Insights into the Properties of the Deep Earth from Computational Mineral Physics

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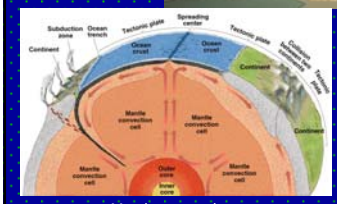
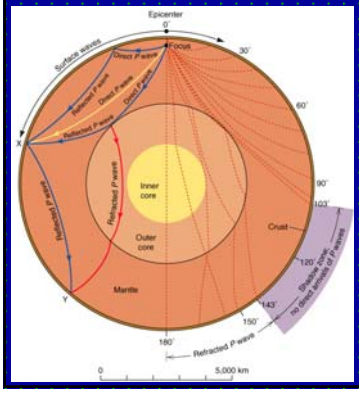
Understanding is hidden inside…



Mantle convection

Core convection

Earth's internal structure is known from seismological studies, but its interpretation needs mineral physics



1906: Oldham infers liquid core.

1914: Gutenberg deduces depth of CMB.

1936: Lehmann finds solid inner core.

1981: Dziewonski creates global Earth's model.

1983: Lay discovers D" discontinuity.

2002: Ishii & Dziewonski find innermost inner core.

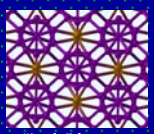
Pressure at the centre = 3.65 million atmospheres.

Materials properties change dramatically under pressure, so: DON'T use extrapolations!

- Metallisation ("Turning Wood Into Copper": SmS – at 0.6 GPa, Ne – at 158 TPa).
- Disappearace of magnetism (Fe at 13 GPa).
- Profound structural changes.

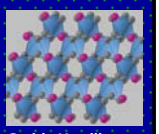
Superconductivity
In many elements

s→d transition
In K, Rb, Cs
(Schwarz`99)



"Ionic" boron
(ARO'06)

Tetrahedral carbonates: $CaCO_3$ (ARO`06)



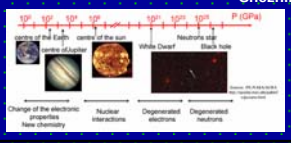
Stable Xe silicates
(Jung & ARO'07)

High-pressure experiments are extremely difficult

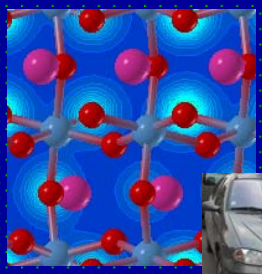
Multianvil press
P < 25-55 GPa

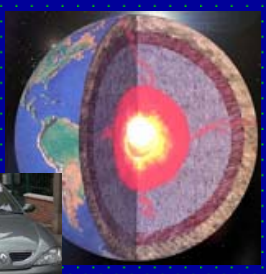
Diamond anvil cell
P < 300 GPa

Shock-wave gun
Caltech, LLNL: P< 500 GPa
Snezhinsk: P < 10^4-10^5 GPa



We simulate Earth's materials under pressure using quantum mechanics





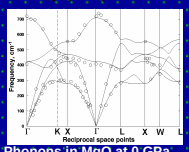
Density functional theory (DFT): $E=F[\rho]$

DFT enables accurate calculations of many properties

$$E = E_{n-e}[\rho] + \int V_{n-e}\rho(\mathbf{r})d\mathbf{r} + E_H[\rho] + E_{XC}[\rho] + E_{ion}[\psi \to \rho] \quad \to \text{standard DFT}$$

$$f_i = -\frac{\partial E}{\partial x_i} = -\left[\frac{\partial E_{n-e}}{\partial x_i} + \int \frac{\partial V_{n-e}}{\partial x_i}\rho(\mathbf{r})d\mathbf{r}\right] \quad \to \text{molecular dynamics}$$

$$\frac{\partial^2 E}{\partial x_i \partial x_j} = \frac{\partial^2 E_{n-n}}{\partial x_i \partial x_j} + \int \frac{\partial^2 V_{n-e}}{\partial x_i \partial x_j}\rho(\mathbf{r})d\mathbf{r} + \int \frac{\partial V_{n-e}}{\partial x_i}\frac{\partial \rho(\mathbf{r})}{\partial x_j}d\mathbf{r} \to \text{phonons}$$



Phonons in MgO at 0 GPa
(ARO et al., *J.Chem.Phys.* 2003)

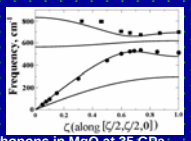
Equations of state of phases in the MgO-SiO_2 system: theory and experiment.

	V_0, Å^3	K_0, GPa	K_0'
MgO			
Theory	76.2	168.7	4.258
Exp.	74.7	160.2	3.99
Stishovite			
Theory	46.3	318.3	4.373
Exp.	46.9	312.9	4.8
$MgSiO_3$ perovskite			
Theory	163.3	261.4	4.032
Exp.	162.3	259.5	5.69

Thermodynamic properties of phases in the MgO-SiO_2 system: theory and experiment @ GPa, 300 K).

	MgO periclase		SiO_2 Stishovite		$MgSiO_3$ perovskite	
	theory	Exp.	theory	Exp.	theory	Exp.
C_V	36.58	36.87	41.3	42.2	80.73	77.3
S	26.81	27.13	24.6	25.9	57.14	57.2

(ARO *et al.*, 2003-2005)

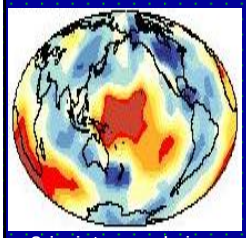


Phonons in MgO at 35 GPa
(Ghose, Krisch, ARO, *PRL* 2006)

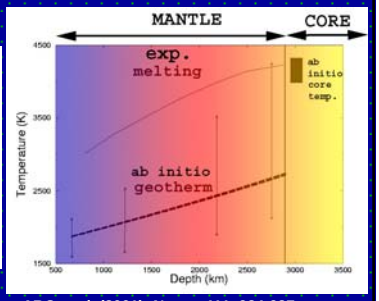
$$F(T) = E_0 + \int_0^{\omega_{max}} \frac{1}{2}\hbar\omega\, g(\omega)d\omega + k_B T \int_0^{\omega_{max}} \ln[1-\exp(-\frac{\hbar\omega}{k_B T})]g(\omega)d\omega$$

G=F-V(d*F*/d*V*).

Temperature distribution can be inferred from mineral properties



Seismic tomography image
(Masters et al., 2000)



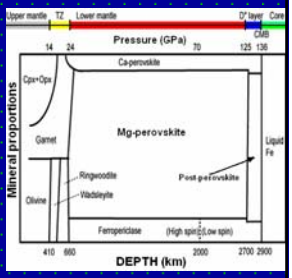
ARO et al. (2001), *Nature* 411, 934-937;
Ono & ARO (2005), *EPSL* 236, 914-932

Deep Earth's mineralogy is not as primitive as once thought

1. "Soup a la mantle":
$1.2MgO + 1SiO_2 + 0.1FeO + 0.1Al_2O_3 + 0.1CaO$

2. $(Mg,Fe)SiO_3$ perovskite - 75 vol.% of lower mantle, 40 vol.% of the Earth!

3. Metallic iron and Fe^{3+} in the lower mantle and D" layer:
$3Fe^{2+} \rightarrow 2Fe^{3+} + Fe^0$
(Frost'04; Sinmyo'06; Zhang & ARO'06)



Ono & ARO, *EPSL* (2005)

Novel simulation methods are a powerful tool for discovery in Earth sciences

1. New mineral in Earth's mantle

Density-functional perturbation theory

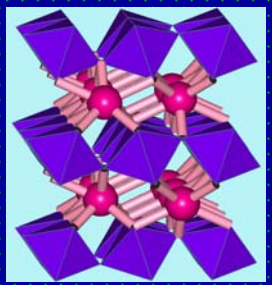
2. Anisotropy of the D" layer

Ab initio metadynamics

3. Crystal structure prediction

Ab initio evolutionary algorithm

1. New mineral in the Earth's mantle

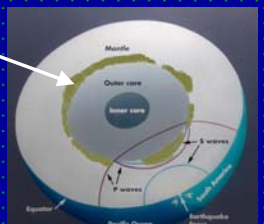


Post-perovskite explains anomalies of Earth's D" layer (2700-2890 km depths)

Post-perovskite:
75 vol.% of D" layer

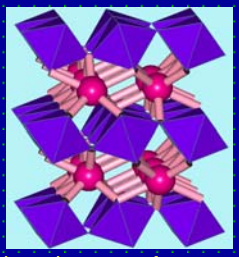
Discovered in 2004
(Murakami *et al.*, *Science*'2004; ARO & Ono, *Nature*'2004)
following S. Ono's work on Fe_2O_3.

Family of related structures predicted
(ARO et al., *Nature*'2005)
and verified
(Tschauner et al., under review)

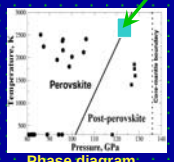


D" is the root of "hot spots"

Properties of post-perovskite explain most mysteries and imply that D" layer is growing with time



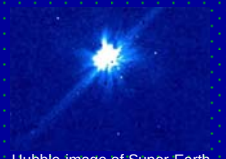
Anisotropic structure of post-perovskite
Explains D" anisotropy and electrical conductivity
Conductivity explains decadal variations of the length of day



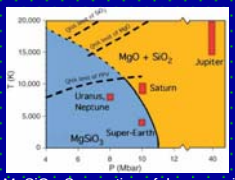
Phase diagram
Explains D" discontinuity and its variability
Predicts growth of D" due to cooling of Earth
Increases Earth's cooling rate (Tackley'05)
D" layer should not exist in Mercury and Mars

Predicted related minerals
Explain plastic deformation of D" layer

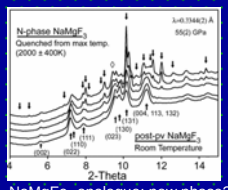
What's beyond post-perovskite?



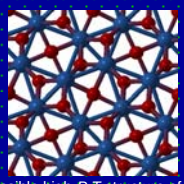
Hubble-image of Super-Earth



$MgSiO_3$: Suggestion of decomposition (Umemoto et al., *Science* 2006)

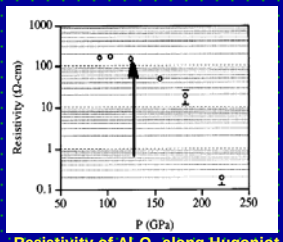


$NaMgFe_3$ analogue: new phase? (Martin et al., *GRL* 2006)

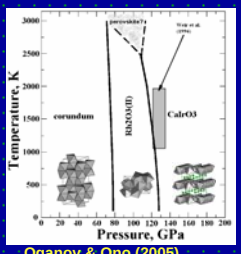


Possible high-*P,T* structure of $MgSiO_3$

Al_2O_3: jump of electrical conductivity at 130 GPa coincides with a "*PPV*" transition



Resistivity of Al_2O_3 along Hugoniot (Weir *et al.*, 1996)



Oganov & Ono (2005), *PNAS* 102, 10828-10831

Our prediction agrees with (Caracas & Cohen, 2005; Tsuchiya *et al.*, 2005).
Experimental confirmation – Oganov & Ono (PNAS'05), Ono (EPSL'06)

Conductivity is likely due to diffusion of O^{2-} ions.

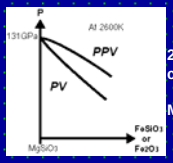
Elements partition strongly between *PV* and *PPV*

[Ono & Oganov (2005), *EPSL* **236**, 914-932]

At 120 GPa:

Cation	ΔH_{perov}, eV	$K_{PV\text{-}PPV}$(4000 K)
Be^{2+}	0.821	0.092
Ca^{2+}	0.154	0.64
Sr^{2+}	0.925	0.068
Ba^{2+}	2.271	0.0014
Ni^{2+}	0.397	0.32
Fe^{2+}	-0.239	2.00
Al^{3+}-Al^{3+}	0.286	0.44

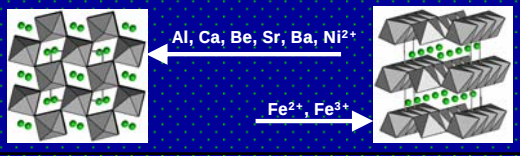
K < 1 indicate better solubility in perovskite



2-phase coexistence loop can be very wide (Akber'05)

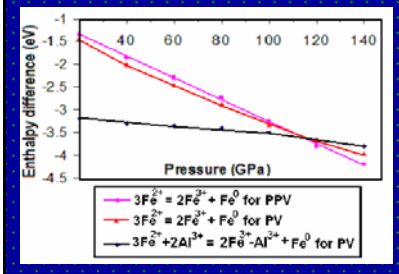
Makes transition invisible?

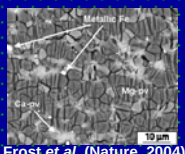
Agree with Mao'04; Kobayashi'05.
Disagree with Murakami'05.



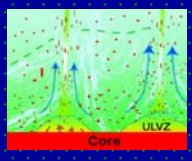
Iron impurities in *PV* and *PPV* are Fe^{3+}, and there is free metallic iron in the lower mantle

$(Mg,Fe^{2+})SiO_3+MgO=(Mg,Fe^{3+})(Si,Fe^{3+})O_3+Fe$





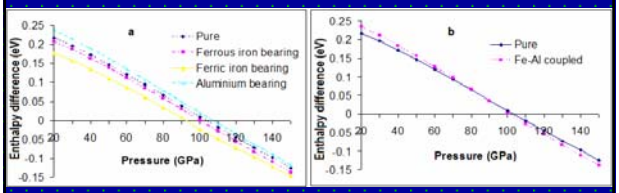
Frost *et al.* (Nature, 2004)



Theory (Zhang & ARO, EPSL 2006) consistent with experiment (Frost *et al.*, *Nature* 2004).

Metallic Fe in lower mantle. Extracts siderophiles. Core growth?

At mantle compositions, impurities stabilise *PPV* by several GPa

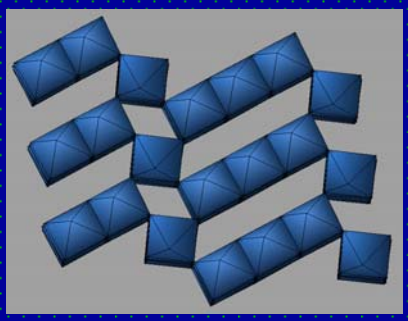


***PPV-PV* enthalpy difference: effects of chemistry**

$$\frac{\partial P_{tr}}{\partial x_{Al_2O_3}} = 0.950 \text{ GPa}, \quad \frac{\partial P_{tr}}{\partial x_{FeO}} = -0.997 \text{ GPa}, \quad \frac{\partial P_{tr}}{\partial x_{Fe_2O_3}} = -3.904 \text{ GPa}, \quad \frac{\partial P_{tr}}{\partial x_{FeAlO_3}} = -0.866 \text{ GPa}$$

$K_{PV\text{-}PPV}(Fe^{3+})$= 39 for Al-free system
4.8 for Al-saturated system (120 GPa, 3000 K).

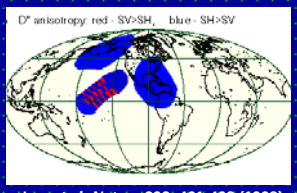
2. Anisotropy of the D” Layer



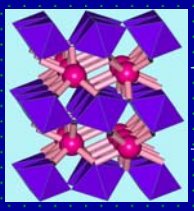
It has been very difficult to explain the anisotropy of the D” layer

2004: $MgSiO_3$ post-perovskite with {010} plastic slip produces correct type of anisotropy.

But: the amount of preferred orientation needed to explain observations is ~50-100%.

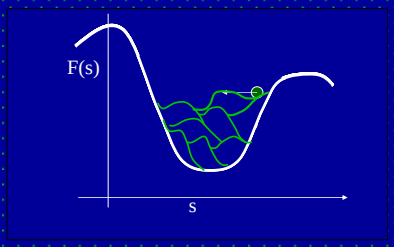


Lay et al, *Nature* 392, 461-468 (1998)



We use metadynamics to study plastic deformation of post-perovskite

Metadynamics can find: phase transition mechanisms, new crystal structures, plastic deformation mechanisms.



(Laio & Parrinello, 2002; Martonak et al., 2003)

Predicted {110} slip was not expected, but makes sense

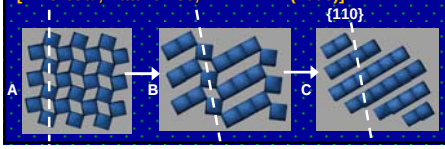
(modified from Ballentine’02)

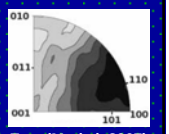
Subduction: ~40% preferred orientation gives $V_{SH}>V_{SV}$, tilted axis.
(*cf.* Garnero’04; Wookey’05)

Horizontal flow: $V_{SH}<V_{SV}$

Plumes: $V_{SH}>V_{SV}$ or $V_{SH}=V_{SV}$

[ARO et al, *Nature* 438, 1142-1144 (2005)]

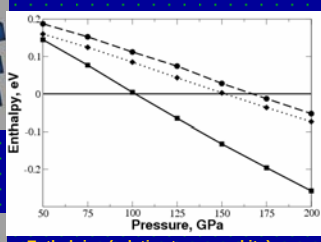




Exp. (Merkel, 2007)

New structures are energetically competitive and may exist in the mantle (synthesized by Tschauner’07)

Perovskite



2x2-structure

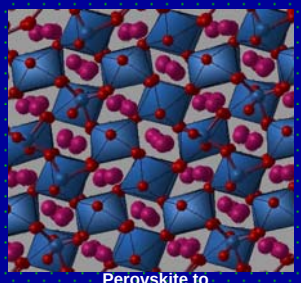
3x1-structure

Enthalpies (relative to perovskite):
solid – post-perovskite
dotted – 3x1 structure
dashed – 2x2 structure

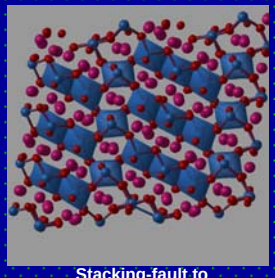
[ARO et al, *Nature* 438, 1142-1144 (2005)]

Post-perovskite

More detailed picture of the post-perovskite transition

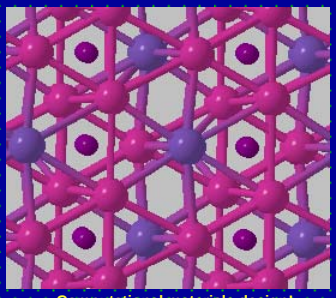


Perovskite to stacking-fault



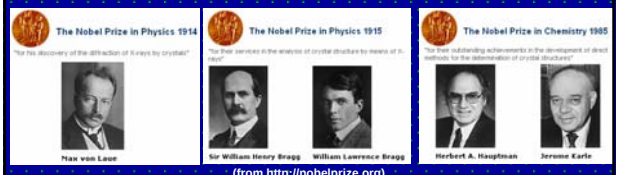
Stacking-fault to post-perovskite

3. Are Crystal Structures Predictable?



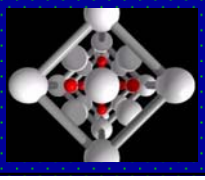
-Computational materials design!
-Find new Earth's minerals!
-Chemistry at extreme conditions!

Structure is the basis for understanding materials and their properties



(from http://nobelprize.org)

Zincblende ZnS.
First structure solved by Braggs in 1913.



It is believed that prediction of stable structure just from the chemical formula is impossible

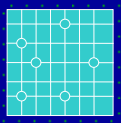
> One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition. Who, for example, would guess that graphite, not diamond, is the thermodynamically stable allotrope of carbon at ordinary temperature and pressure? Solids such as crystalline water (ice) are still thought to lie beyond mortals' ken.

J. Maddox, editorial comment in *Nature* (1988)

Crystal structure prediction is hard, because of the enormous number of possible structures

Need to find GLOBAL minimum of free energy.
Trying all combinations is impossible:

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



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

USPEX (Universal Structure Predictor: Evolutionary Xtallography)

- Evolutionary algorithm

Compatible with expected landscape shape

- Local optimisation

Eliminate „noise"

- Requires only chemical composition

Random initialisation (start from random structures)
No experimental data required

INPUT:
- Number of atoms of each type
- *P,T* conditions (usually T= 0 K)
- Parameter values
- Optional: Experimental lattice parameters
- Optional: Starting structures

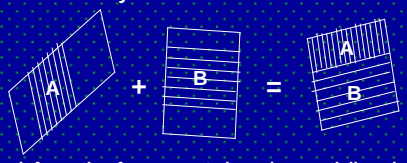
ARO, Glass, Ono (2006). *Earth Planet. Sci. Lett.* **241**, 95.
ARO, Glass (2006). *J. Chem. Phys.* **124**, art. 244704.
Glass, ARO, Hansen (2006). *Comp. Phys. Comm.* **175**, 713.

USPEX in a Nutshell

- Initialise (First population)
- Assign a fitness value to each individual using the evaluation function
- Select individuals (parents) based on their fitness
- Use variation operators on parents to create new individuals (offspring)
- Choose new population from old population + offspring

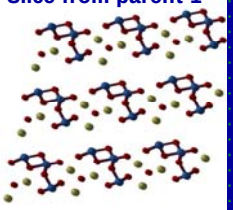
Selection:
- Stochastic
- Better fitness rank leads to higher probability of being chosen. Usually linear or quadratic dependance.
- A predefined amount of worst individuals are discarded from selection (~40%)

USPEX: Heredity

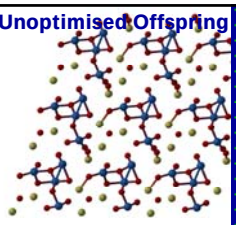


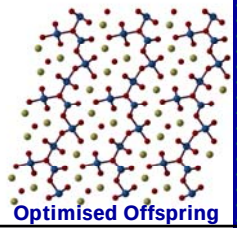
- Conserve information from parents by using spatially coherent pieces:
- Match planar slices of two parents.
- [0,X] and [X,1] on random lattice vector. Cut parallel to other vectors.
- Shift prior to cut, to avoid biasing substructure "position"
- Adjust number of atoms of each kind.
- Lattice: Weighted average
- Allows sampling "in between" two parents

Slice from parent 1



Unoptimised Offspring

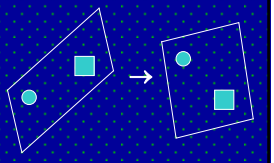




Optimised Offspring

USPEX: Lattice Mutation

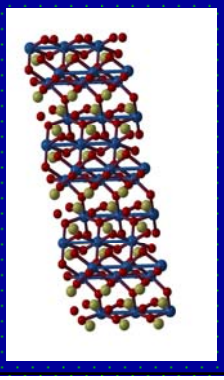
$$(\mathbf{I}+\varepsilon)=\begin{pmatrix} 1+\varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1+\varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1+\varepsilon_3 \end{pmatrix}$$

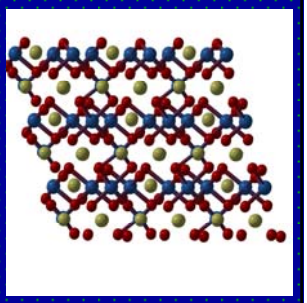


- Apply strain matrix with zero-mean Gaussian random strains
- Leave fractional coordinates as they are.
- Investigate neighbourhood of good individuals.
- Often structures of similar quality differ essentially in lattice (Metadynamics)
- Avoids premature convergence of lattice.

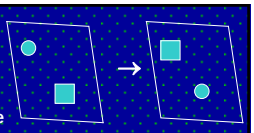
- And/or add zero mean Gaussian random variables to coordinates (we never use this, but in principle it could be useful)

Lattice Mutation: Example

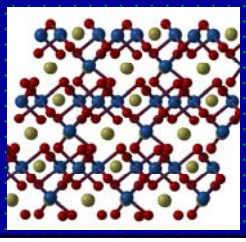


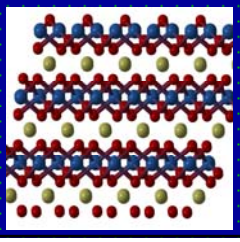


USPEX: Permutation

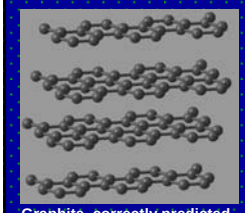


- Swap always two atoms of different type
- Especially if chemically similar atoms are present, structures of similar quality can be found by permutation
- Enables sensible steps that are very far and difficult in Euclidian distance

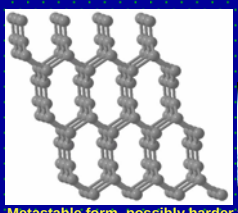




Test 1: „Who would guess that graphite is the stable allotrope of carbon at ordinary pressure?" (Maddox, 1988)



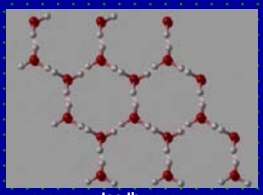
Graphite, correctly predicted to be the stable phase at 1 atm



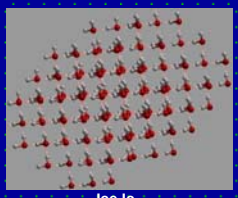
Metastable form, possibly harder than diamond.

Test 2: „Solids such as crystalline water (ice) are still thought to lie beyond mortals' ken" (Maddox, 1988)

Main component of Neptune and Uranus (~60 mol.%)
Proton-disordered structures
Previous methods failed to predict the structure of ice
USPEX find both known ices (Ih and Ic) in a single simulation at 1 atm

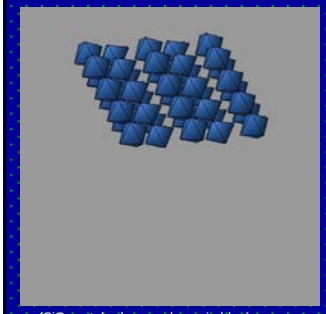


Ice Ih

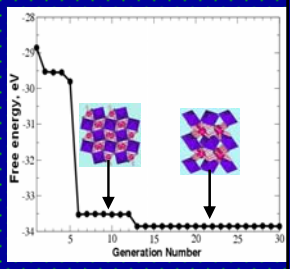


Ice Ic

Test 3: without any experimental information we find $MgSiO_3$ post-perovskite as the stable phase at 120 GPa



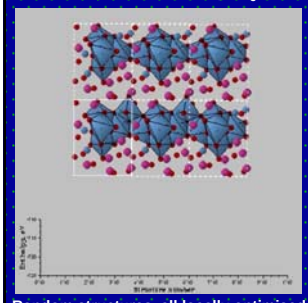
(SiO_6-octahedra are shown in blue)



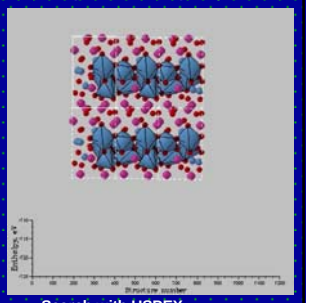
Free energy of the best structure in each generation.

Test 4: USPEX is vastly superior to random sampling

Test case: 40-atom cell of $MgSiO_3$ with fixed lattice parameters of post-perovskite



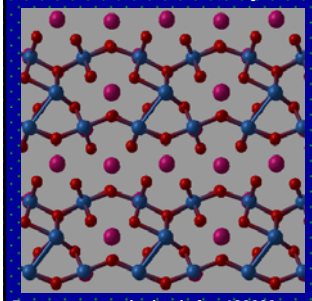
Random structures, all locally optimised
Did not find PPV after 120000 steps



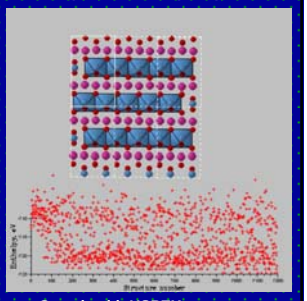
Search with USPEX
Found PPV after 950 steps

Test 4: USPEX is vastly superior to random sampling

Test case: 40-atom cell of $MgSiO_3$ with fixed lattice parameters of post-perovskite



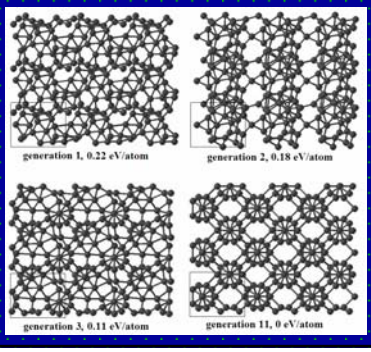
Best structure obtained after 120000 steps
Is *not* PPV



Search with USPEX
Found PPV after 950 steps

Evolutionary simulation is self-learning, self-improving

Example of Boron at 1 atm: we easily find the complex α-B structure



Most of Earth's carbon is in high-pressure carbonates C

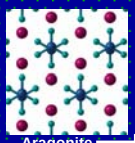
Carbon is the element of life. However, its greatest part is hidden in the Earth's mantle in the form of carbonates of Ca and Mg.

"*Jigoku*" at Mt. Karakuni (Japan): hot water and volcanic gases (H_2S, CO_2, ...)

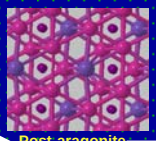
Newly discovered forms of carbonates – main reservoirs of carbon in the Earth

C

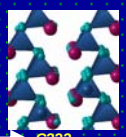
$CaCO_3$



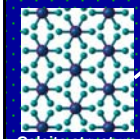
Aragonite
4-42 GPa, known



Post-aragonite
42-137 GPa, verified



$C222_1$
>137 GPa, verified



Calcite structure

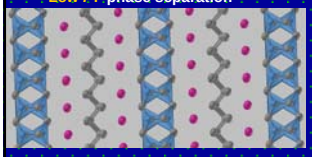
phase II, 82-138 GPa

ARO et al., *EPSL* 241, 95-103 (2006).

Investigating chemical reactions: Xe is not inert in the Earth's mantle

Xe

Low *P*: phase separation



Normally, Xe does not participate in chemical reactions. Only a few Xe compounds are known.

High *P*: xenon silicate ($XeSiO_4$) forms

Xe paradox: ~90% of Xe is missing in in the Earth's atmosphere.

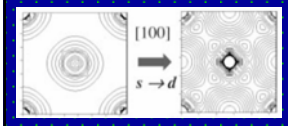
Is Xe chemically bonded in the mantle or core?

Sanloup (2006): experimental evidence for a reaction of Xe + SiO_2.

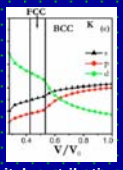
Jung & ARO (2007): insight into the nature of Xe silicates.

Novel chemistry of simple elements under pressure: "orbital alchemy", or how to turn s-elements into d-elements

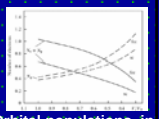
K



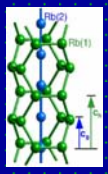
Valence electron density in Cs before and after s-d transition (Tse, 2005)



Orbital contributions for K (Xie, Cui. Tse, ARO, et al., 2007)



Orbital populations in Ca (Maksimov, 2005)

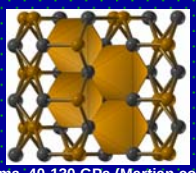


Structure of K(III) at 20 GPa

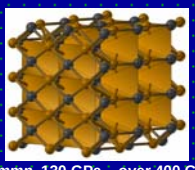
- Radioactive ^{40}K in the core?
- New chapter in geochemistry.

New phases of FeS in Martian and terrestrial cores

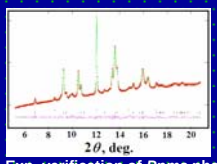
FeS



Pnma, 40-130 GPa (Martian core)



Pmmn, 130 GPa – over 400 GPa (Earth's core)



Exp. verification of *Pnma* phase

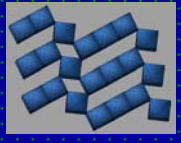
•*Pmmn* is a new structure type. Can be described as distorted NaCl-type.

Ono, ARO et al. (2007)

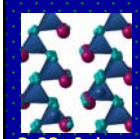
Novel simulation methods are a powerful tool in Earth sciences

1. Post-perovskite and Earth's mantle

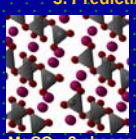
2. Anisotropy of the D" layer



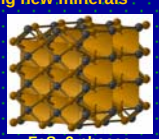
3. Predicting new minerals



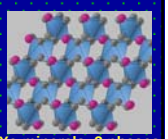
$CaCO_3$: 2 phases



$MgCO_3$: 2 phases



FeS: 2 phases



Xe-minerals: 3 phases

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- ETH Research Grants programme
- ETH Research Equipment programme
- Swiss Supercomputer Centre
- Russian Supercomputer Centre
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