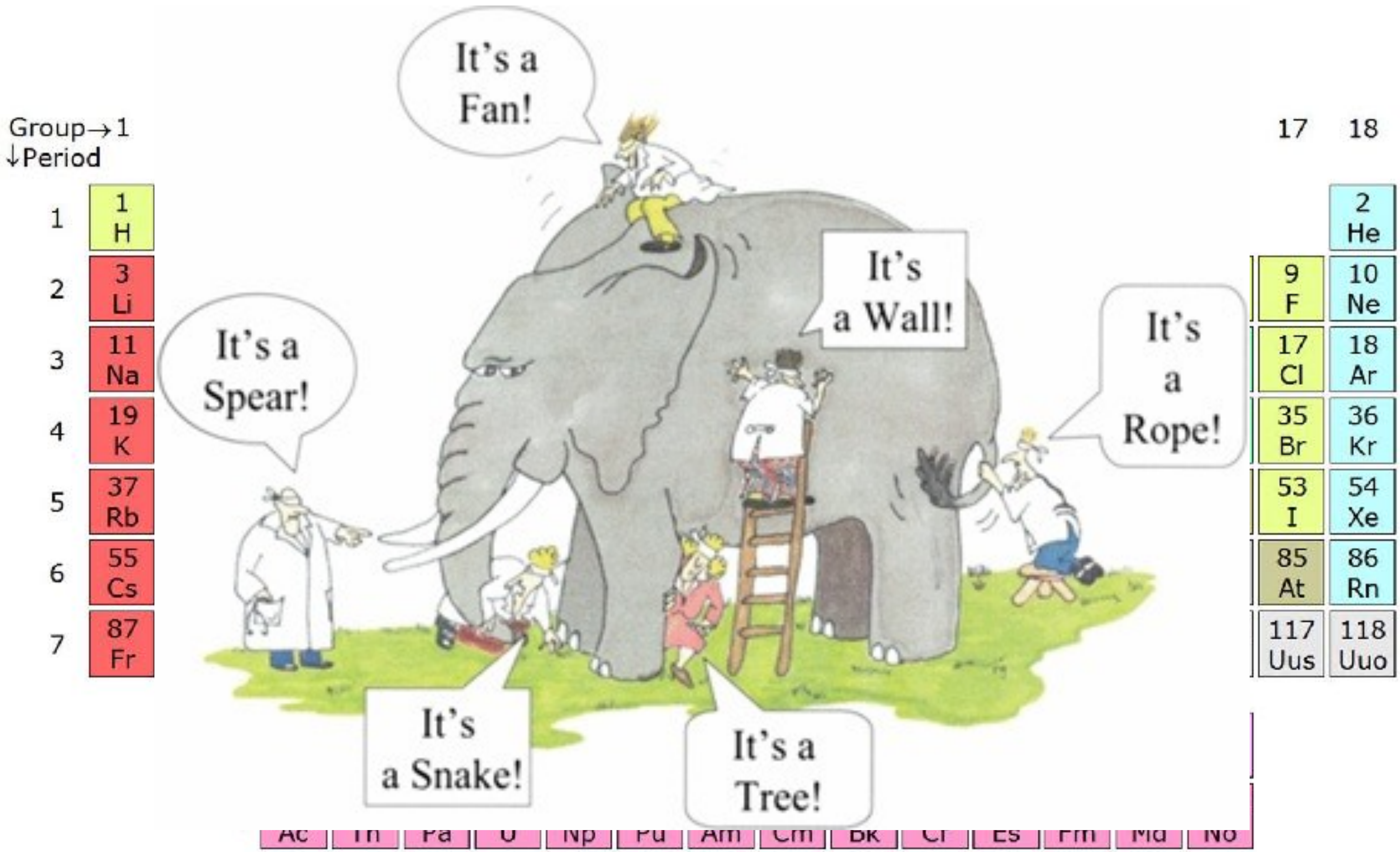


Fig. 2. **Photographs of hydrogen at different stages of compression.** Photos were taken with an iphone camera at the ocular of a modified stereo microscope, using LED illumination in the other optical path of the



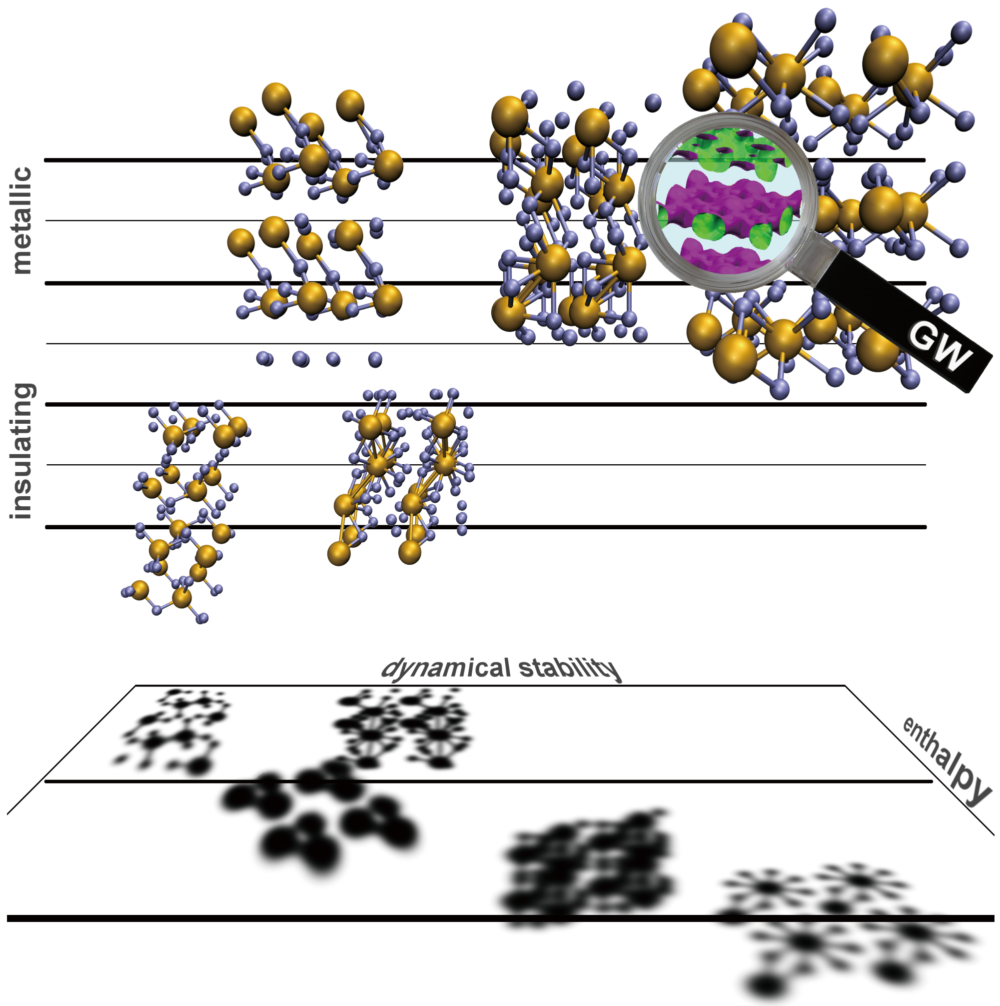
Conventional wisdom ?



Pressure can be regarded as an additional dimension of science

computational approaches

Electronic structure analysis



Atomic position predictions

USPEX

Universal Structure Predictor: Evolutionary Xtallography

Ab Initio Random Structure Searching

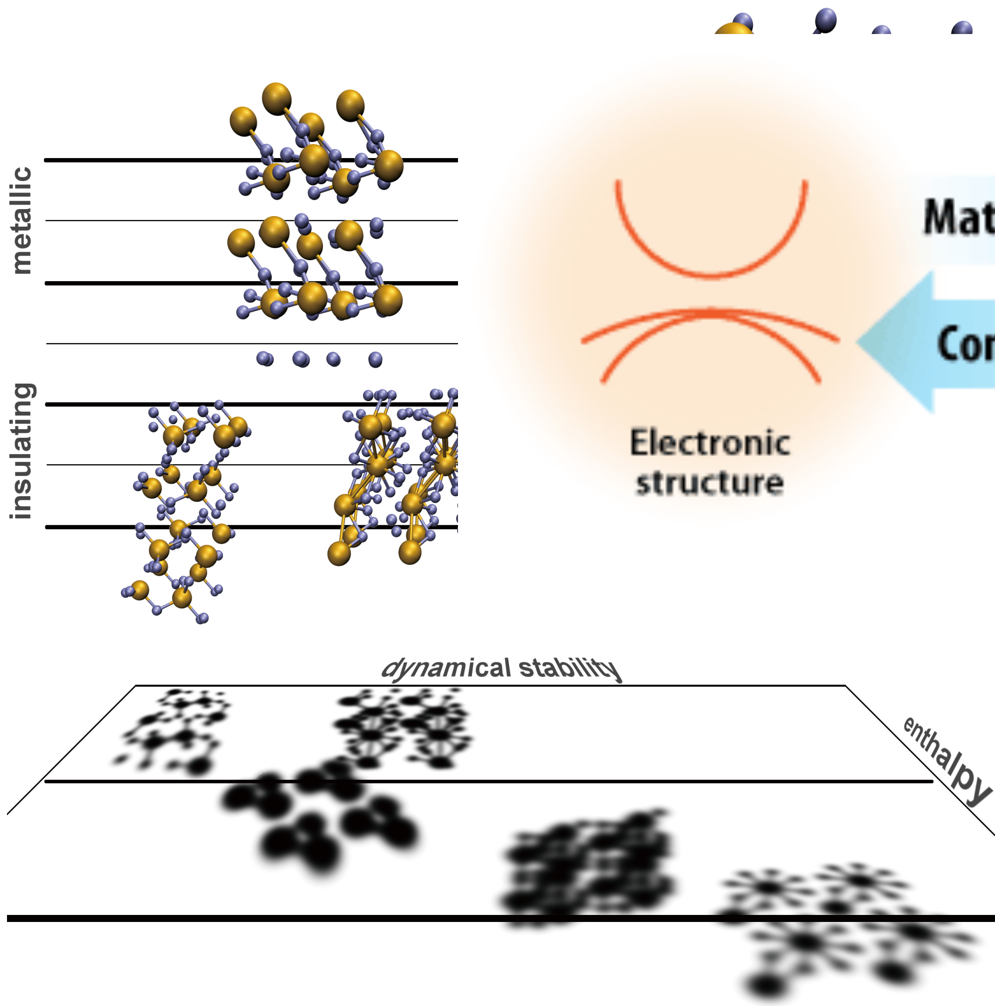
UCL

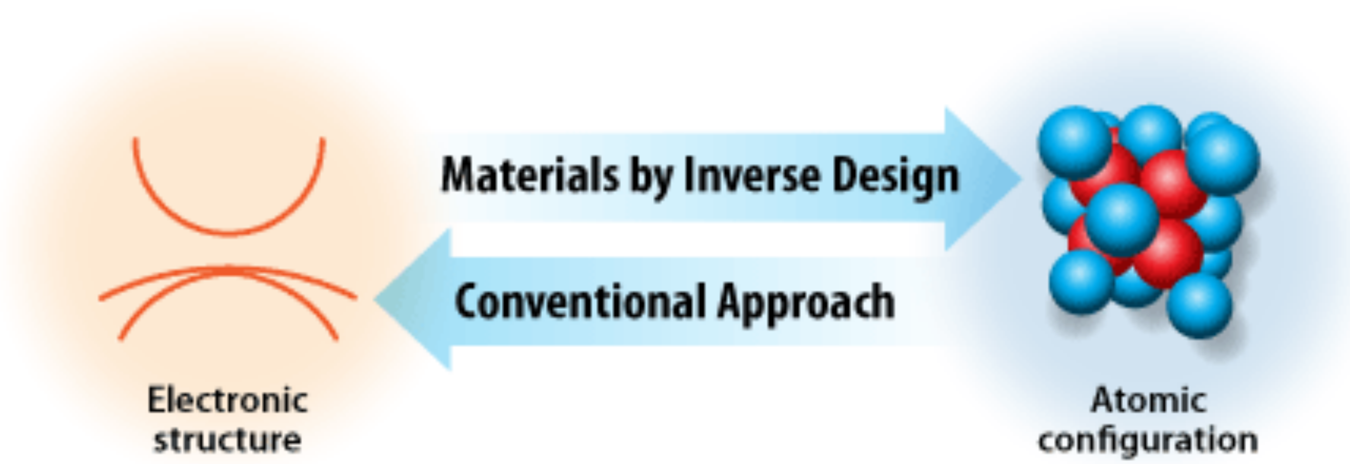
Meta – dynamics

computational approaches

Electronic structure analysis

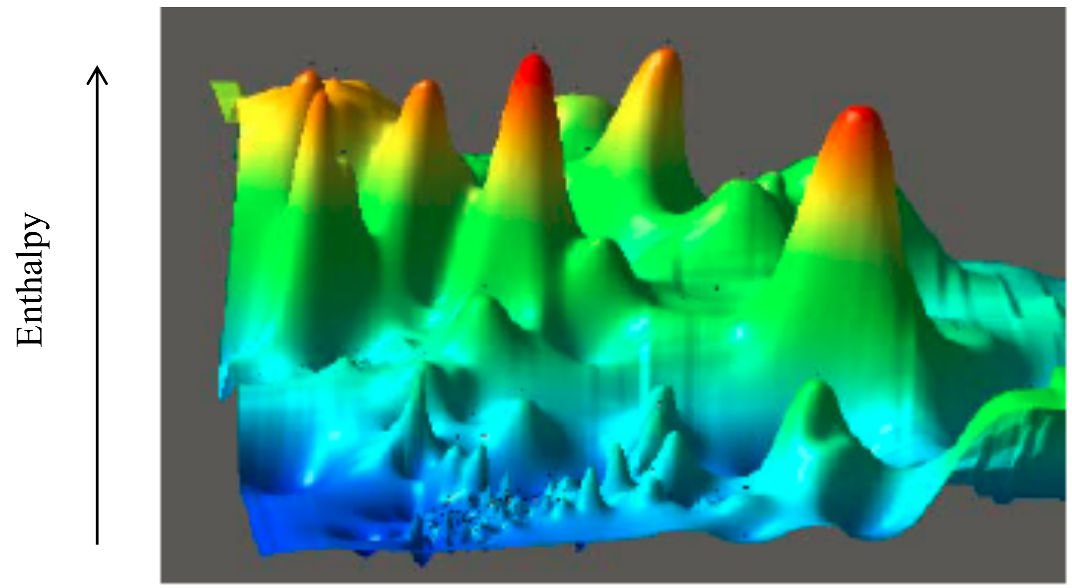
Atomic position predictions





Meta – dynamics

Prediction crystal structure



- Make a random unit cell
- Throw the required numbers of each atom type into the cell at random
- Relax under the quantum mechanical forces and stresses
- Look at lowest-energy or other interesting structures

Searching method + First principles calculations

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

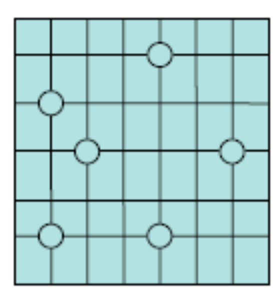
Are Crystal Structures Predictable?

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

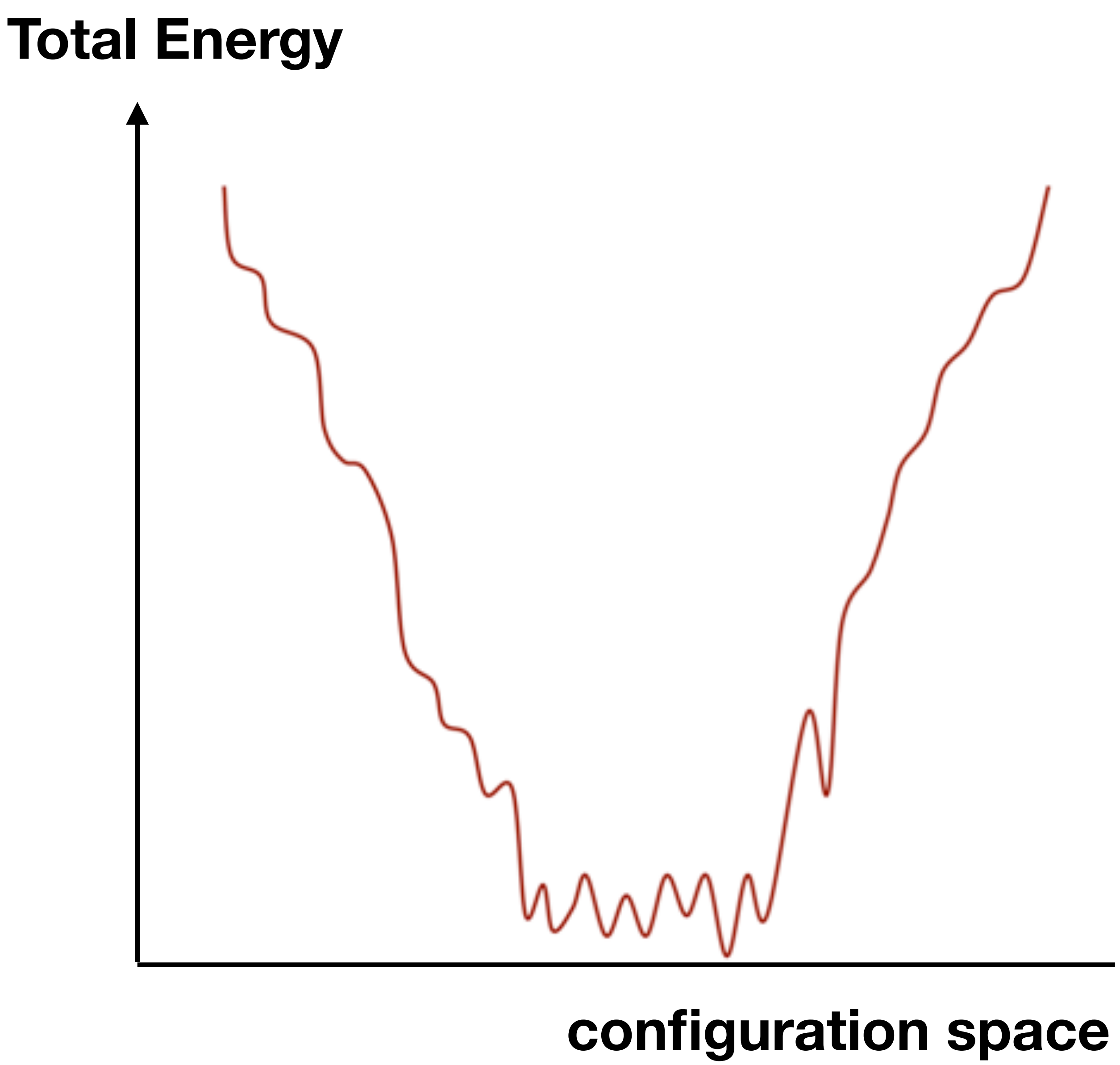
Need to find GLOBAL energy minimum.
Trying all structures is impossible:

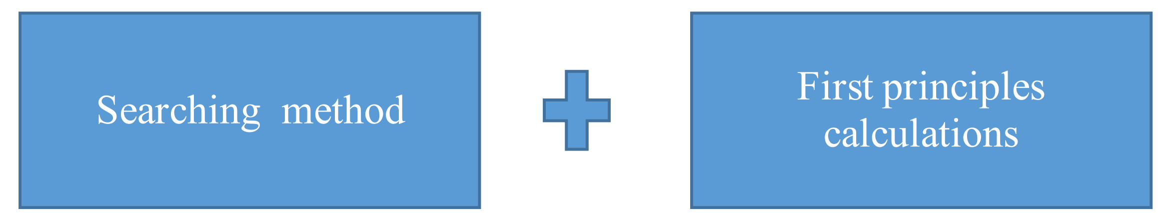
$$C = \frac{1}{(V/\delta^3)} \frac{(V/\delta^3)!}{[(V/\delta^3) - N]!N!}$$



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.

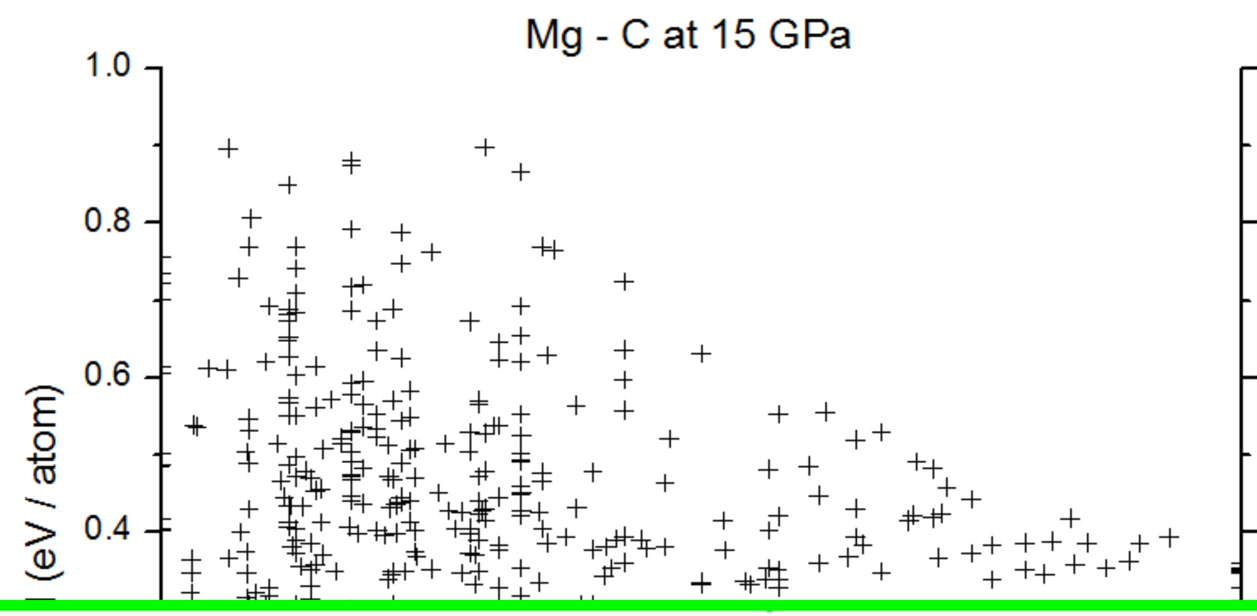
Computational structure prediction



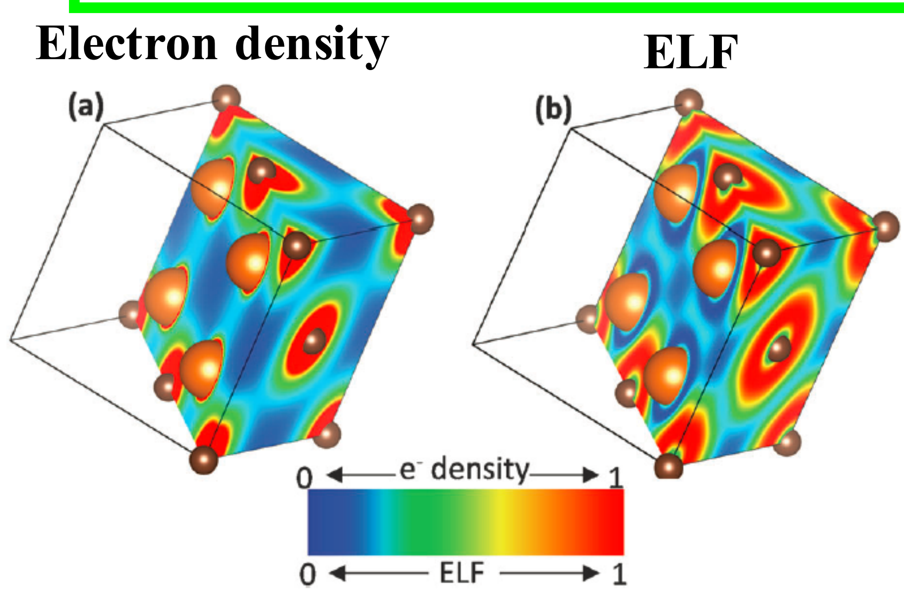


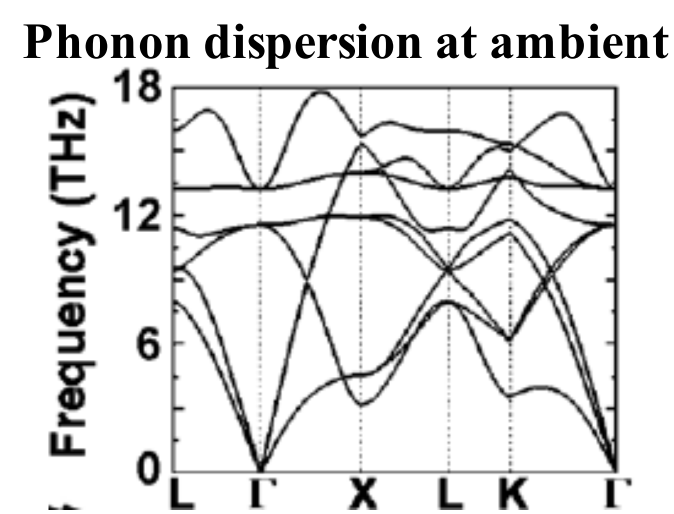
- Make a random unit cell
- Throw the required numbers of each atom type into the cell at random
- Relax under the quantum mechanical forces and stresses
- Look at lowest-energy or other interesting structures

In silico experiments

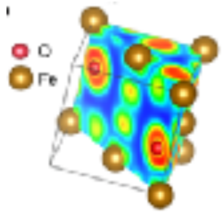


contain the rare $[C{=}C{=}C]^{4-}$ group. Herein, we present the formation of a third carbide of magnesium, namely Mg_2C. This compound is stabilized at pressures above 15 GPa, but is fully recoverable to ambient conditions and contains the very unusual C^{4-} methanide anion.[12,15]





Anger. Chem. Int. Ed. **53** 8930 (2013)



Contents of FeO_2 presentation

FeO_2 : prediction and experimental synthesis

FeO_2 : Detailed theoretical work

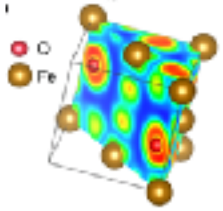
What should be done

LETTER

doi:10.1038/nature18018

FeO_2 and FeOOH under deep lower-mantle conditions and Earth's oxygen–hydrogen cycles

Qingyang Hu[1,2]*, Duck Young Kim[1,2]*, Wenge Yang[1,3]*, Liuxiang Yang[1,3], Yue Meng[4], Li Zhang[1,2] & Ho-Kwang Mao[1,2]



Computational prediction *in 2014*

duckyoung, I am interested in
new Fe-O compound at high pressure

especially iron-rich oxides

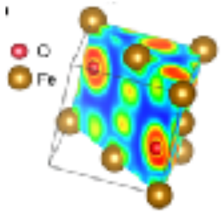
I can try but ……

Binary crystal structure searching is easy !

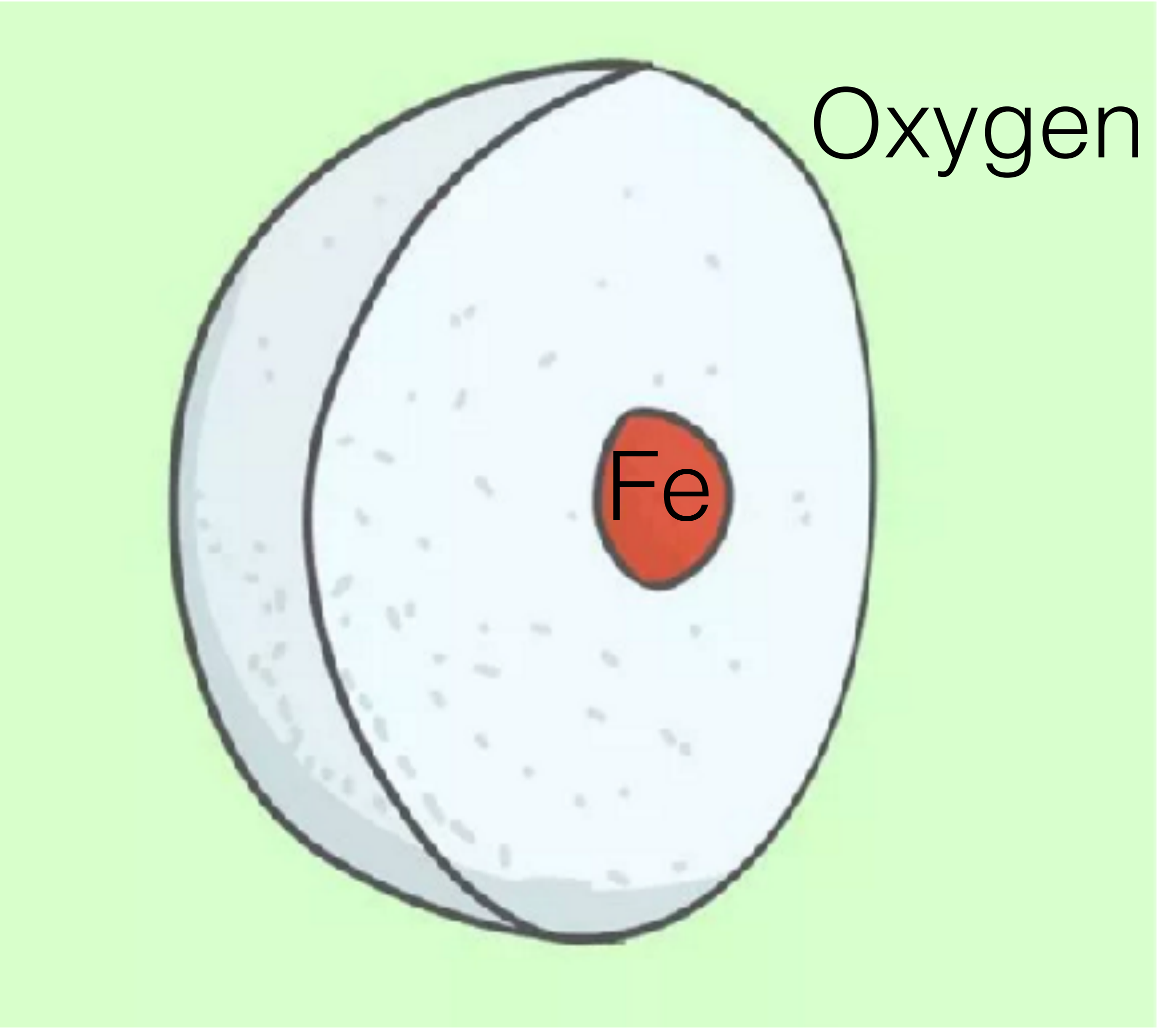
standard DFT calculations for Fe and Fe-O compounds are not reliable

But pressure reduces e-e correlation effects in general

It is not straightforward to determine reliable pressure regime
for standard DFT calculations to Fe-O systems



The simplest model of the earth

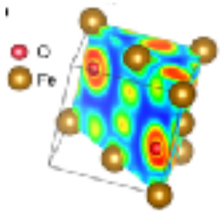


For realistic model,we need Si, Mg, O ……

Fe-O compounds are important to understand the Earth

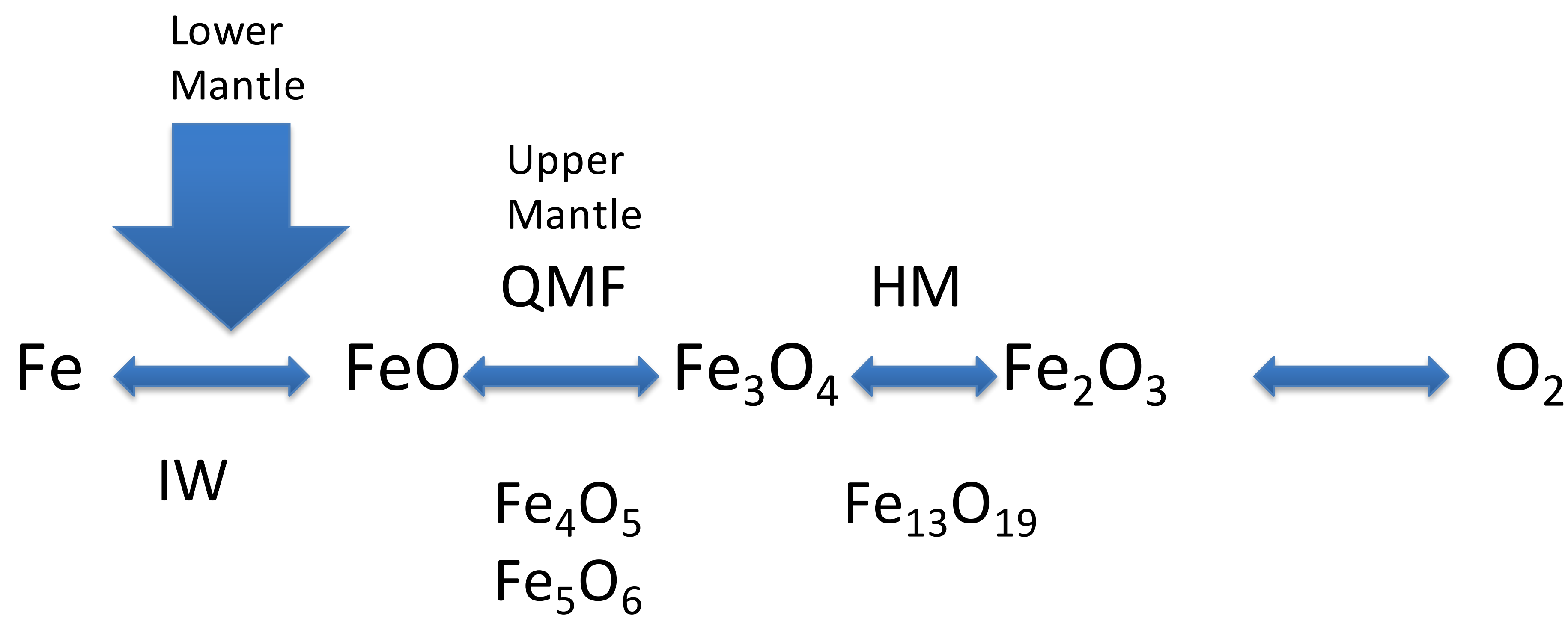
There are many iron compounds with two end members - FeO and Fe_2O_3

such as Fe_4O_5, $Fe_{32}O_{25}$, Fe_7O_9, Fe_3O_4, and Fe_5O_7



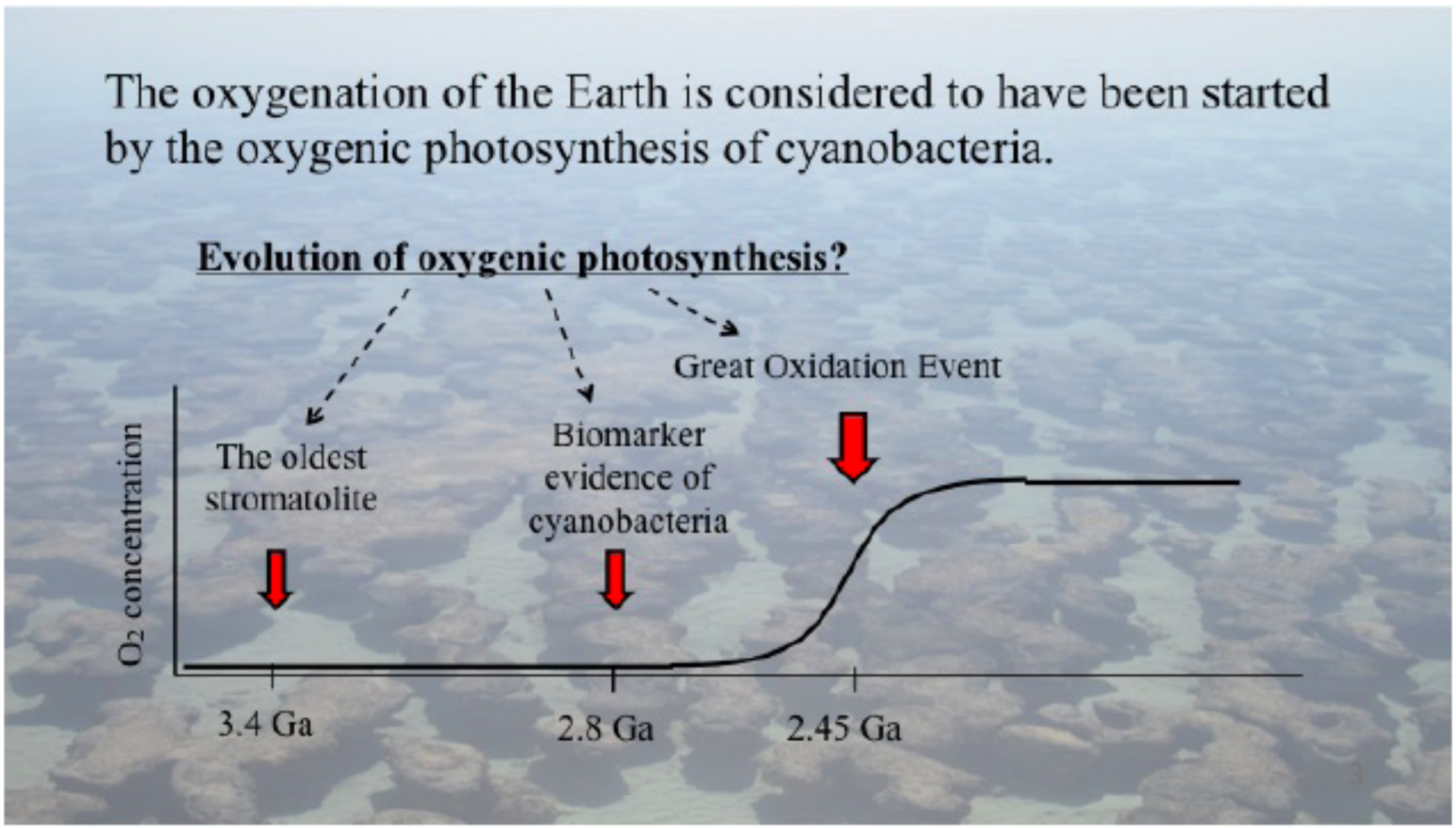
Conventional Wisdom # 1

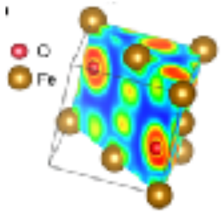
The mantle is uniformly reducing toward Fe



Conventional Wisdom # 2

The GOE is solely biogenic





Conventional Wisdom # 2

The GOE is solely biogenic

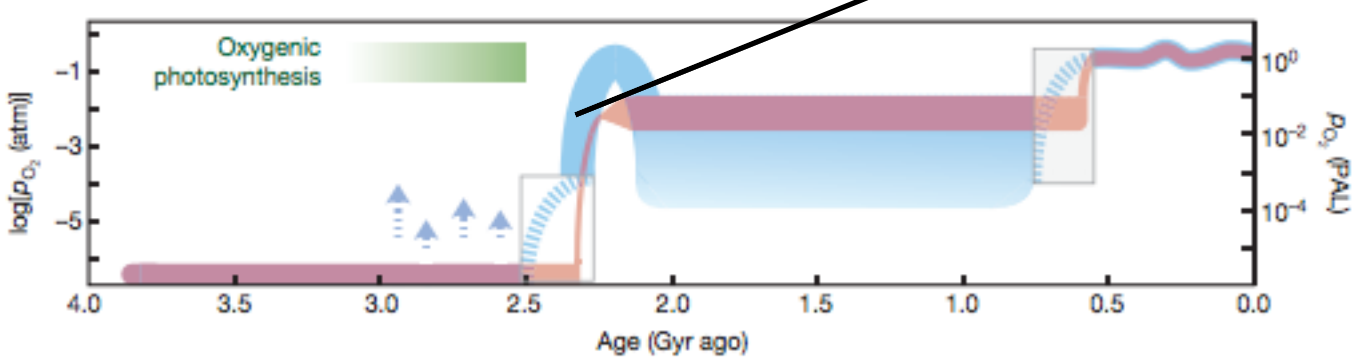
REVIEW

doi:10.1038/nature13068

The rise of oxygen in Earth's early ocean and atmosphere

Timothy W. Lyons[1], Christopher T. Reinhard[1,2,3] & Noah J. Planavsky[1,4]

oxygenic photosynthesis of cyanobacteria

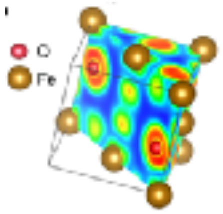


Evidence for oxygen-producing photosynthesis before the GOE

Current Biology *19*, R567–R574, July 28, 2009 ©2009 Elsevier Ltd All rights reserved DOI 10.1016/j.cub.2009.05.054

The Continuing Puzzle of the Great Oxidation Event

Review



Conventional Wisdom # 3

Hydrogen cycle is dictated by hydrous Mg and Al silicates

LETTER 13 MARCH 2014 | VOL 507 | NATURE | 221
doi:10.1038/nature13080

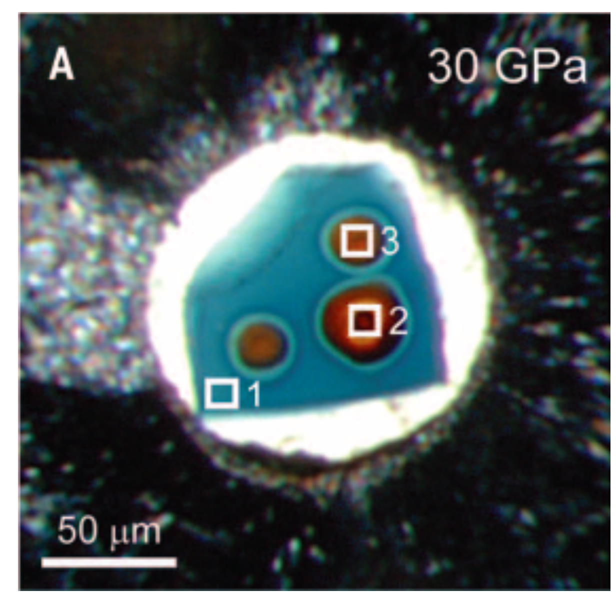
Hydrous mantle transition zone indicated by ringwoodite included within diamond

D. G. Pearson[1], F. E. Brenker[2], F. Nestola[3], J. McNeill[4], L. Nasdala[5], M. T. Hutchison[6], S. Matveev[1], K. Mather[4], G. Silversmit[7], S. Schmitz[2], B. Vekemans[7] & L. Vincze[7]

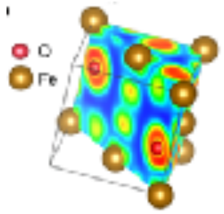
EARTH'S INTERIOR

Dehydration melting at the top of the lower mantle

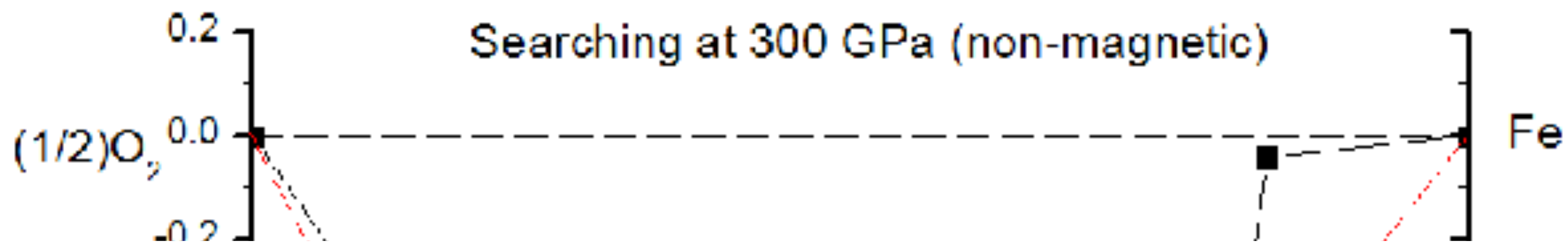
Brandon Schmandt,[1*] Steven D. Jacobsen,[2*] Thorsten W. Becker,[3] Zhenxian Liu,[4] Kenneth G. Dueker[5]



$(Fe,Mg)_2SiO_4$ with H_2O releases hydrogen



First attempt at 300 GPa



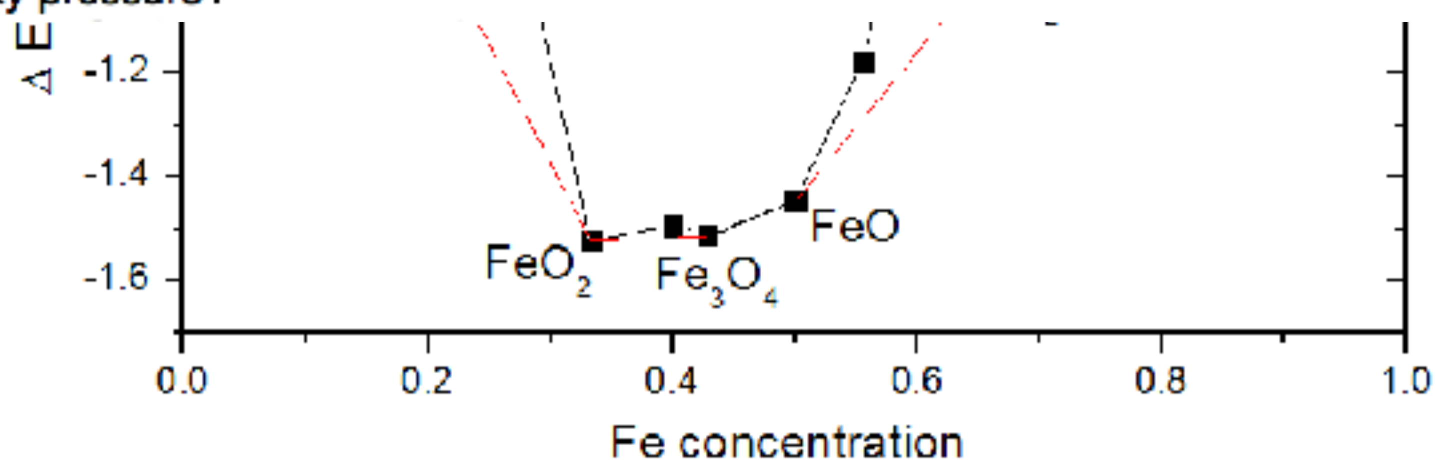
Hokwang Mao March 3, 2015 at 9:39 AM

To: Kim, DuckYoung Cc: Hokwang Mao

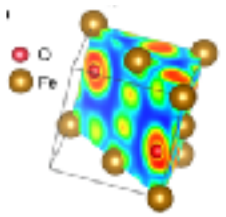
Re: Fe-O at 300 GPa

HM

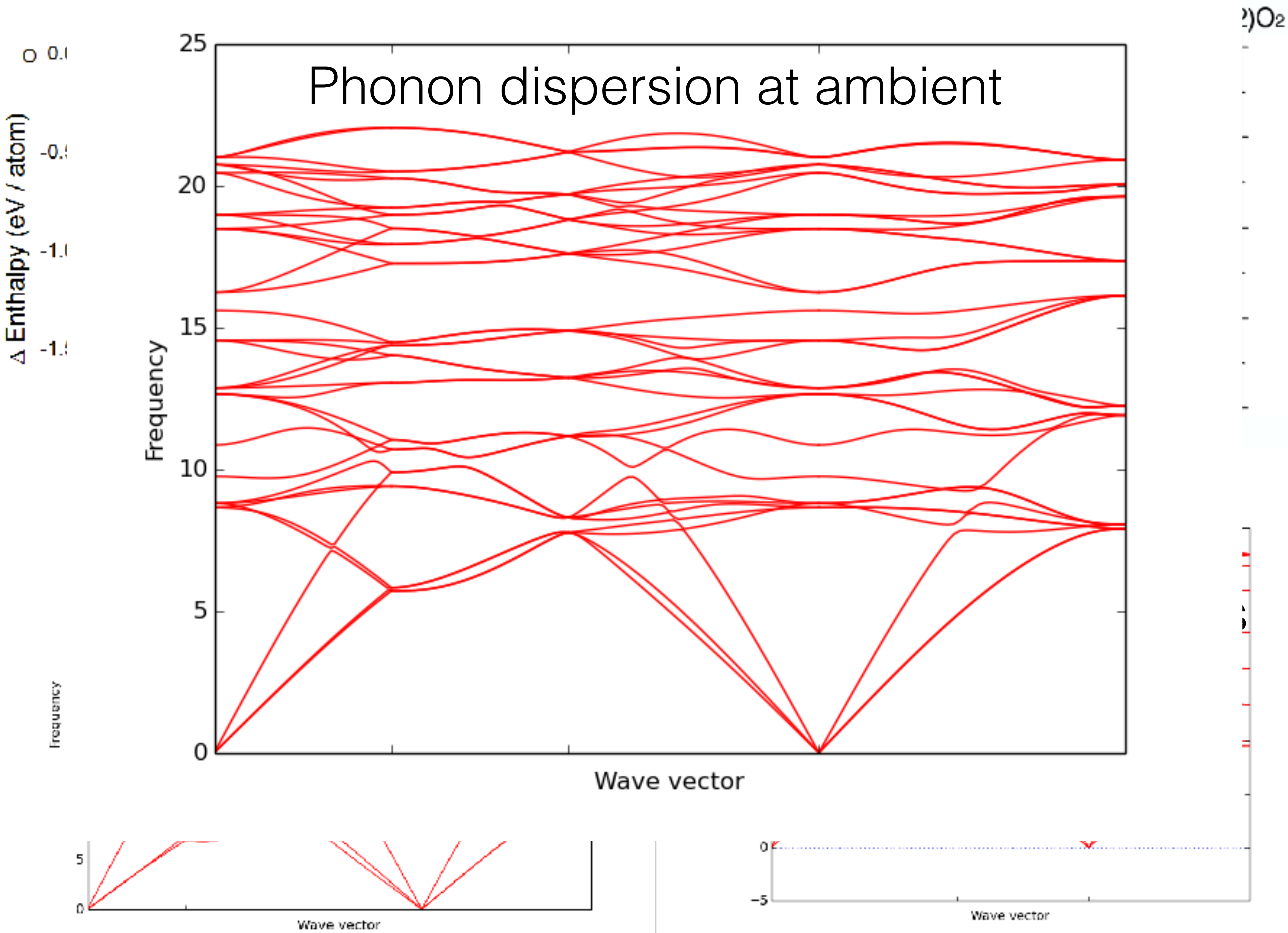
It is surprising that you found FeO2 to be very stable. Fe2O3 is the highest known compound. A straight line should be drawn between Fe2O3 and Fe, instead of Fe3O4 and Fe. In either case FeO2 is very stable. Can you find its minimum stability pressure?

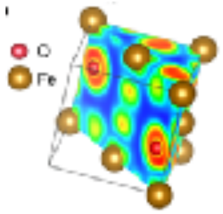


We chose the highest pressure at the Earth as a starting point because then standard DFT might not fail to calculate total energy



Lowering pressures …





As far as standard DFT works

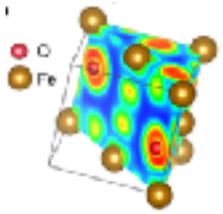
FeO_2 is stable phase at high pressures

FeO_2 is a metastable form even at ambient pressure

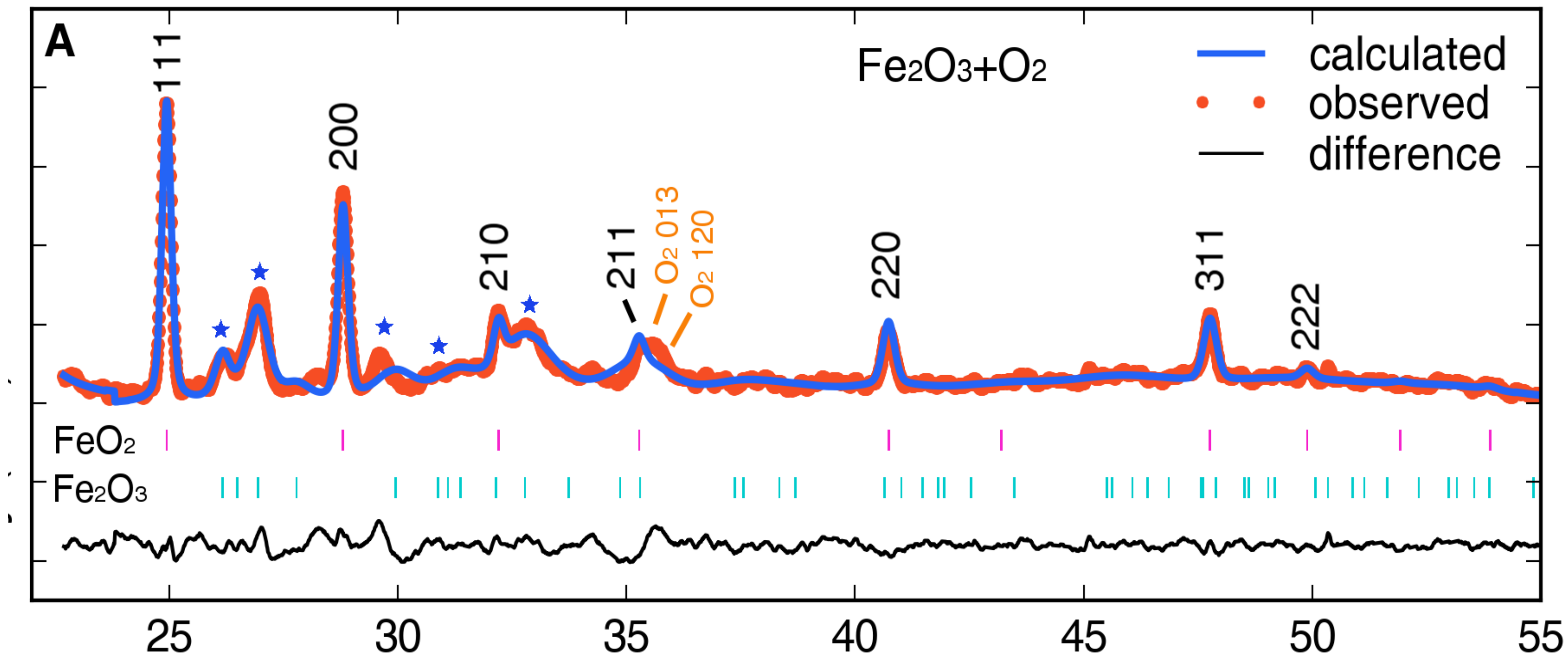
Computational searches for iron oxides at high pressures

Gihan L Weerasinghe[1], Chris J Pickard[2] and R J Needs[1]

Published 16 October 2015 • © 2015 IOP Publishing Ltd
Journal of Physics: Condensed Matter, Volume 27, Number 45



Experimental synthesis



with $Fe_2O_3 + O_2$, we found a pyrite-phase of Pa-3 peroxide - FeO_2 at 76 GPa

All ca ... ern

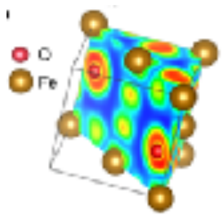
An interest ... oscience

SCIENTIFIC REPORTS

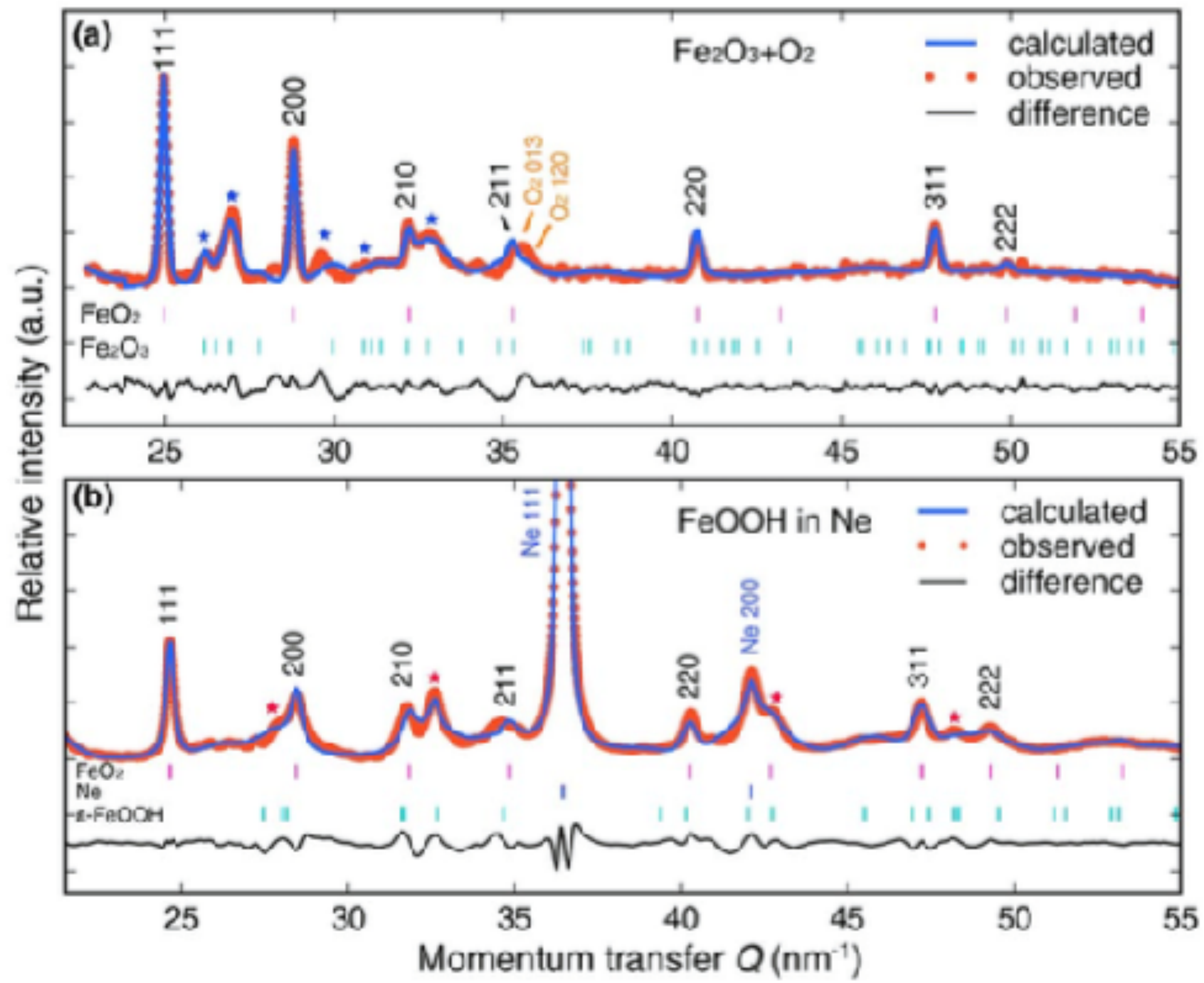
OPEN

Stable magnesium peroxide at high pressure

Sergey S. Lobanov[1,2], Qiang Zhu[3], Nicholas Holtgrewe[1,4], Clemens Prescher[5], Vitali B. Prakapenka[5], Artem R. Oganov[3,6,7,10] & Alexander F. Goncharov[1,8,9]



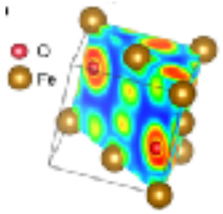
Several chemical routes are found



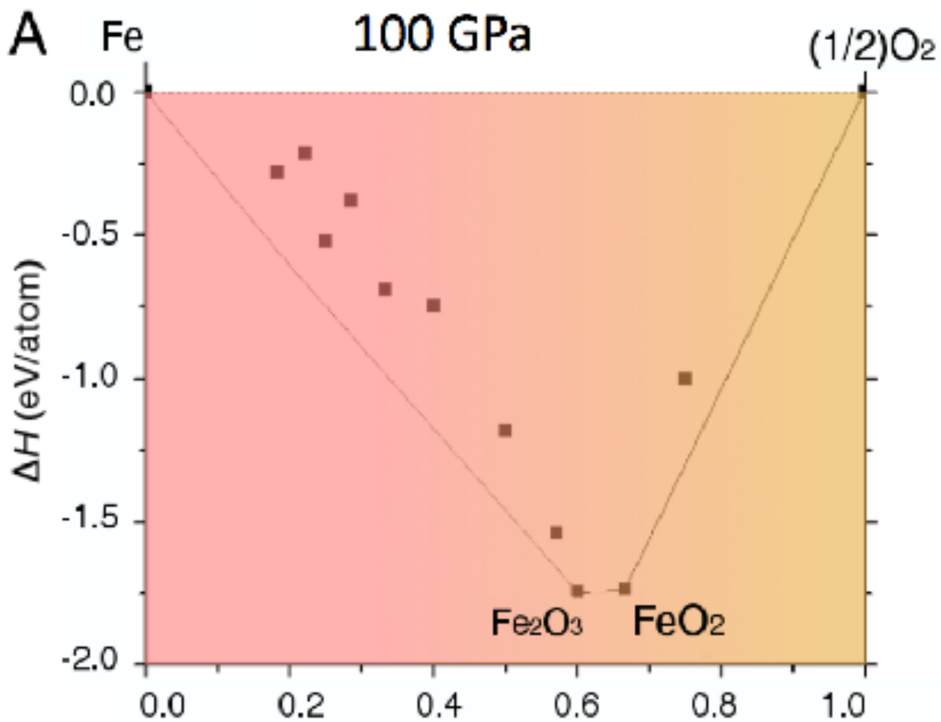
$Fe_2O_3 + 1/2O_2 = FeO_2$

$2FeOOH = 2FeO_2 + H_2$

Now, it becomes more interesting story to geoscience

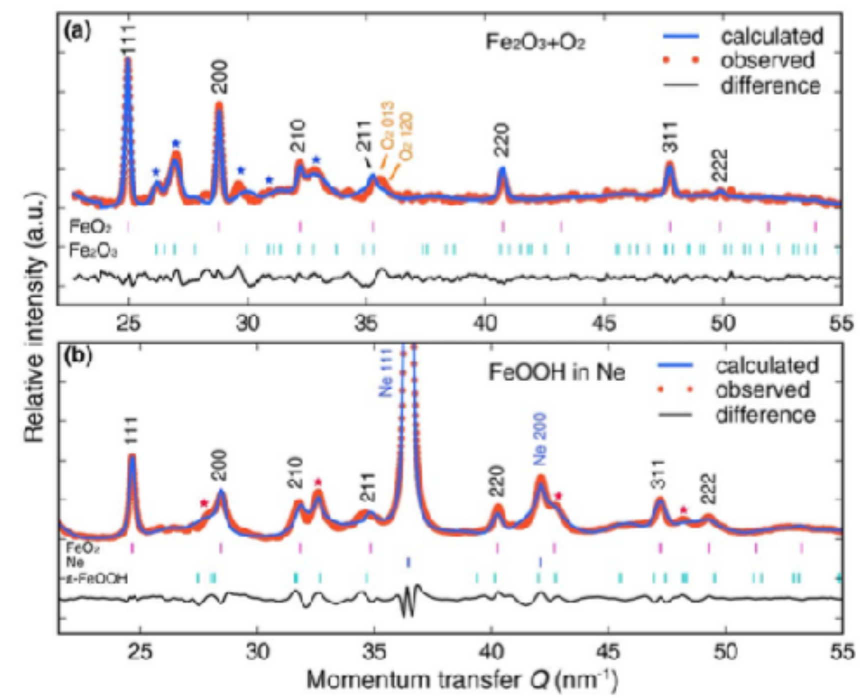


Observation of FeO_2 at the DLM conditions

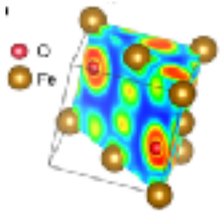


Oxygen concentration

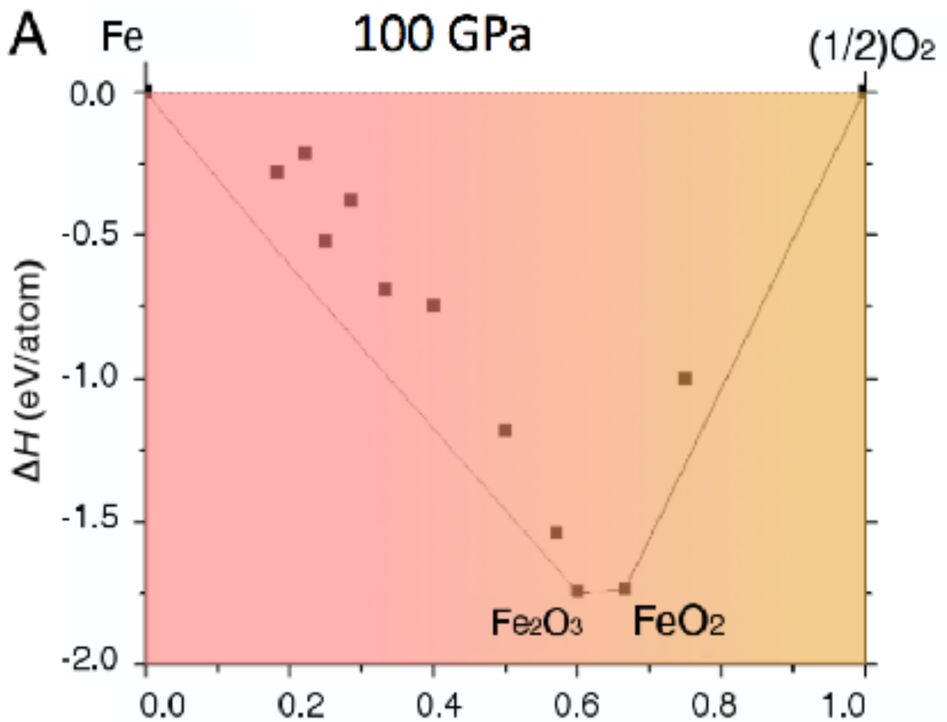
Computationally we predicted the formation of FeO_2



Experimentally we confirmed :



Observation of FeO_2 at the DLM conditions



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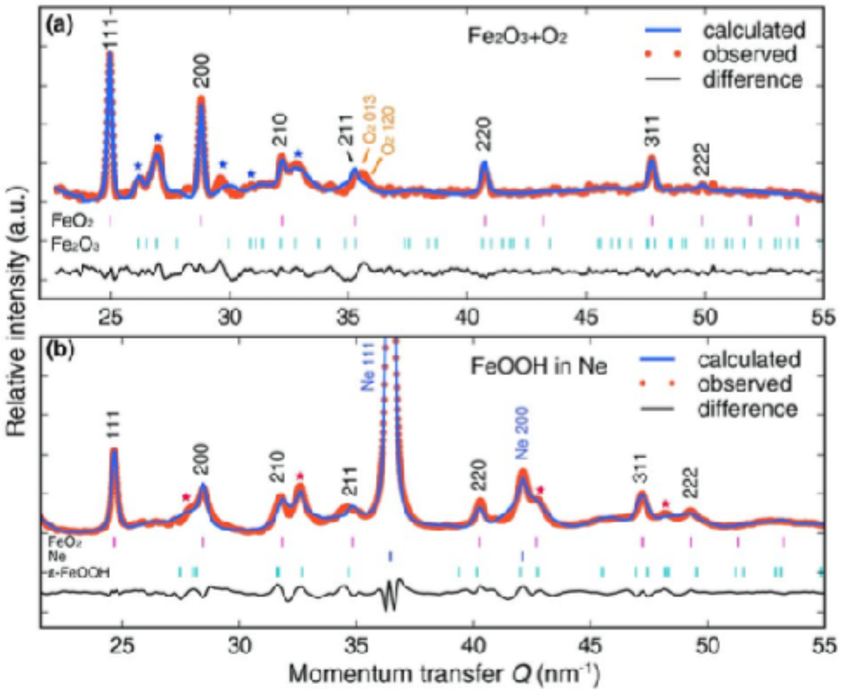
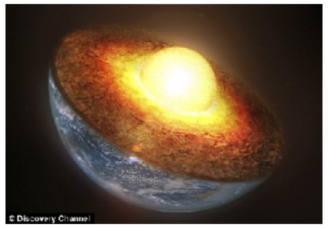


Experimentally we confirmed :

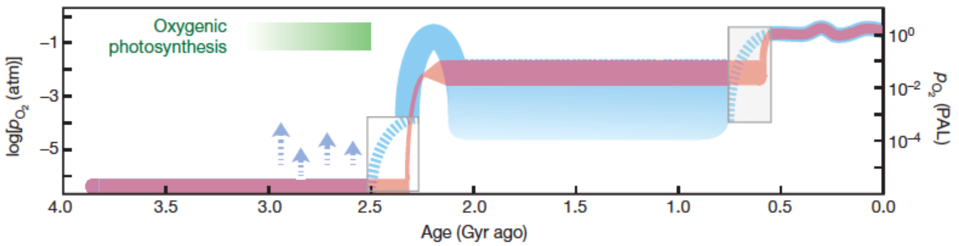
$Fe_2O_3 + 1/2O_2 = FeO_2$

$2FeOOH = 2FeO_2 + H_2$

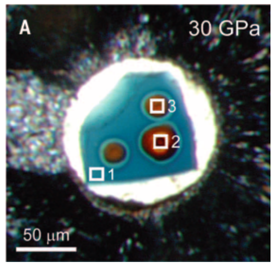
A scenario based on our study



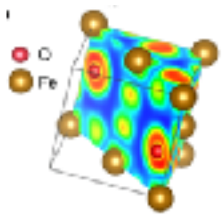
FeO_2 in DLM



FeO_2 plays as a oxygen reservoir (GOE may be abiogenic)



Fe oxidation dictates hydrogen cycle



Conventional Wisdom # 1

The mantle is NOT uniformly reducing toward Fe

Lower Mantle

QMF HM

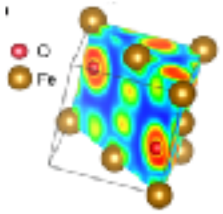
Fe ⟷ FeO ⟷ Fe_3O_4 ⟷ Fe_2O_3 ⟷ FeO_2 O_2

IW

Fe_4O_5

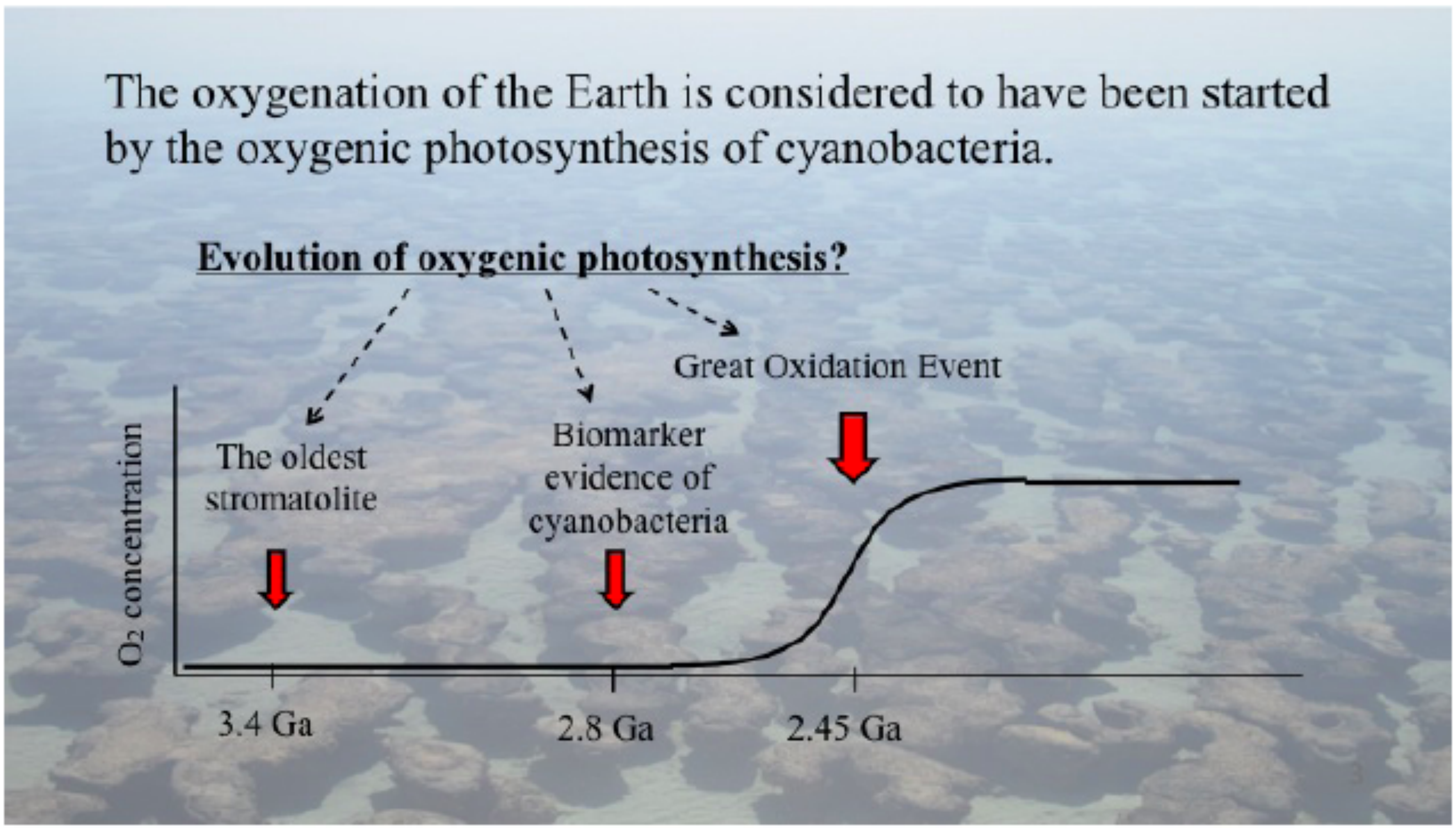
Fe_5O_6

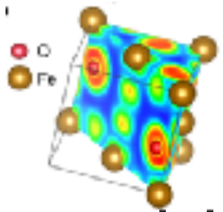
$Fe_{13}O_{19}$



Conventional Wisdom # 2

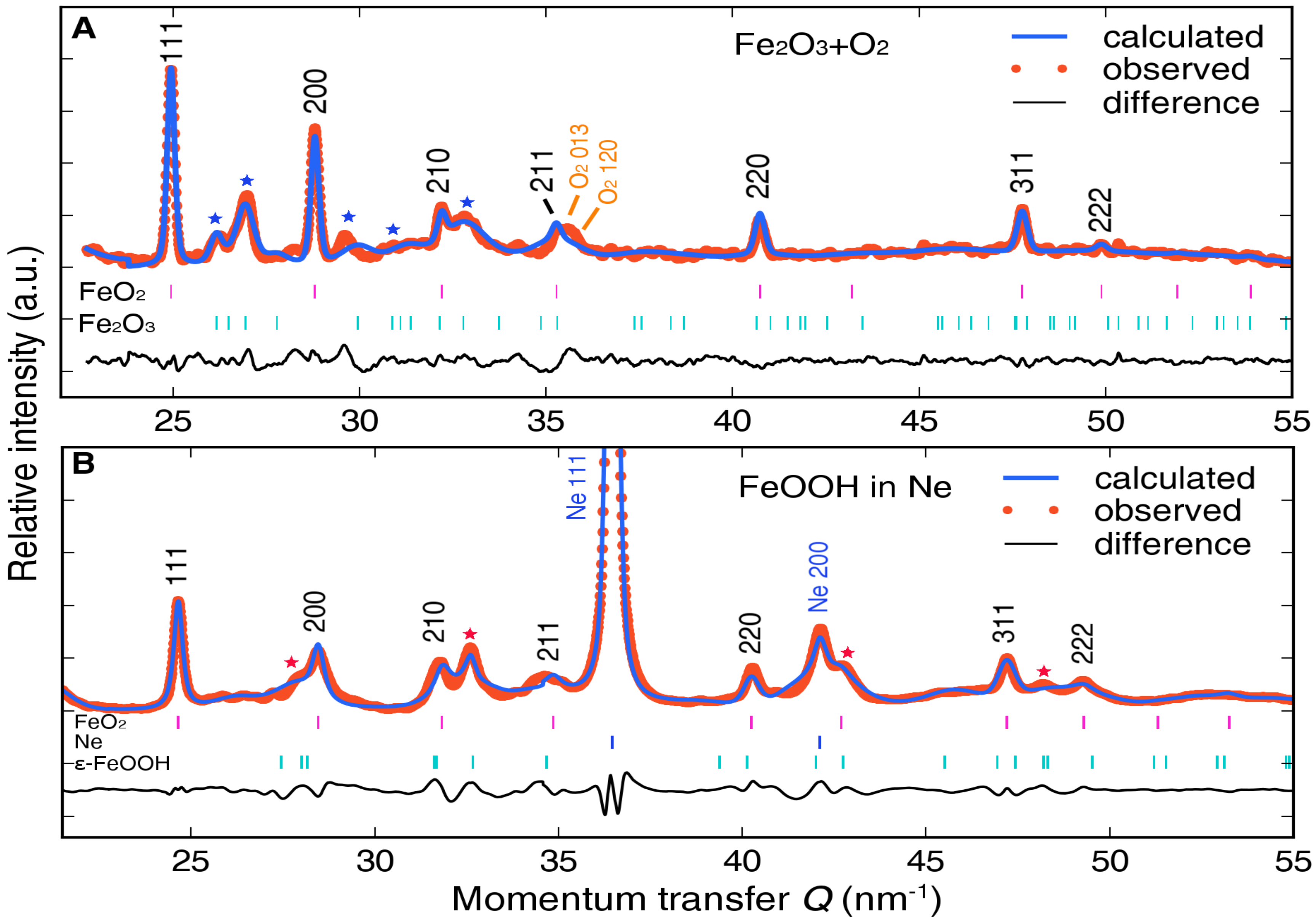
The GOE is NOT solely biogenic, maybe…..

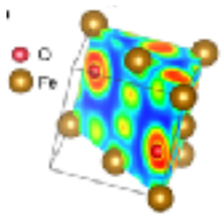




Conventional Wisdom # 3

Hydrogen cycle is NOT dictated by hydrous Mg and Al silicates, but Fe oxidation





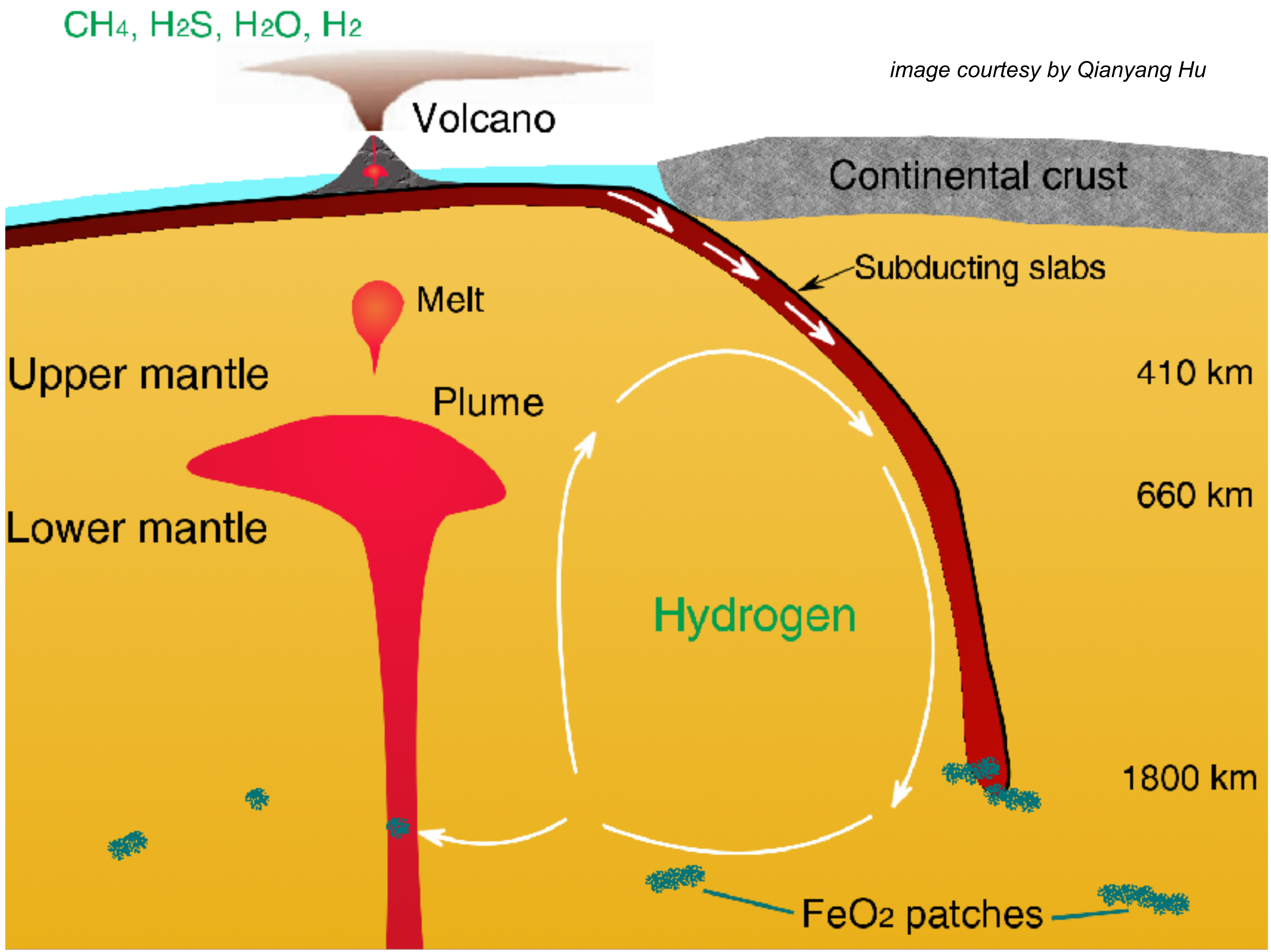


image courtesy by Qianyang Hu

We are at starting point

Theory

- What is correct band structure (e-e correlation in FeO_2)
- Spin transition of Fe compounds
- computationally, can we predict chemical paths to FeO_2
- What's physical properties of FeO_2

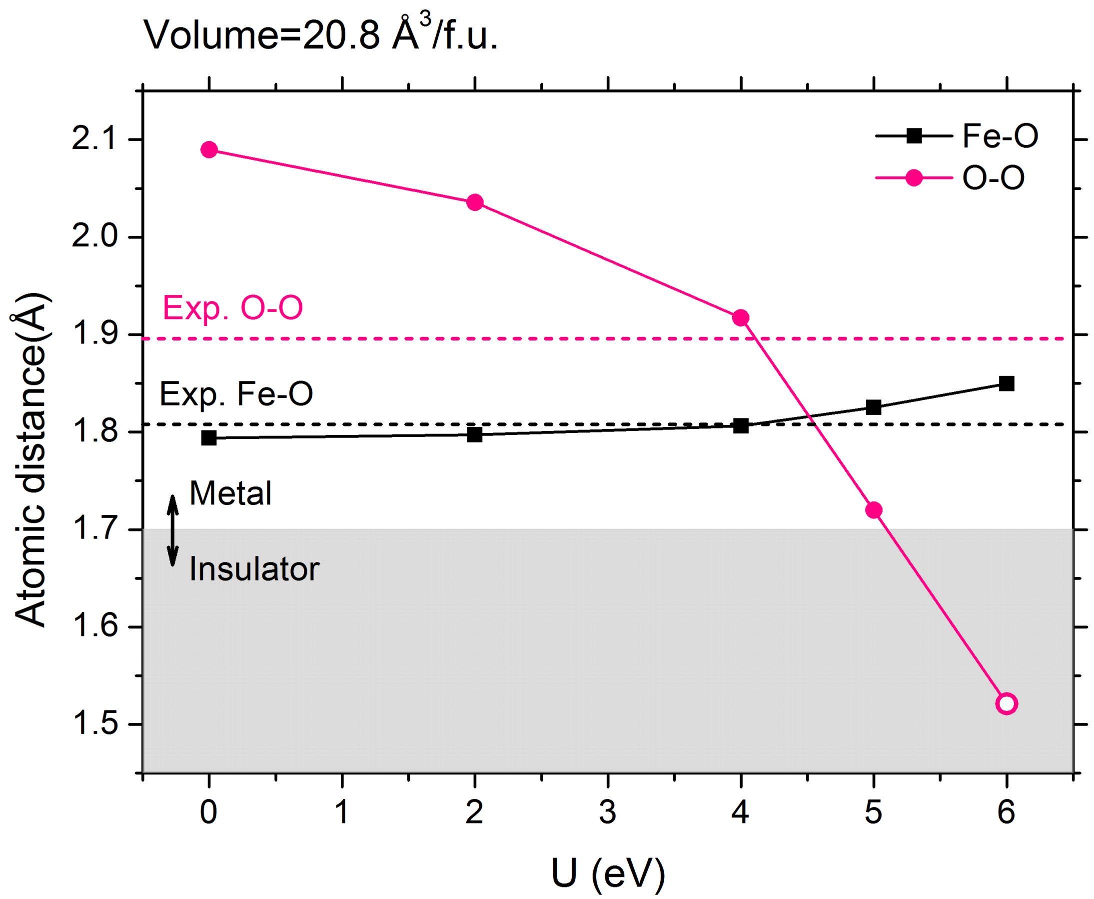
Experimentally

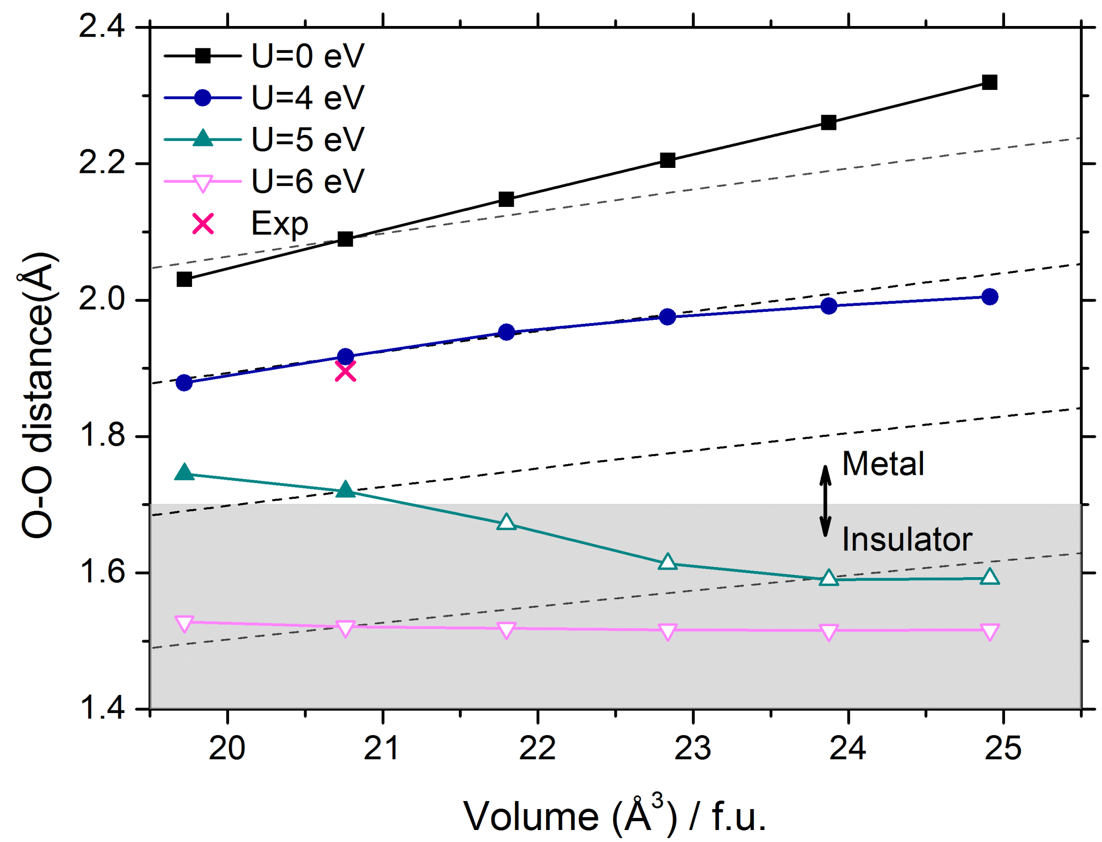
- How Fe can meet H_2O at the deep lower mantle ?
- Is FeO_2 stable against environment ?

Commonly

- Can FeO2 survive in real mantle environment?
- Does it match with established geological observations?

e-e correlation in FeO_2

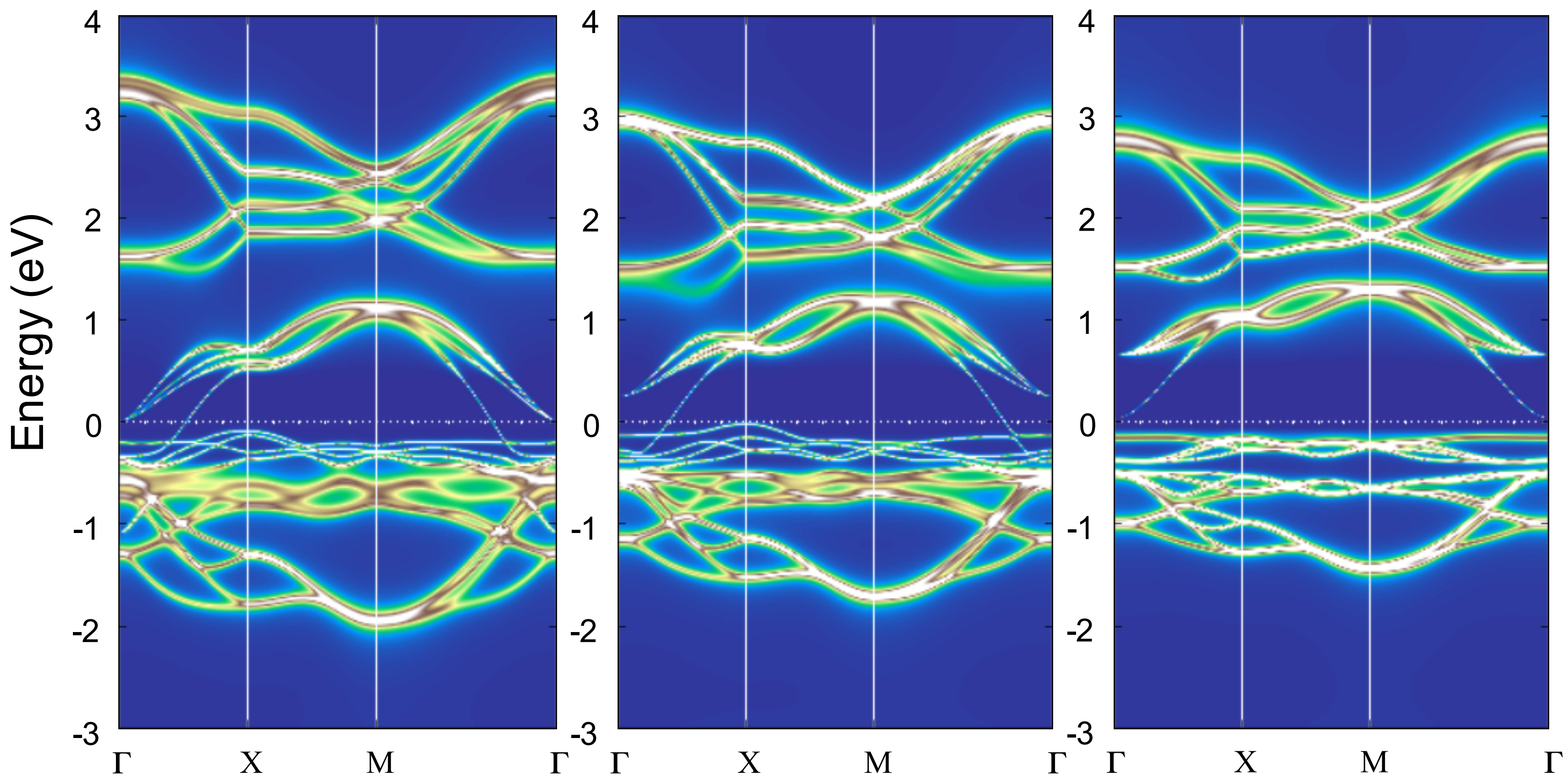




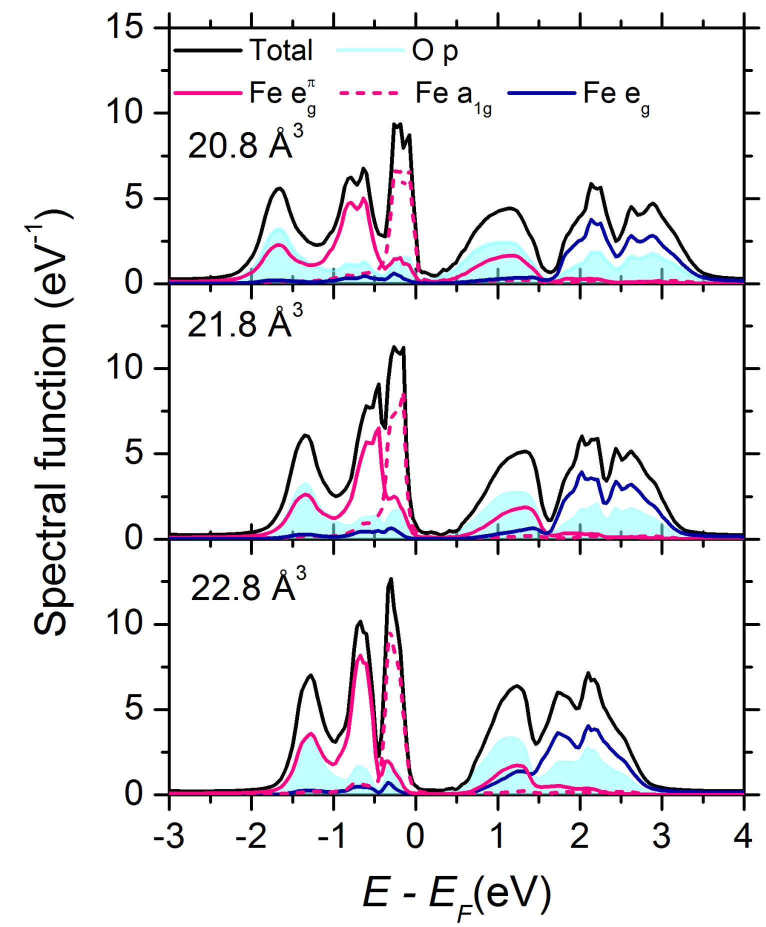
@ 76 GPa, LDA + U calculations tells U = 5 eV and J=0.8 eV gives best match to experimental bond lengths

Phys. Rev. B **95** 075114 (2017)

Band structure with DMFT calculations



20.8 Å^3 / f.u.　　21.8 Å^3 / f.u.　　22.8 Å^3 / f.u.

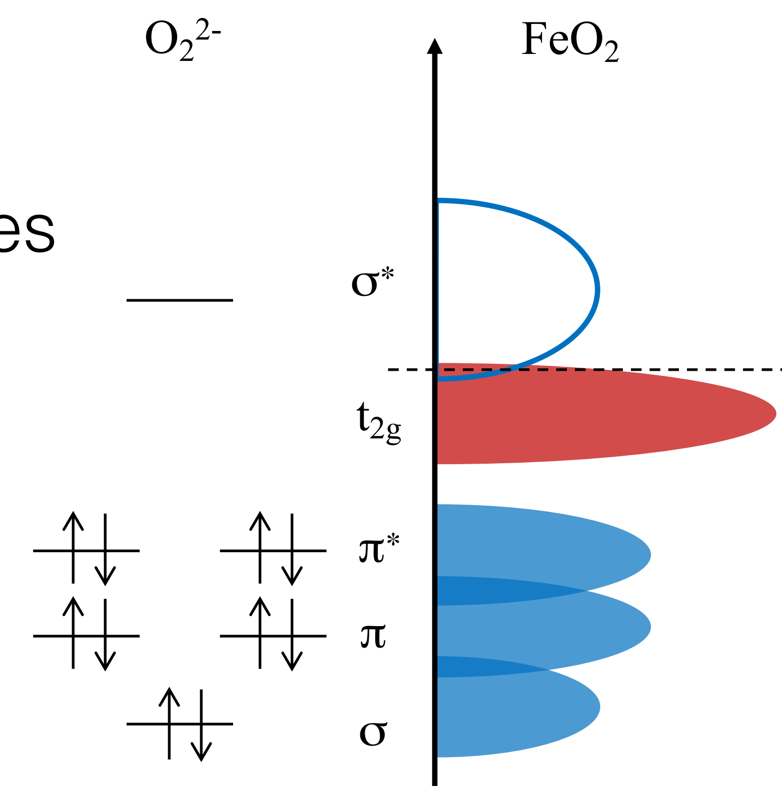


Calculated momentum resolved spectral function at 200 K

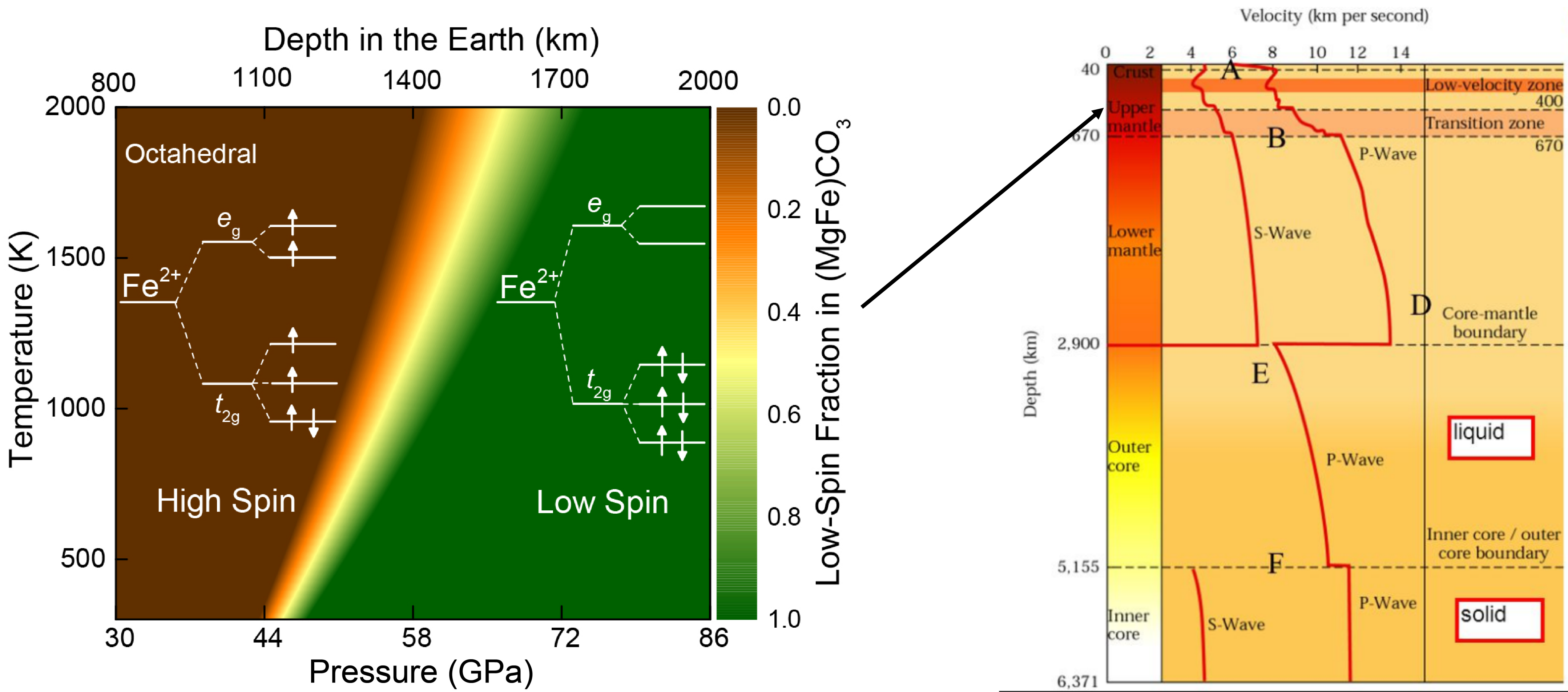
It shows metal to insulator transition with increasing volumes

FeO_2 show metallic behavior due to the broad O_2 σ* band

Small spectral weight near Fermi level disappear as O_2 σ* band width decreases



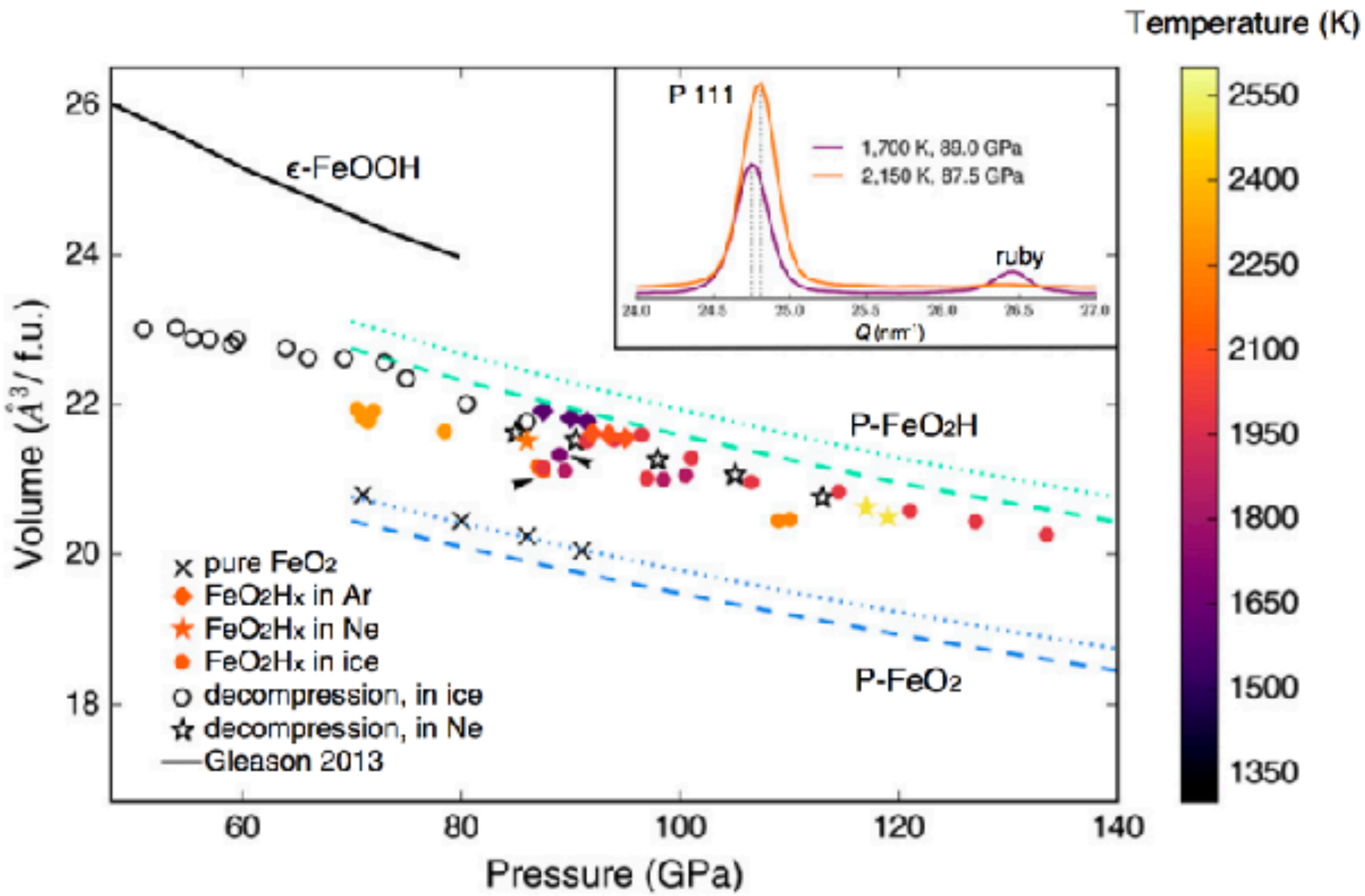
Spin transition softens seismic velocity

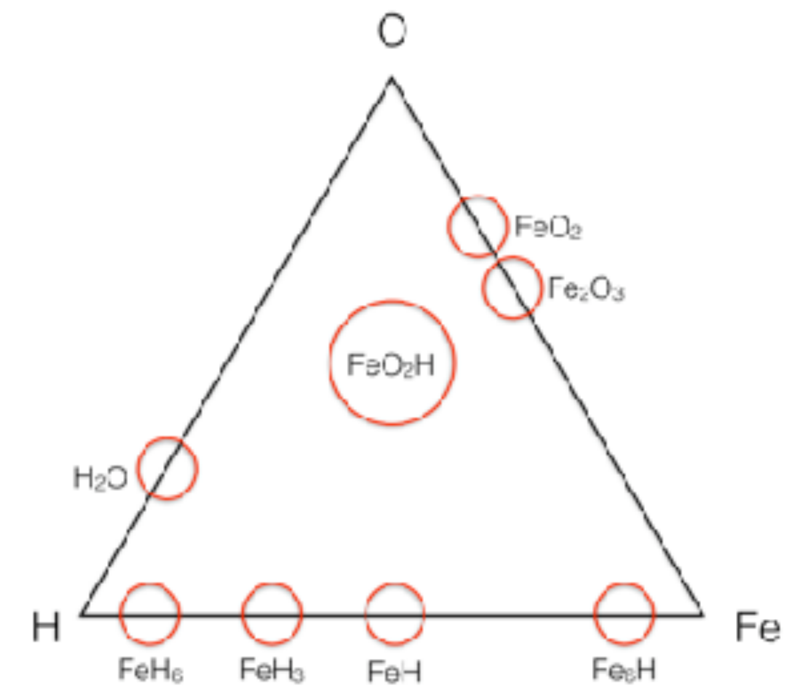


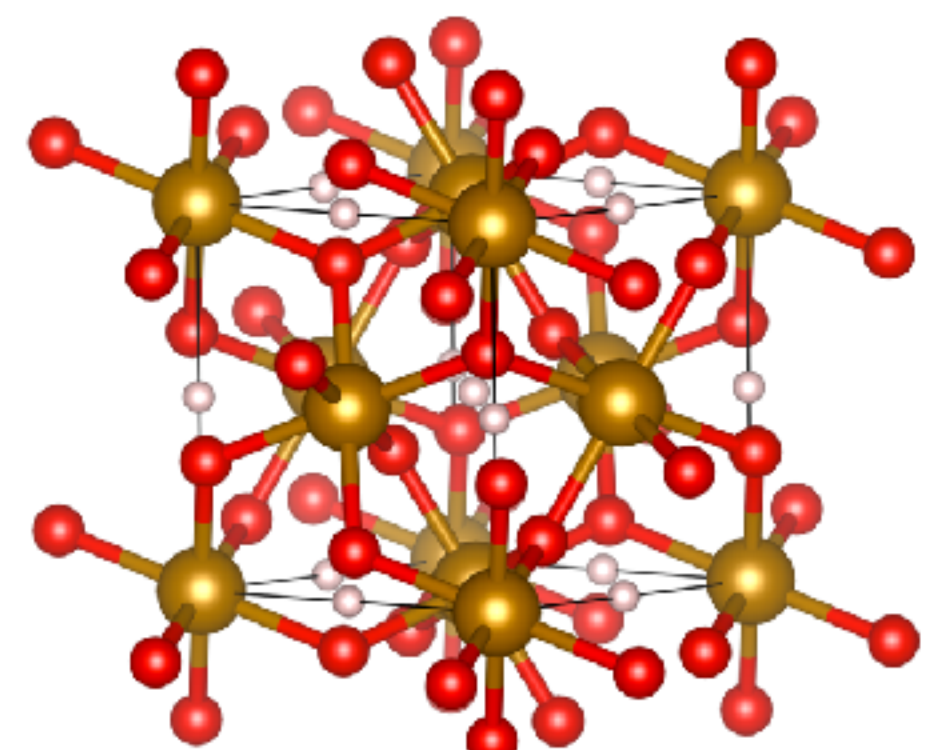
HS to LS transition with pressure induces a volume collapse
Bulk modulus become soft at the spin crossover zone

image courtesy: Afu Lin's group

The relation between FeO_2H and FeO_2



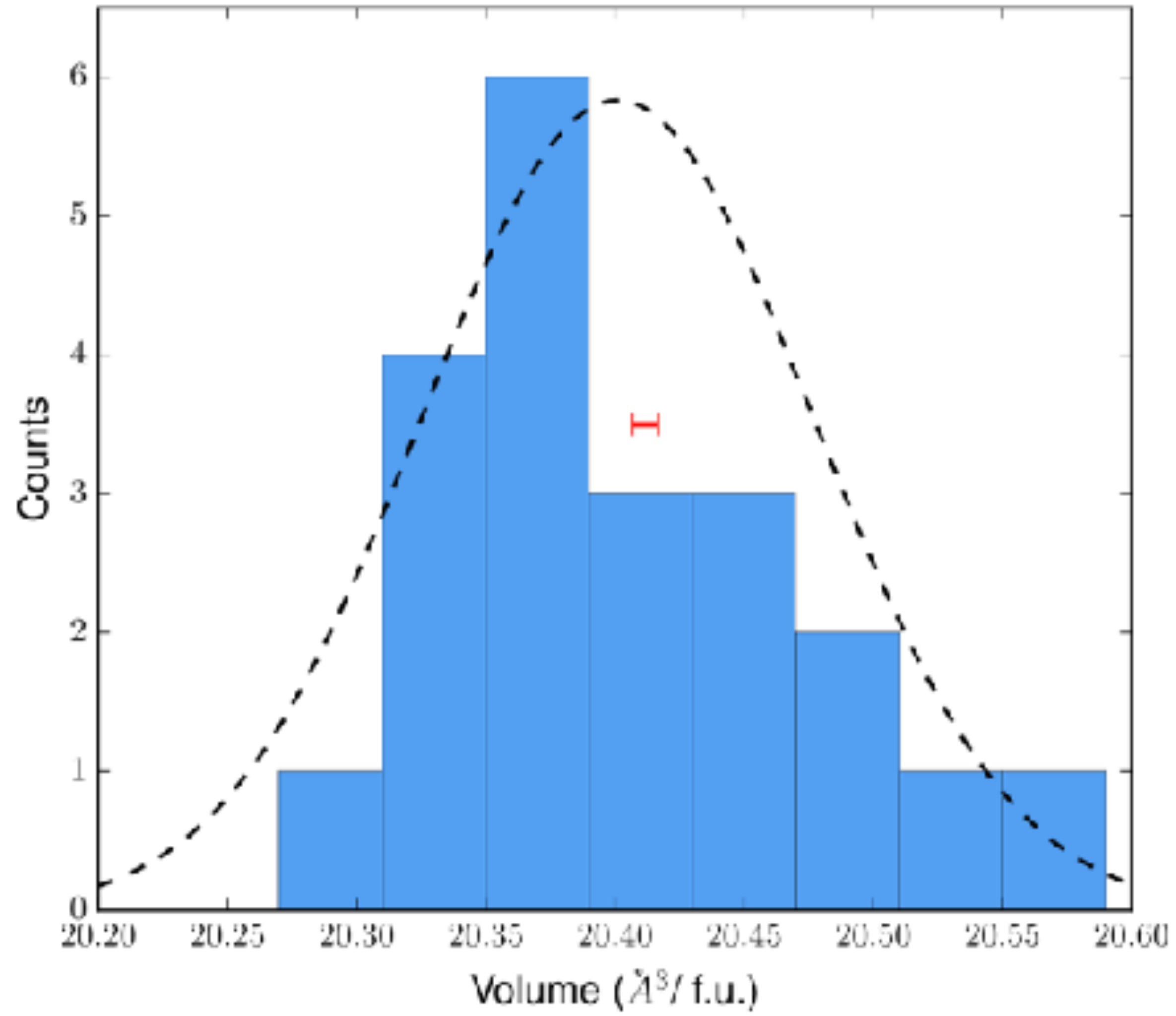




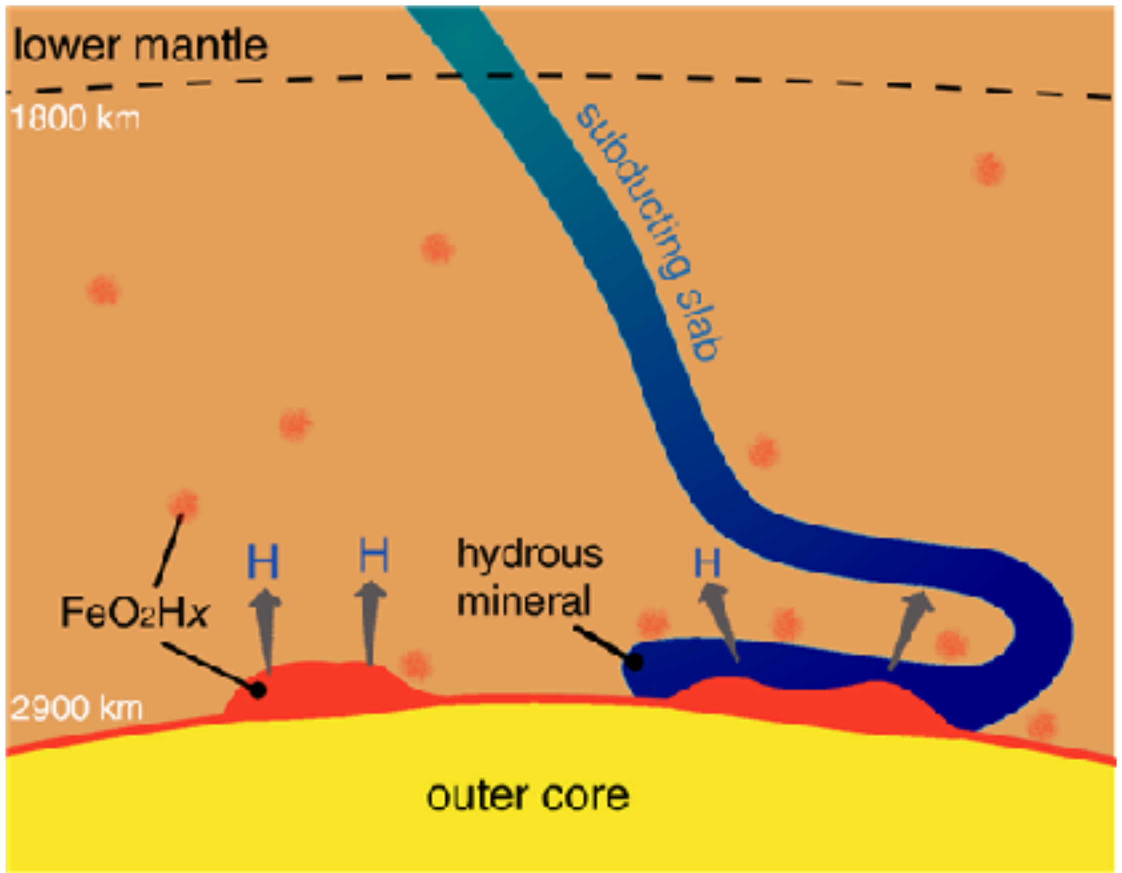
$$2FeO_2H = 2FeO_2Hx + (1-x)H_2,$$

PNAS **114** 1498-1501 (2017)

FeO_2H releases hydrogen at DLM



Volume scattering in an FeO_2H_x at 100 GPa

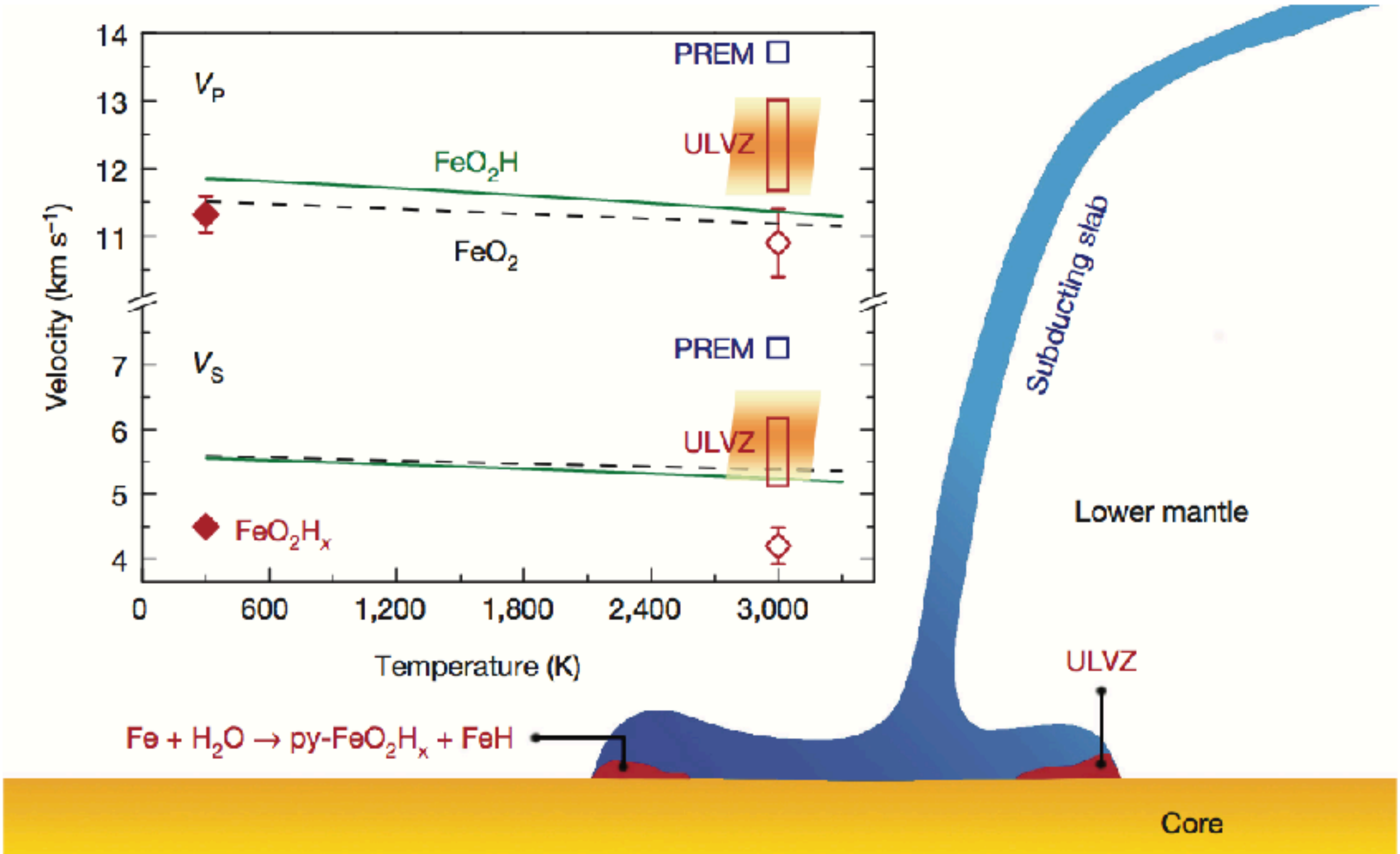


Schematic view of hydrogen circulation

but, hydrogen release in FeO_2H is contradicting

PNAS **114** 1498-1501 (2017)

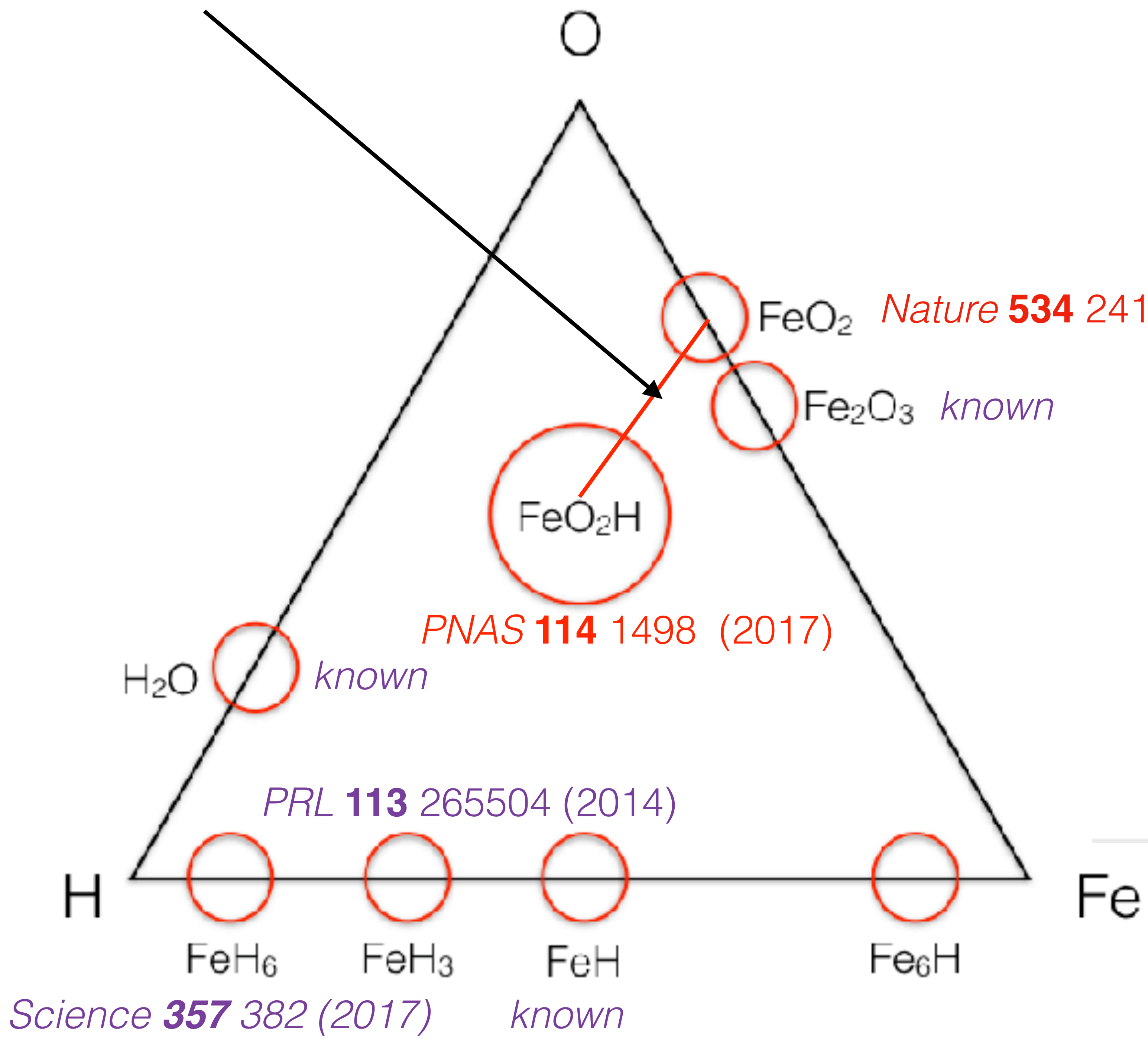
FeO_2H explains seismic velocity at DLM

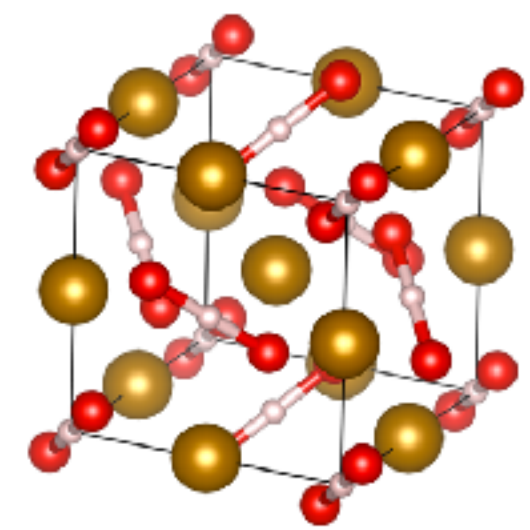


Nature in press

How much can be done using DFT ?

1. Hydrogen-bearing iron peroxide and the origins of ultralow velocity zones, *accepted in Nature (2017)*
2. When water meets iron at Earth's core-mantle boundary, *accepted in National Science Review (2017)*



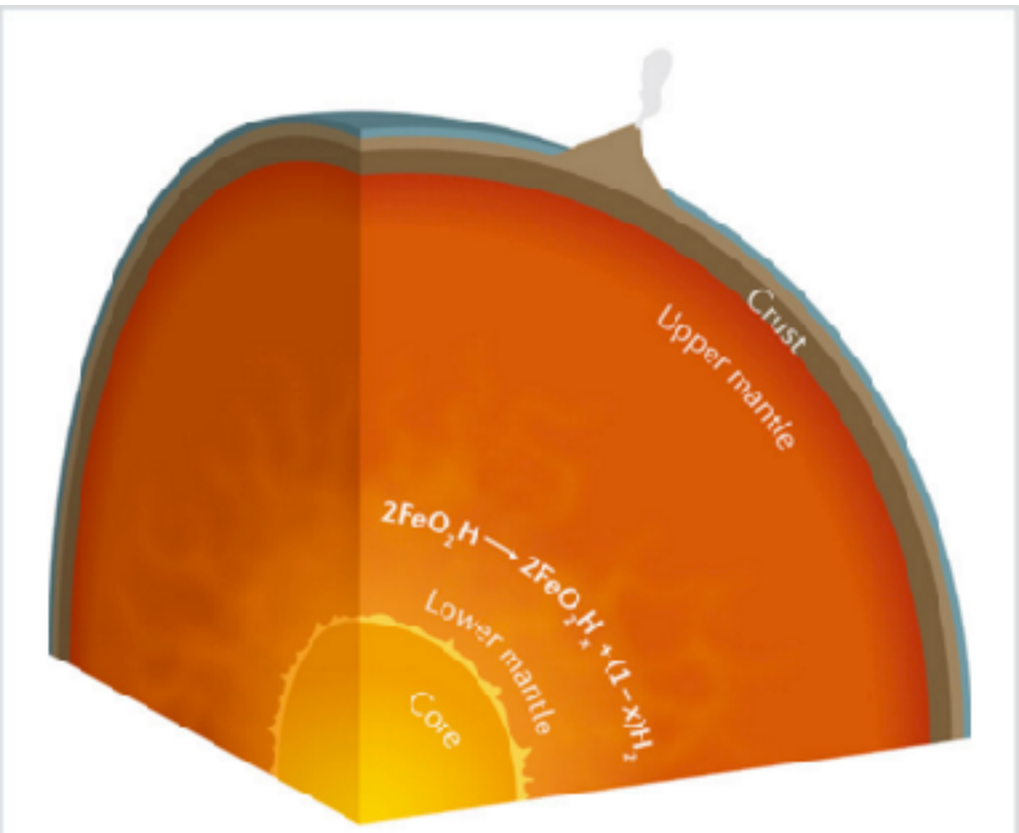


MENU
nature REVIEWS CHEMISTRY

Research Highlight

Geochemistry: A journey to the oxidized centre of the Earth

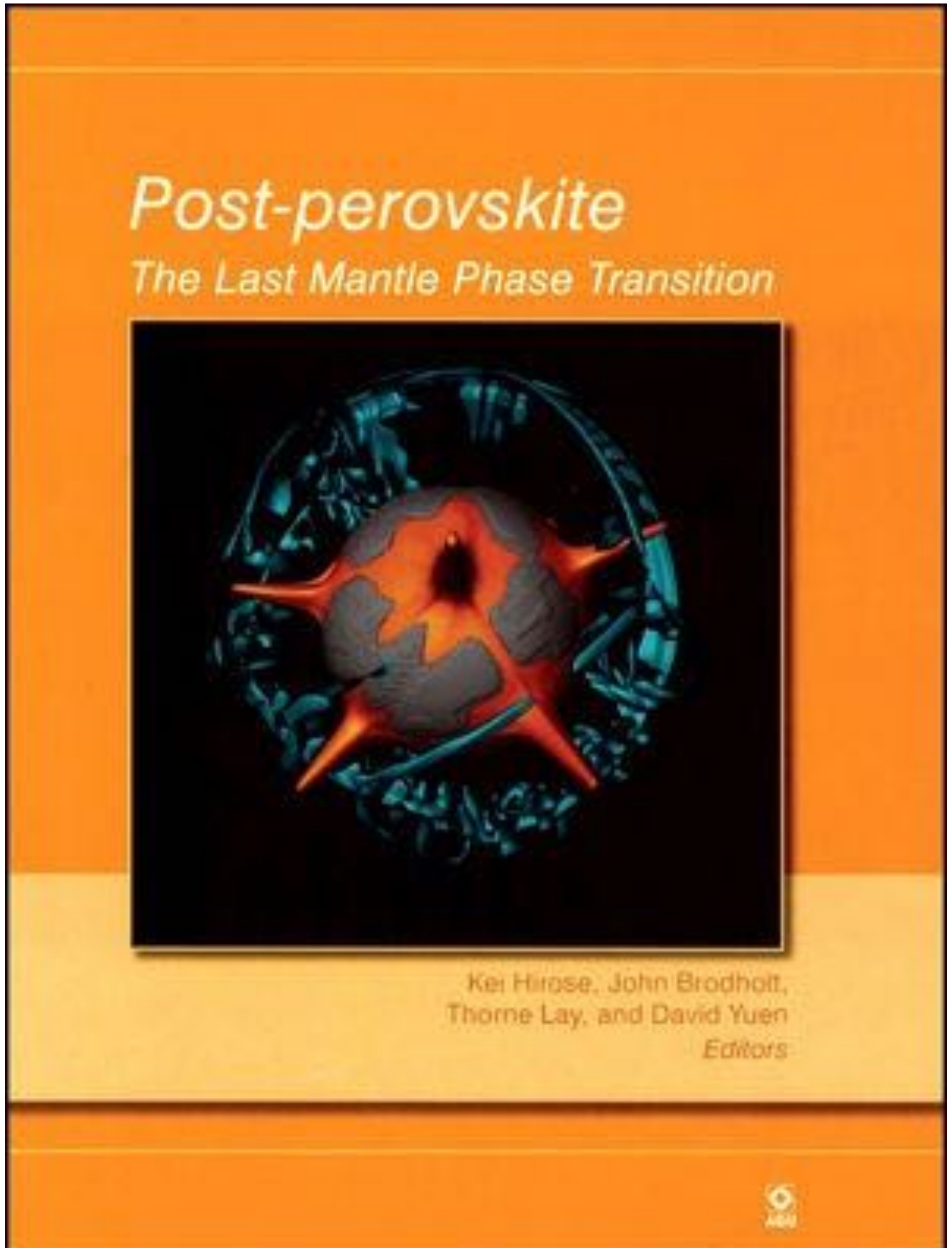
Gabriella Graziano



Rachael Tremlett/Macmillan Publishers Limited

Iron is present in various forms in the different layers of the Earth – metallic iron in the core, bridgmanite ($(Mg,Fe)SiO_3$) and ferropericlase ($(Mg,Fe)O$) in the mantle, and olivine ($(Mg,Fe)_2SiO_4$), haematite (Fe_2O_3) and goethite in the crust. Another form of iron that is present in the mantle is FeO_2, which can be generated by either haematite oxidation or goethite dehydrogenation, two processes that occur at the high pressures (~78 GPa) and temperatures (~1,800 K) in the deep lower mantle of the Earth. In previous work, the Mao group found that the unit cell of the FeO_2 mineral derived from goethite dehydrogenation was quite variable owing to the presence of residual hydrogen in the form of FeO_2H_x. Mao and co-workers have now moved forward: by combining diamond anvil cell compressions, state-of-the-art X-ray diffraction measurements and first-principles simulations, they have quantified the amount of hydrogen lost by goethite and proposed a two-step mechanism for goethite dehydrogenation.

Pyrite, a post DLM phase after post perovskite ?



An Introduction to Post-Perovskite: The Last Mantle Phase Transition

Kei Hirose[1], John Brodholt[2], Thorne Lay[3], and David A. Yuen[4]

Discovery of the perovskite to post-perovskite phase transition in $MgSiO_3$, expected to occur for deep mantle conditions, was first announced in April 2004. This immediately stimulated numerous studies in experimental and theoretical mineral physics, seismology, and geodynamics evaluating the implications of a major lower mantle phase change. A resulting revolution in our understanding of the D″ region in the lowermost mantle is well underway. This monograph presents the multidisciplinary advances to date ensuing from interpreting deep mantle seismological structures and dynamical processes in the context of the experimentally and theoretically determined properties of the post-perovskite phase change; the last silicate phase change likely to occur with increasing pressure in lowermost mantle rocks.

A pyrite of FeO_2 is not alone
- MgO_2, FeS_2, SiO_2, AlOOH

Recently, we have obtained seismic velocity data of FeO_2 and FeOOH

Conclusion / perspective

High-Pressure science can provide an alternative view of states of matter ; another dimension of science

Crystal structure search using first principle calculations gives a practical tool to predict atomic configuration of materials at a given constraints without experimental inputs

Computational condensed matter physics can play a critical role in studying geoscience and an emerging theoretical approach even can change the conventional understanding

We suggest an abundant FeO_2 patches at the lower mantle conditions in the earth and we are working on providing more theoretical/experimental evidence to support our idea, which is a major research topic of our center for 5- 10 years

Post-doctoral positions are available (duckyoung.kim@hpstar.ac.cn)