# COMPUTATIONAL MINERALOGY WITH DENSITY-FUNCTIONAL THEORY

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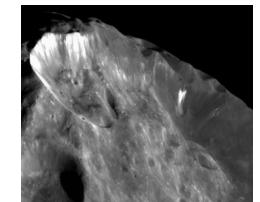
Simplified interior of the Earth
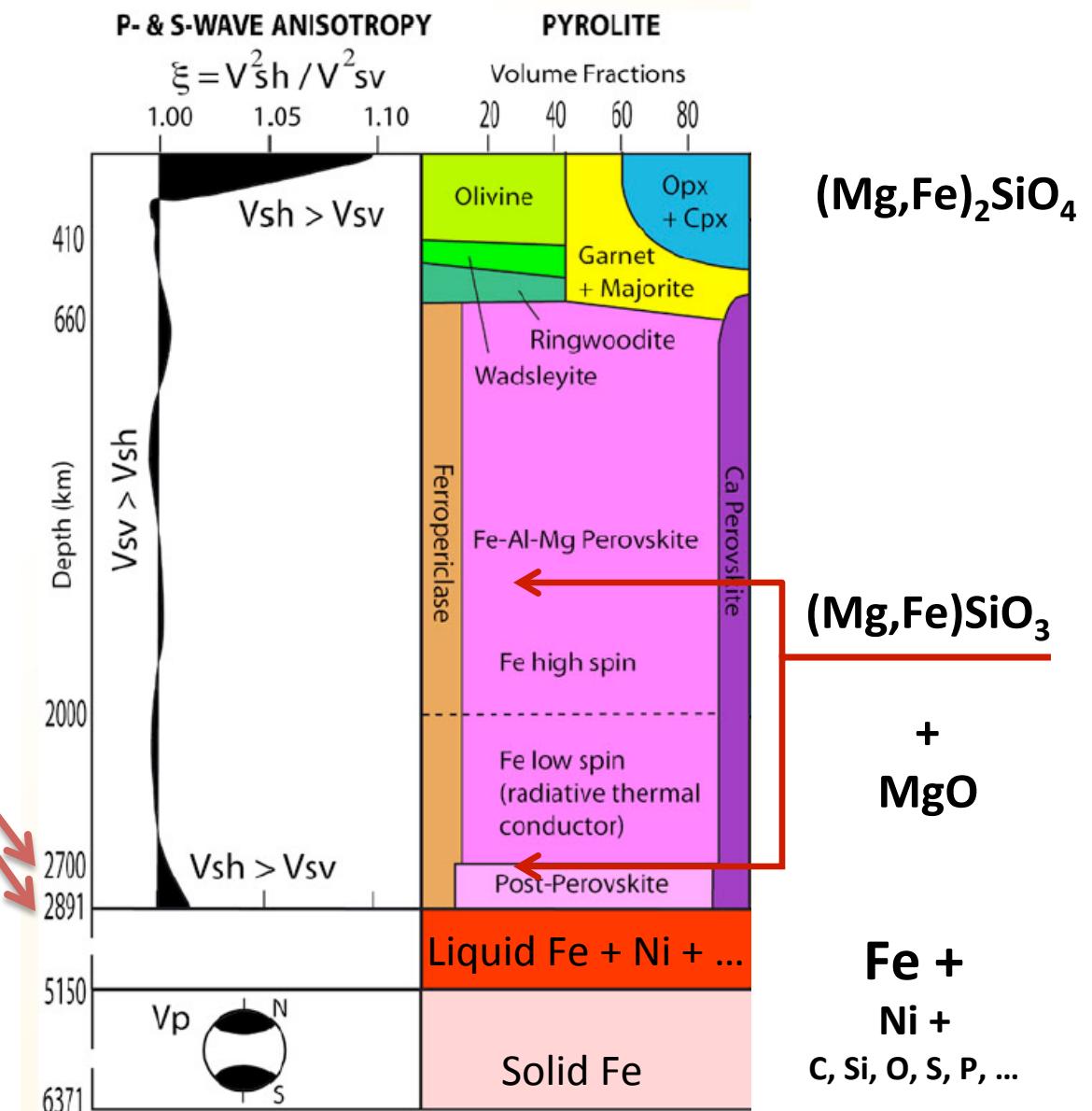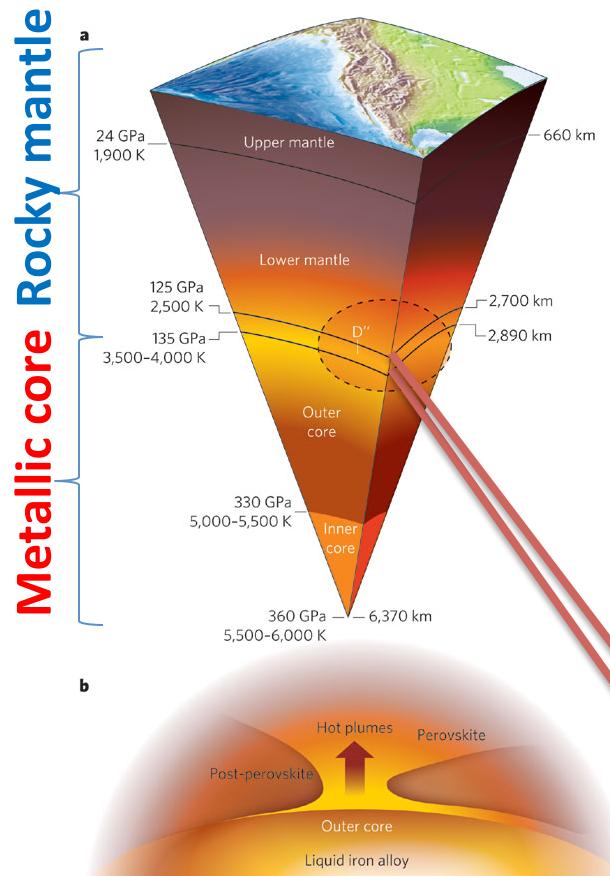
TRANSPORT Flowchart of the calculation

Idea: we obtain the electrical conductivity due to the phonon-induced electron scattering from the electron-phonon coupling matrix. We then need electronic wavefunctions close to the Fermi level, phonon bands, and the electron-phonon coupling matrix.

Perturbation of one atom κ in one direction α for a given vector **q**

$$h^{\kappa\alpha}_{\vec{k}i,\vec{k}'i'} = \langle \psi_{\vec{k}i} \mid \frac{\partial \mathcal{H}}{\partial R_{\kappa;\alpha}} \mid \psi_{\vec{k}'i'} \rangle$$

The electron phonon coupling (EPC) matrix,

$$g^{\vec{q}j}_{\vec{k}i,\vec{k}'i'} = \frac{1}{\sqrt{2\omega_{\vec{q}j}}} \sum_{\alpha\kappa} \frac{1}{\sqrt{M_\kappa}} u^{\vec{q}j}_{\kappa\alpha} h^{\kappa\alpha}_{\vec{k}i,\vec{k}'i'}.$$

With EPC we build the spectral function, summing g over band to calculate a (partial) Fermi surface integral.

$$\alpha^2_{\text{out(in)}}F(\omega) = \frac{1}{N(\epsilon_F)\langle v_x^2\rangle} \sum_\nu \sum_{kjk'j'} |g^{k'-k\nu}_{k'j',kj}|^2 v_x(\mathbf{k}) v_x(\mathbf{k}^{('})}$$

$$\times \delta(\epsilon_{\mathbf{k}j} - \epsilon_F)\delta(\epsilon_{\mathbf{k}'j'} - \epsilon_F)\delta(\omega - \omega_{\mathbf{k}'-\mathbf{k}\nu}).$$

Which are used to compute the T-dependent electrical resistivity

$$\rho(T) = \frac{\pi\Omega_{\text{cell}}k_B T}{N(\epsilon_F)\langle v_x^2\rangle} \int_0^\infty \frac{d\omega}{\omega} \frac{x^2}{\sinh^2 x} \alpha^2_{\text{tr}}F(\omega),$$

*ABINIT implementation by M. Verstraete after theory developed in S. Savrasov and D. Savrasov, **Electron-phonon interactions and related physical properties of metals from linear-response theory**, Phys. Rev. B 54, 16487 (1996).*

Electrical resistivity - hcp Fe
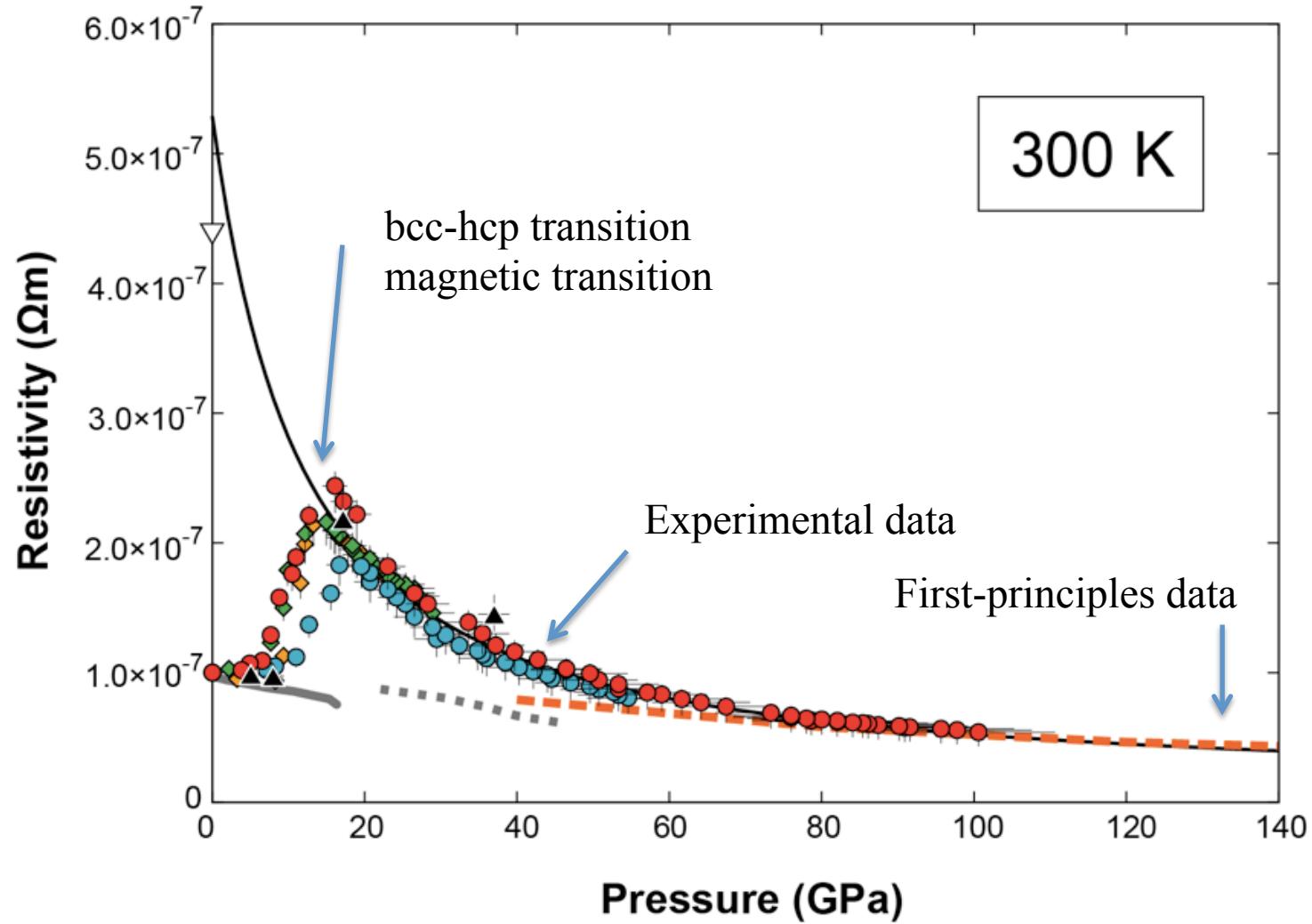
Saturation due to: **Pressure**

Electrical resistivity - hcp Fe + Si

Pure hcp Fe

Fe7Si hcp

FeSi hcp

T = 300K

T = 1000K

T = 2500K

Input into thermodynamical and geodynamical models:
-inner core started to form ~ 1 bil. years after Earth's formation
-stratification in present-day outer core
-long-standing magma ocean at the base of the mantle
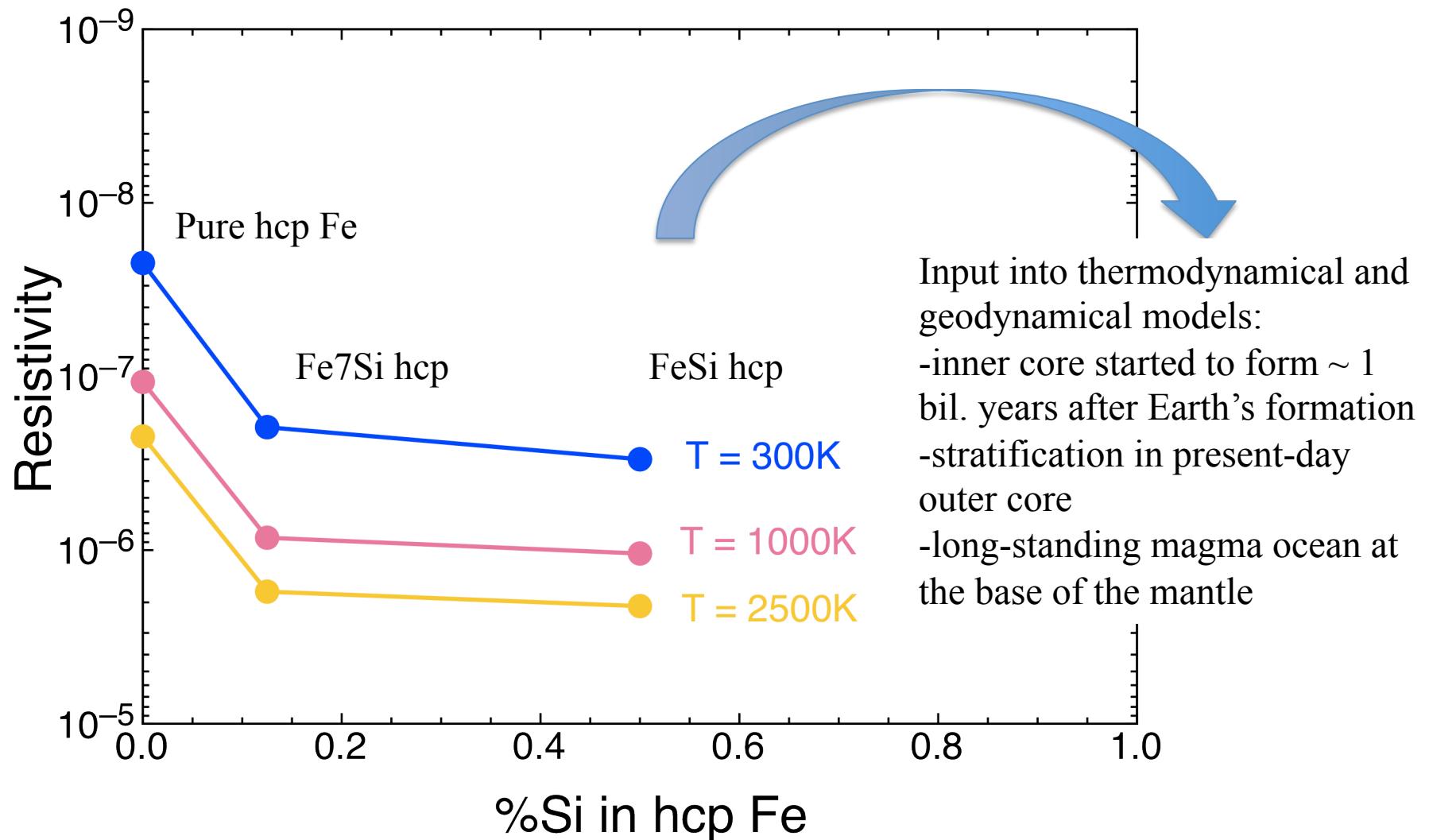
Saturation due to: Pressure, **Composition**
Next question: Temperature (?)

Simplified interior of the Earth
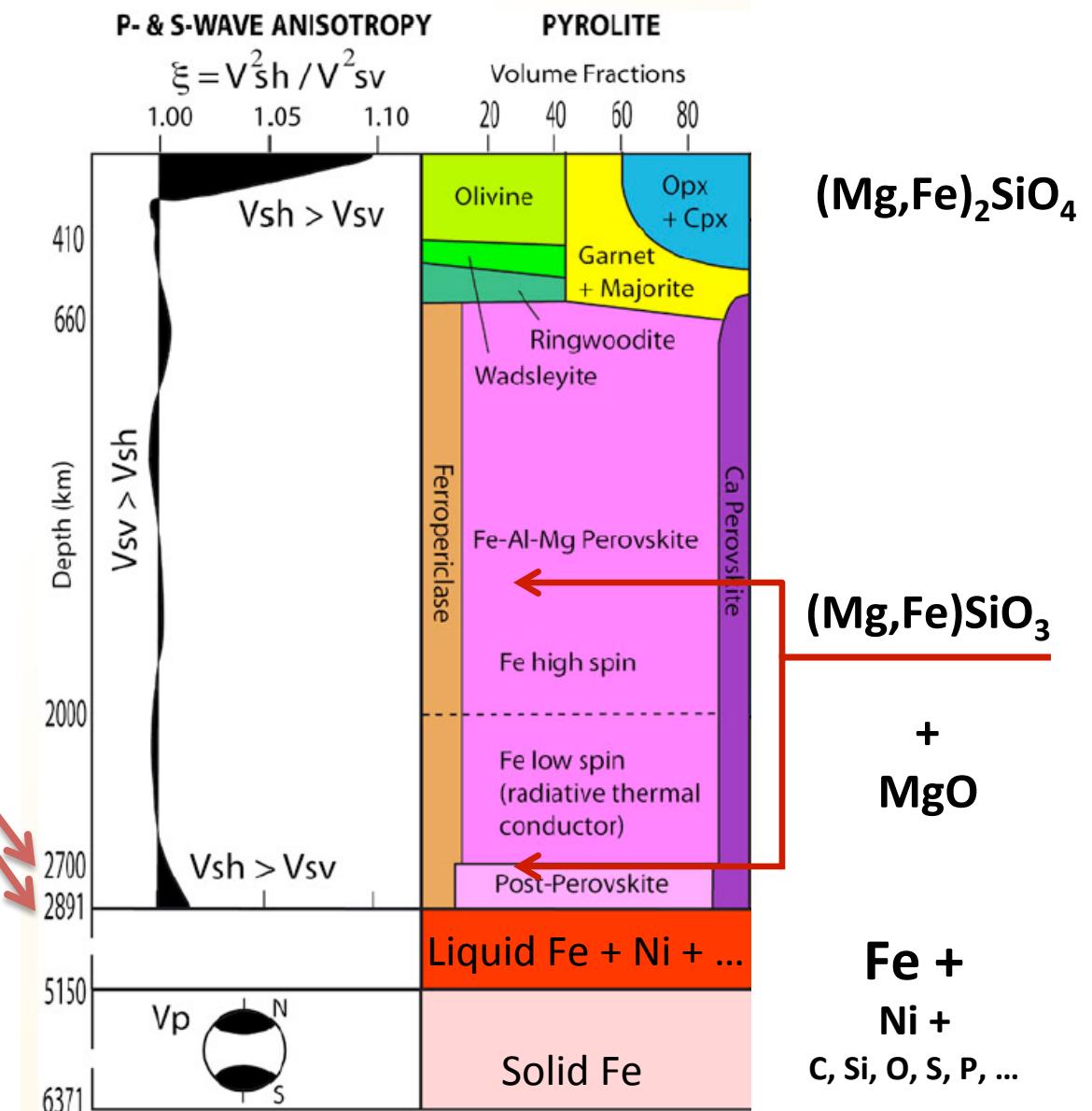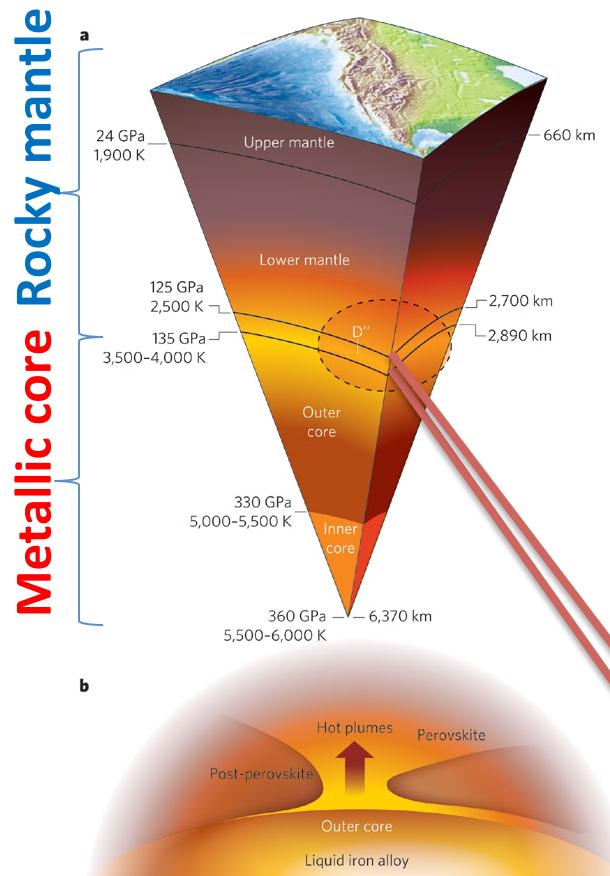
Perovskite – (Mg,Fe)SiO$_3$ – instabilities

Orthorhombic Pbnm structure:

High-Spin (both ferromagnetic and antiferromagnetic)

=> dynamically STABLE

(all phonons have positive frequencies)

Intermediate-Spin and Low-Spin

=> dynamically **UNSTABLE**

*(some phonons have imaginary frequencies)*

Perovskite – FeSiO$_3$ – spin transitions

The Pbnm structure in **low spin** (=non-magnetic) configuration exhibits several strong unstable phonon modes.
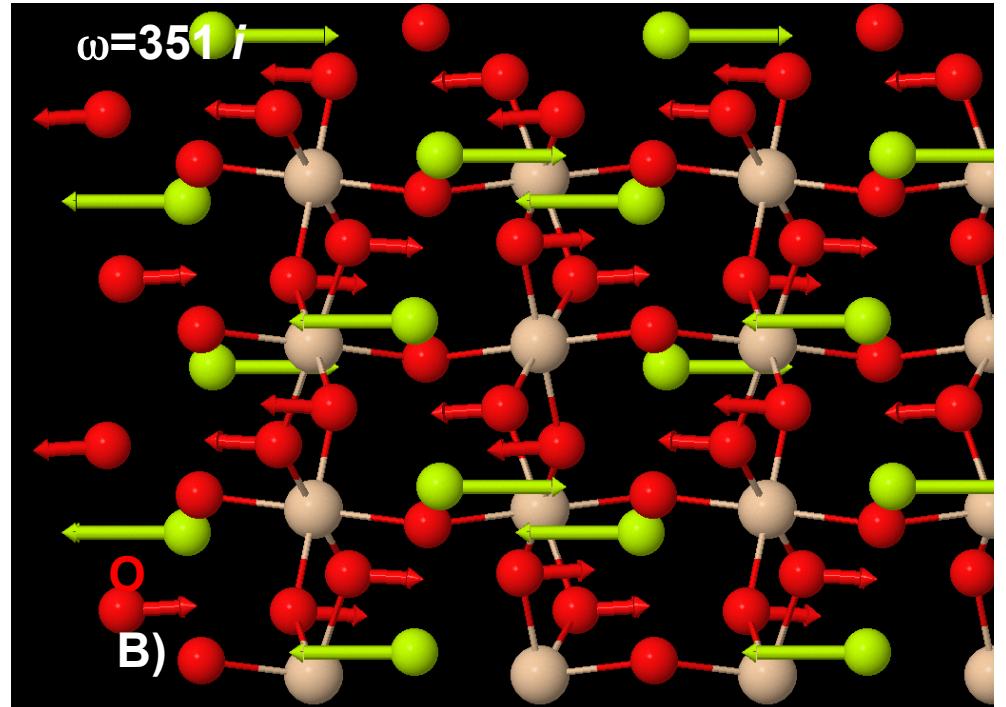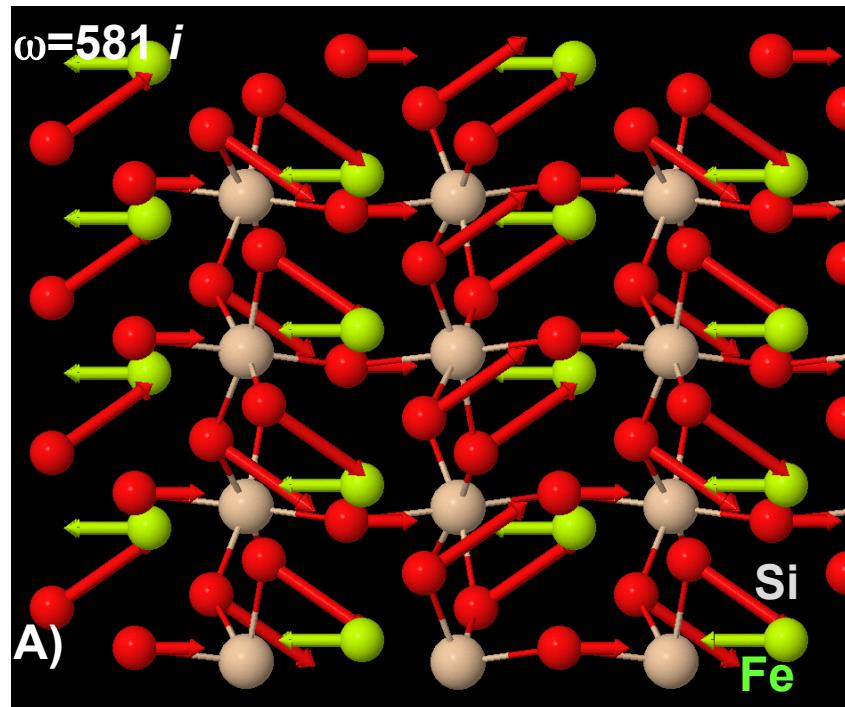
Perovskite – spin & diffraction - Fe 50%
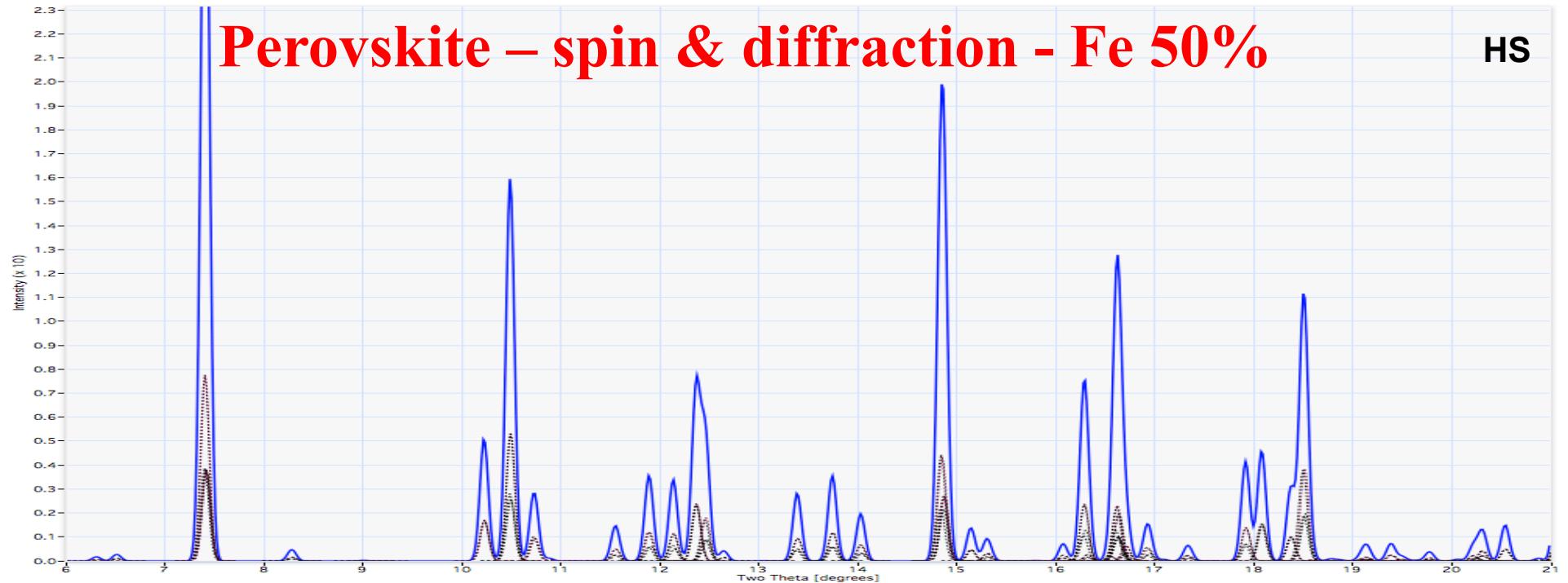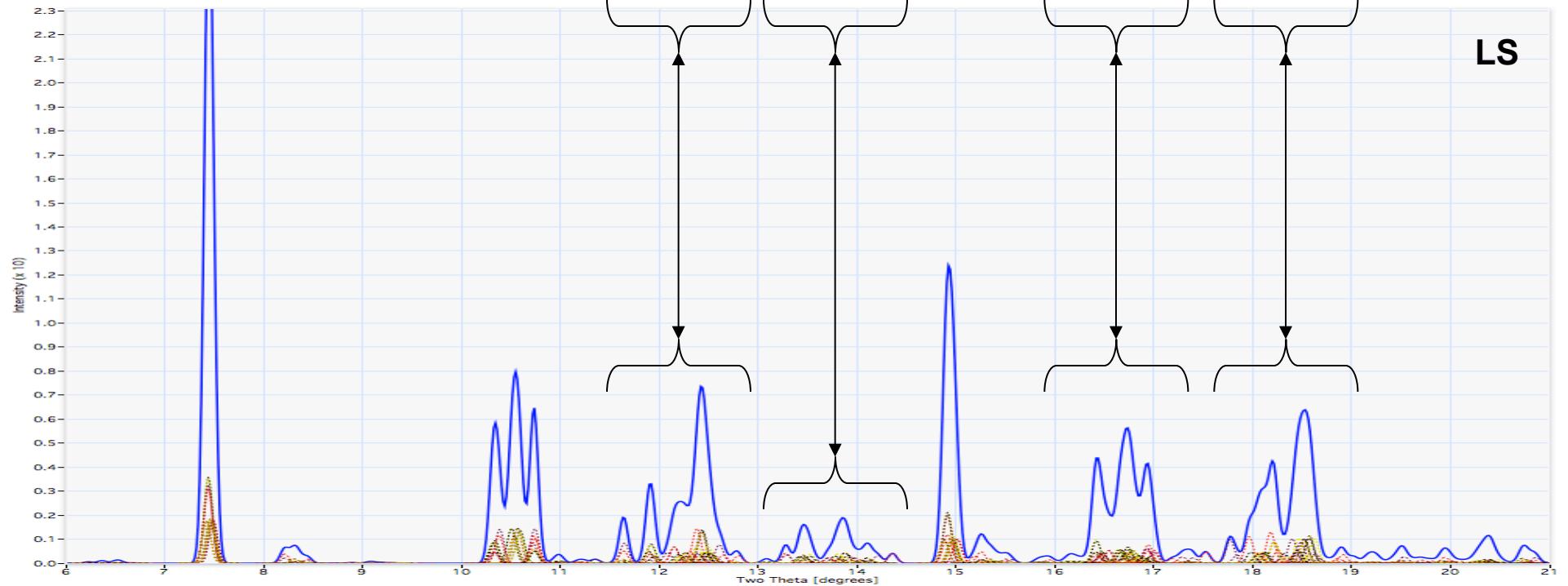
FeSiO$_3$ Perovskite – spin & seismic anisotropy
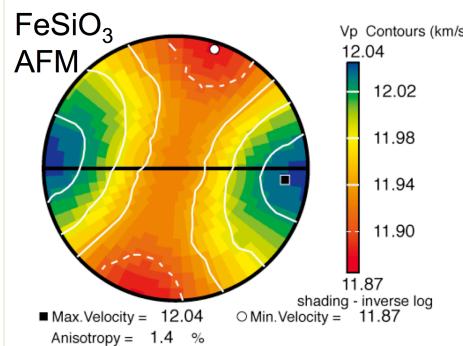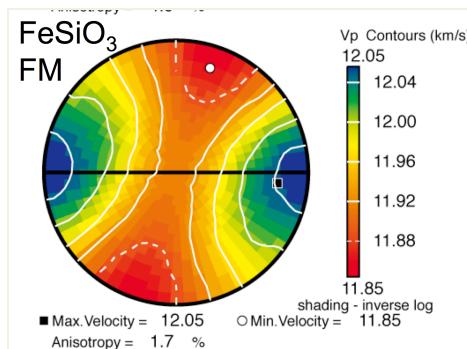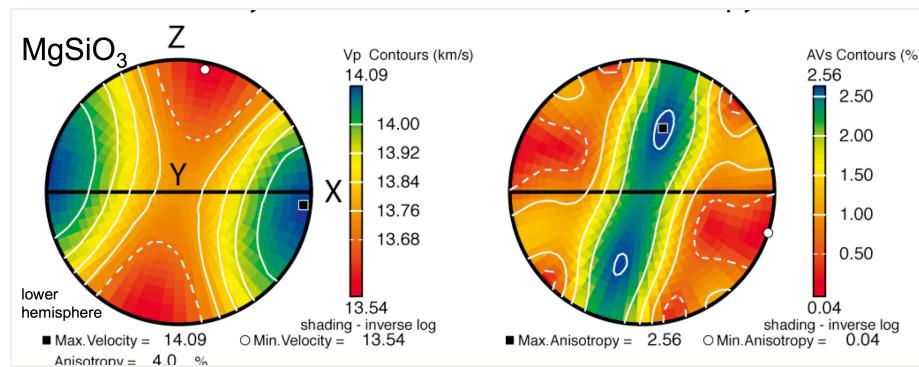
Vp velocity (km/s)   Vs anisotropy (%)
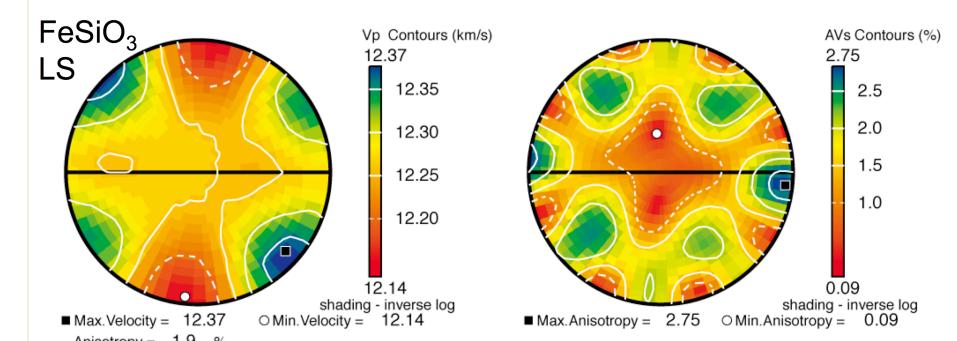
Caracas, Mainprice, Thomas, GRL, 2010

Simplified interior of the Earth
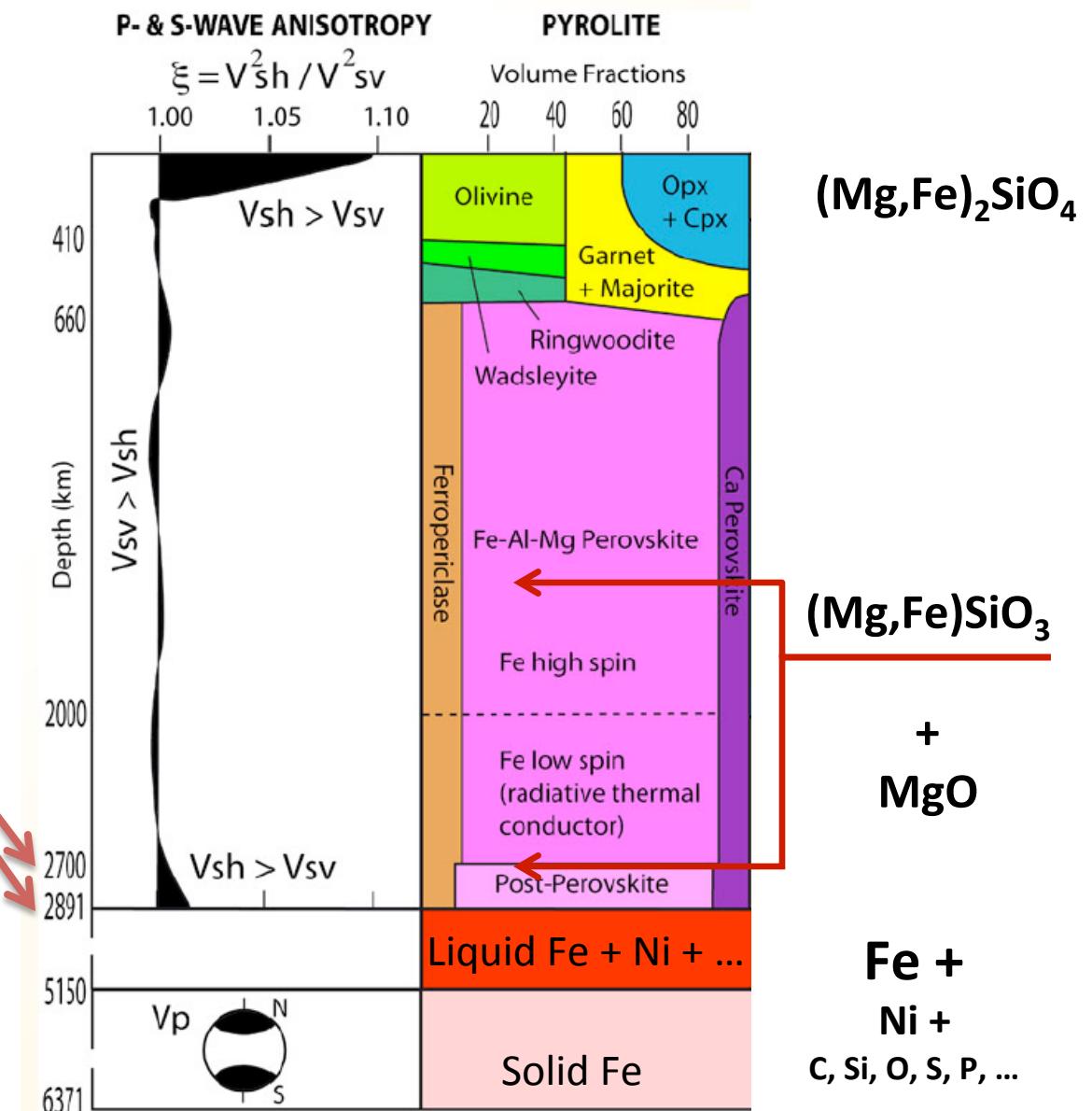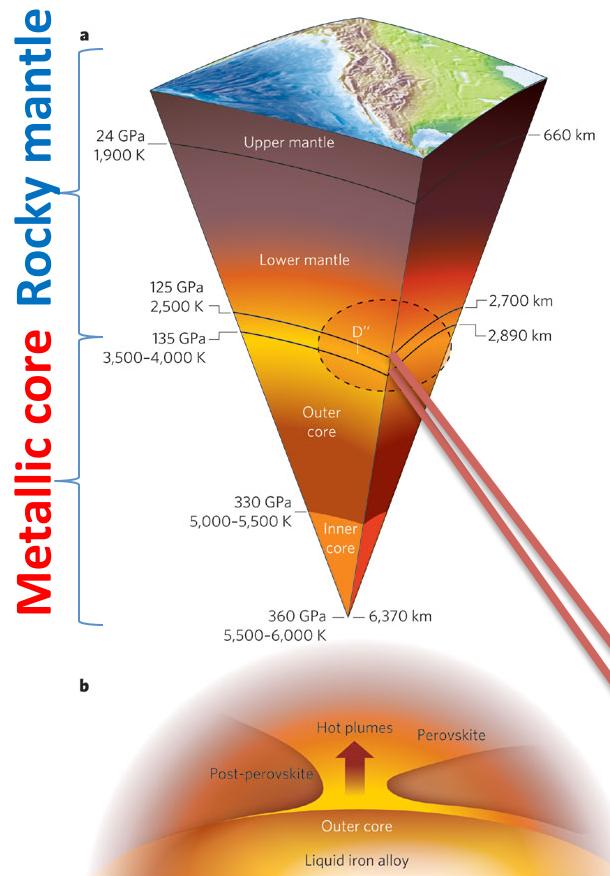
C-BEARING LIQUIDS: from volcanoes to diamonds

(example C-bearing forsterite melt)

Melt

Overheat (5000K) => melt
Cool down (3000K) the melt

We start with forsterite (Mg_2SiO_4) 112 atoms box
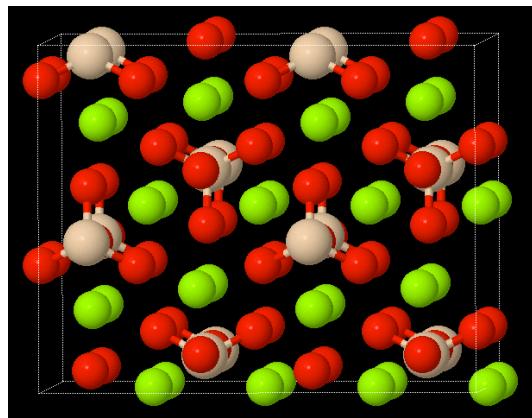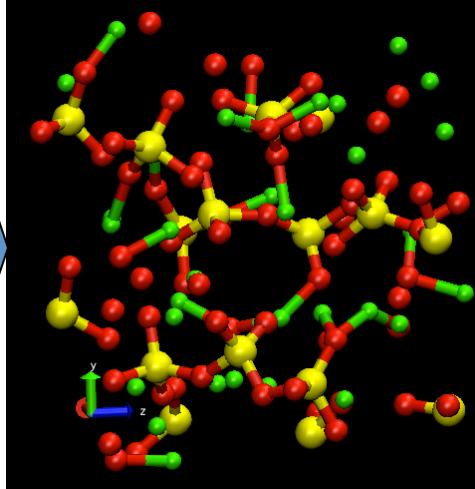
Add Ni, Co, etc. Replace Mg⇔Fe

Play with chemistry:
Add
C, CO_2, $MgCO_3$
Replace
Mg+Si ⇔ 2Fe

LIQUID STRUCTURE : CO$_2$-bearing
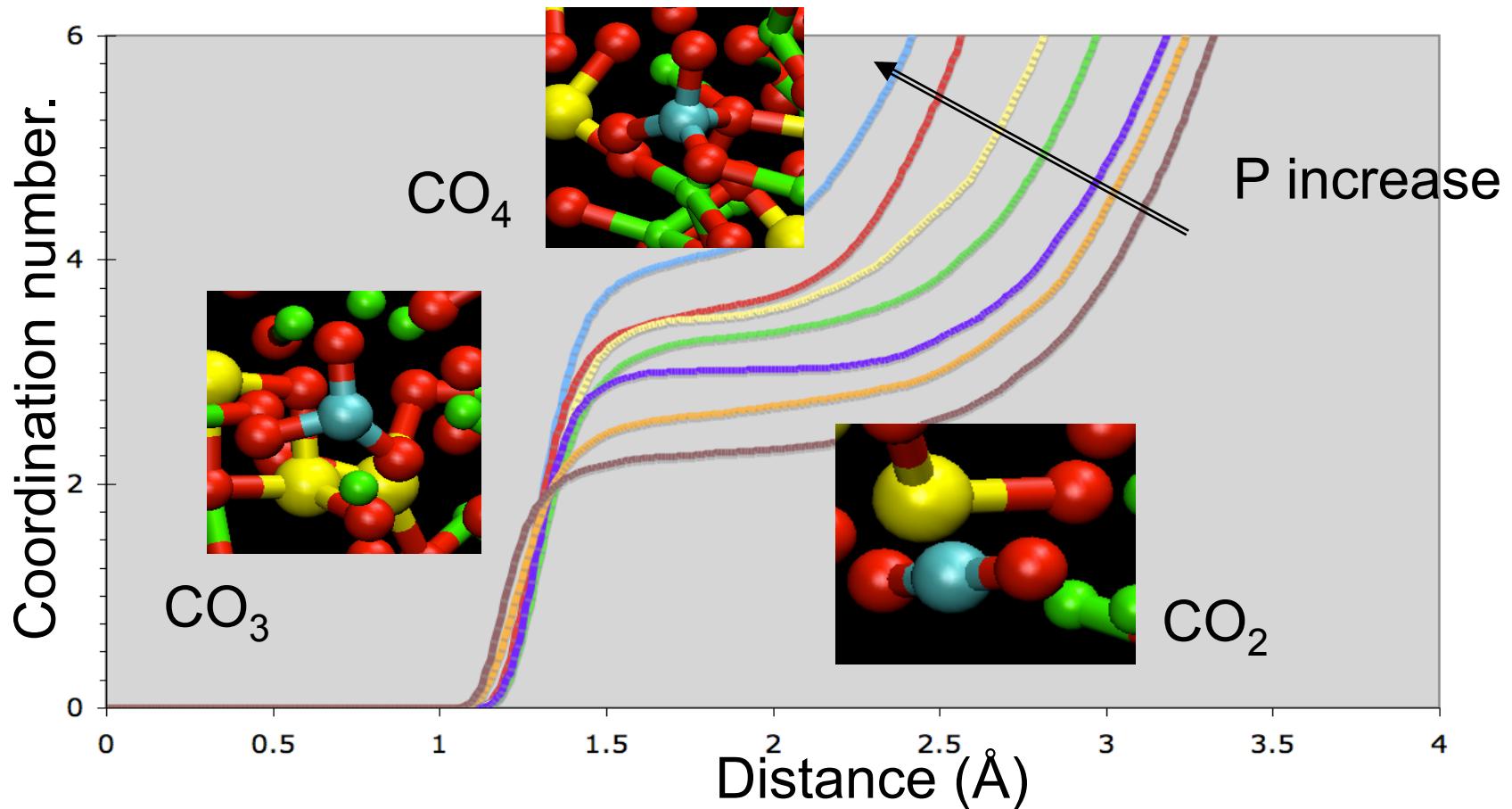
Enters as linear molecular CO$_2$
1. Low-pressure remains linear CO$_2$
2. Moderate pressure starts to form CO$_3$ groups
3. Ultra-high pressure forms CO$_4$
At all lower mantle pressures remains CO$_3$

PARTIAL MOLAR VOLUME OF C-BEARING SPECIES

approx. C diamond @ 3000K
[Correa et al., PRB 78, 024101, (2008)]
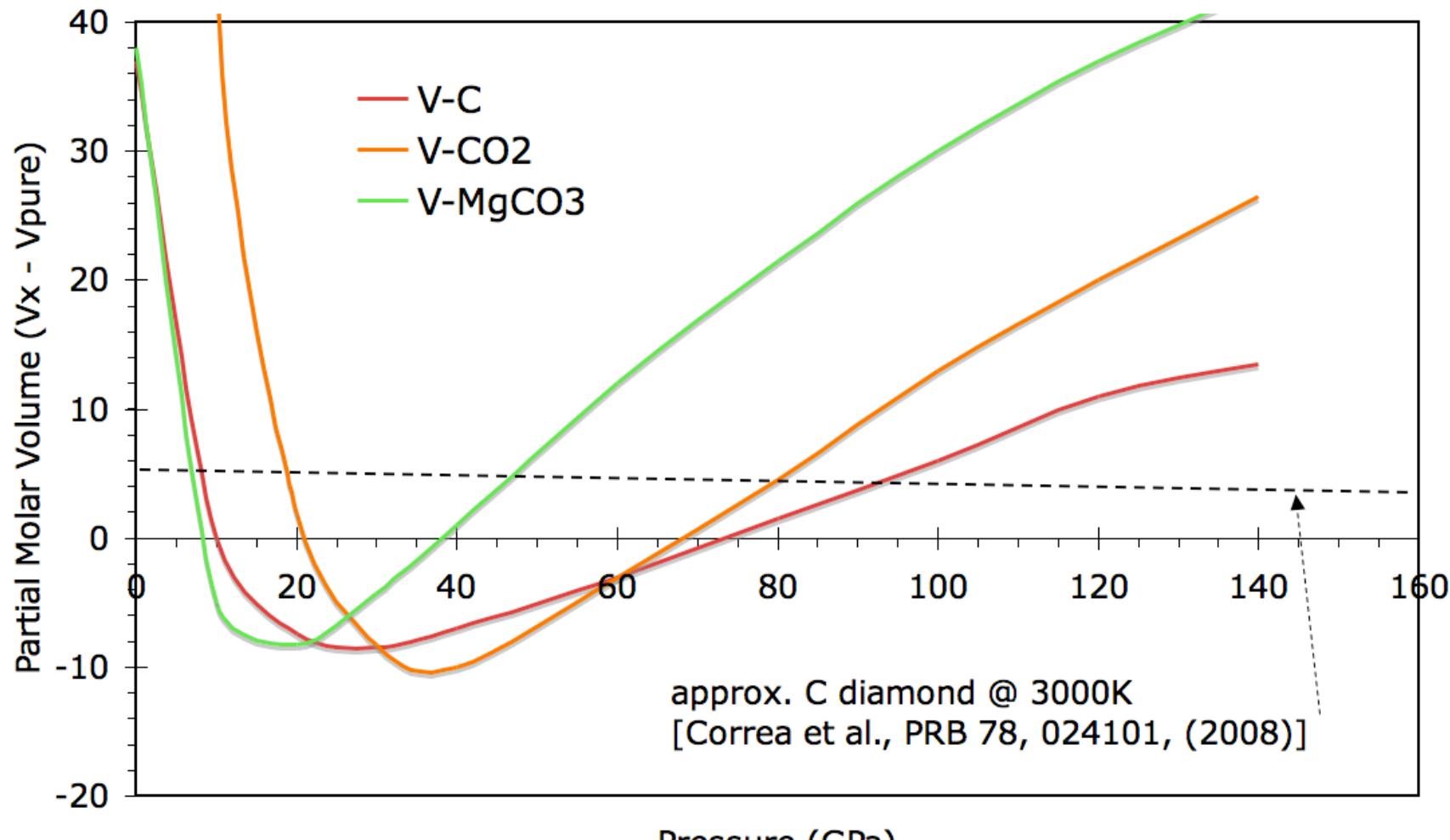
Exsolved
(e.g. volcanic
degassing)

Dissolved
in the melt

Exsolved: origin of
deep diamonds ~ fO_2

Simplified interior of the Earth
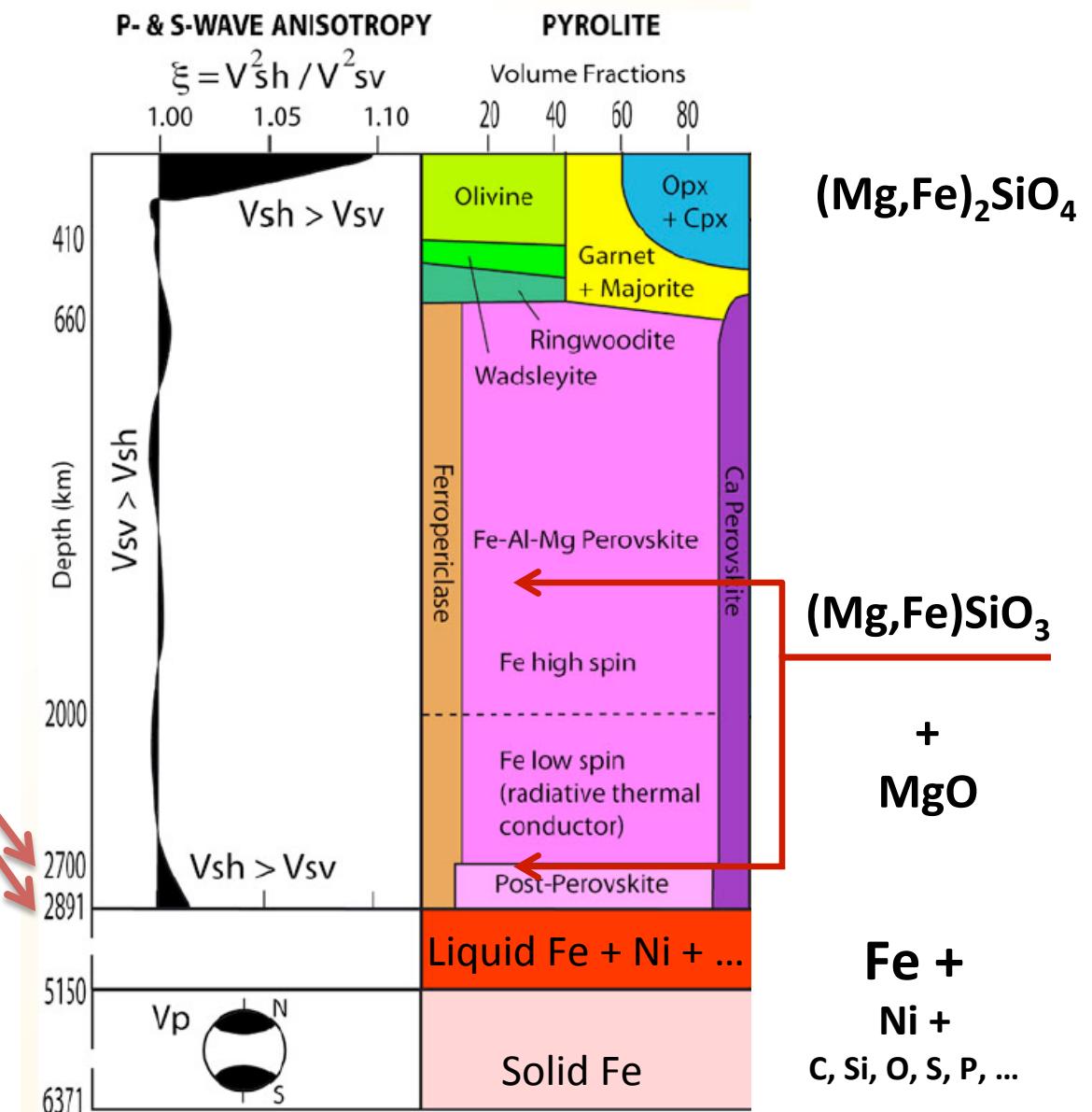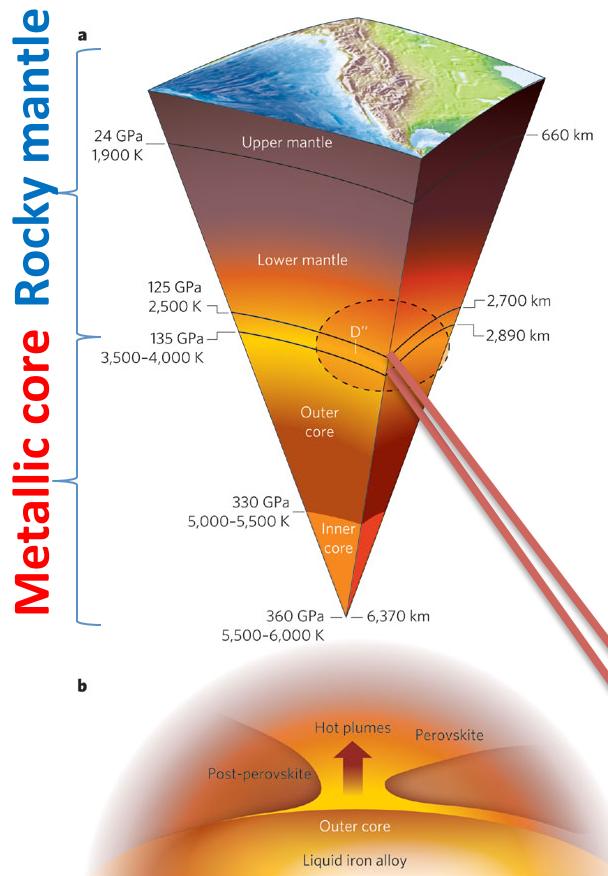
http://wurm.info

Welcome to the WURM project
— a database of computed physical properties of minerals —

The database provides the crystal structure, the parameters of the calculations, the dielectric properties, the Raman spectra with both peak positions and intensities and the infrared spectra with peak positions for minerals. The calculations are performed within the framework of the density-functional theory and the density-functional perturbation theory, using the ABINIT code.

The WURM project provides:

Computed physical properties for natural solid phases

First-principles calculations

minerals and ices
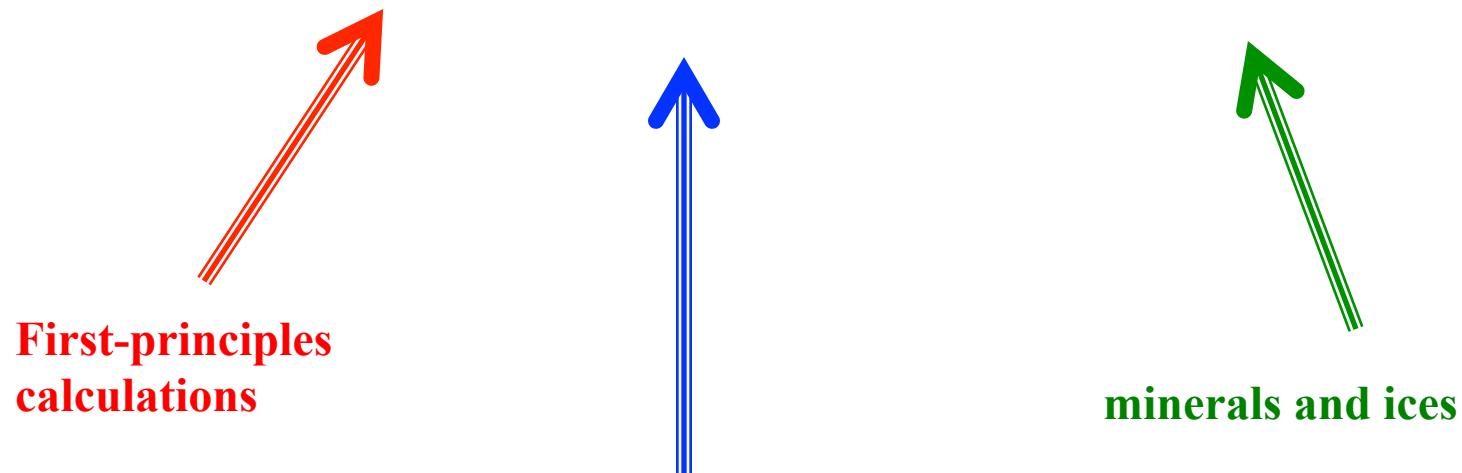
Crystal structure
Dielectric tensors, Atomic charges, Refractive index
Vibrational spectra: Raman and InfraRed

Sister project to RRUFF - same things, but experimental
(same sponsor, aiming search integration)

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w000004 — ANDALUSITE — Al2SiO5

Experimental structure from AMCSD

☑ **Crystal Structure** | ☐ **Parameters of the Calculation** | ☐ **Dielectric Properties** | ☐ **Spectroscopy**

Crystal Structure

Because of the translational symmetry all the calculations are performed in the primitive unit cell and not in the conventional unit cell. The following information regarding the structure is given with respect to this primitive unit cell, which sometimes can take an unintuitive shape.

Symmetry (experimental):

Space group:	58		Pnnm	
Lattice parameters (Å):	7.7930	7.8974	5.5558
Angles (°):	90.0	90.0	90.0

Symmetry (theoretical):

Space group:	58		Pnnm	
Lattice parameters (Å):	7.7930	7.8974	5.5558
Angles (°):	90.0	90.0	90.0

Size:

Nx:	2
Ny:	2
Nz:	2

Display

You can define the size of the supercell to be displayed in the jmol panel as integer translations along the three crystallographic axis.
Please note that the structure is represented using the primitve cell, and not the conventional one.

Visualization of the crystal structure:

Jmol

Cell contents:

Number of atoms:	32
Number of atom types:	3
Chemical composition:	Al, Si, O

Atomic positions (theoretical):

Atom type	X	Y	Z
Al:	0.0000	0.0000	0.2419
Al:	0.3716	0.1395	0.5000
Si:	0.2449	0.2541	0.0000
O:	0.4277	0.3626	0.5000
O:	0.4210	0.3674	0.0000
O:	0.1019	0.4013	0.0000
O:	0.2319	0.1368	0.2406
Al:	0.6284	0.8605	0.5000
Si:	0.7551	0.7459	0.0000
O:	0.5723	0.6374	0.5000
O:	0.5790	0.6326	0.0000
O:	0.8981	0.5987	0.0000

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w000004 — **ANDALUSITE** — Al2SiO5

Experimental structure from AMCSD

☐ **Crystal Structure** | ☐ **Parameters of the Calculation** | ☐ **Dielectric Properties** | ☑ **Spectroscopy**

Raman

Powder Raman spectrum

The intensity of the Raman peaks is computed within the density-functional perturbation theory. The intensity depends on the temperature (for now fixed at 300K), frequency of the input laser (for now fixed at 21834 cm^{-1}, frequency of the phonon mode and the Raman tensor. The Raman tensor represents the derivative of the dielectric tensor during the atomic displacement that corresponds to the phonon vibration. The Raman tensor is related to the polarizability of a specific phonon mode.

Horizontal:

| Xmin: | 0 |
| Xmax: | 1200 |

Vertical:

| Ymin: | 0 |
| Ymax: | 100 |

[Redraw]
[Reset]

Rescale the graph.
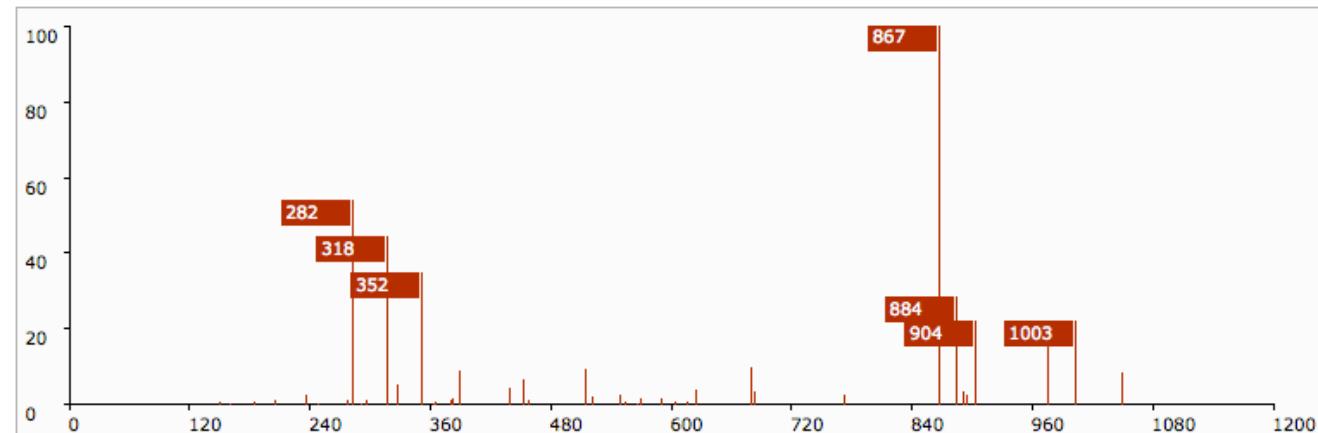
☐ I ∥
☐ I ⊥
☑ I Total

Choose the polarization of the lasers.

Data about the phonon modes

Frequency of the transverse (TO) and longitudinal (LO) phonon modes in the zone-center. The longitudinal modes are computed along

Data about the phonon modes

Frequency of the transverse (TO) and longitudinal (LO) phonon modes in the zone-center. The longitudinal modes are computed along the three cartesian directions. You can visualize the atomic displacement pattern corresponding to each phonon by clicking on the appropriate cell in the table below.

Nx:	2
Ny:	2
Nz:	2

No.	ω TO	ω LOx	ω LOy	ω LOz	I ∥	I ⊥	I Total
81	812	824	812	812			
82	824	861	824	824			
83	861	861	863	861			
84	864	867	864	864			
85	867	883	867	867	2.061e+40	5.713e+37	2.066e+40
86	883	884	883	884			
87	884	892	884	892	2.468e+39	3.394e+39	5.862e+39
88	892	894	89				
89	894	894	89				
90	894	904					
91	904	908	90				

○ Relative
◉ Absolute
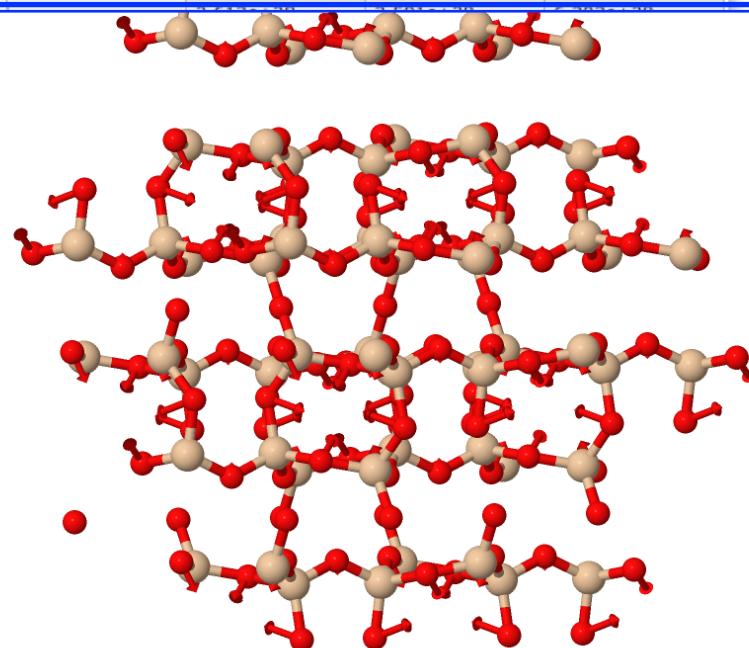
Jmol
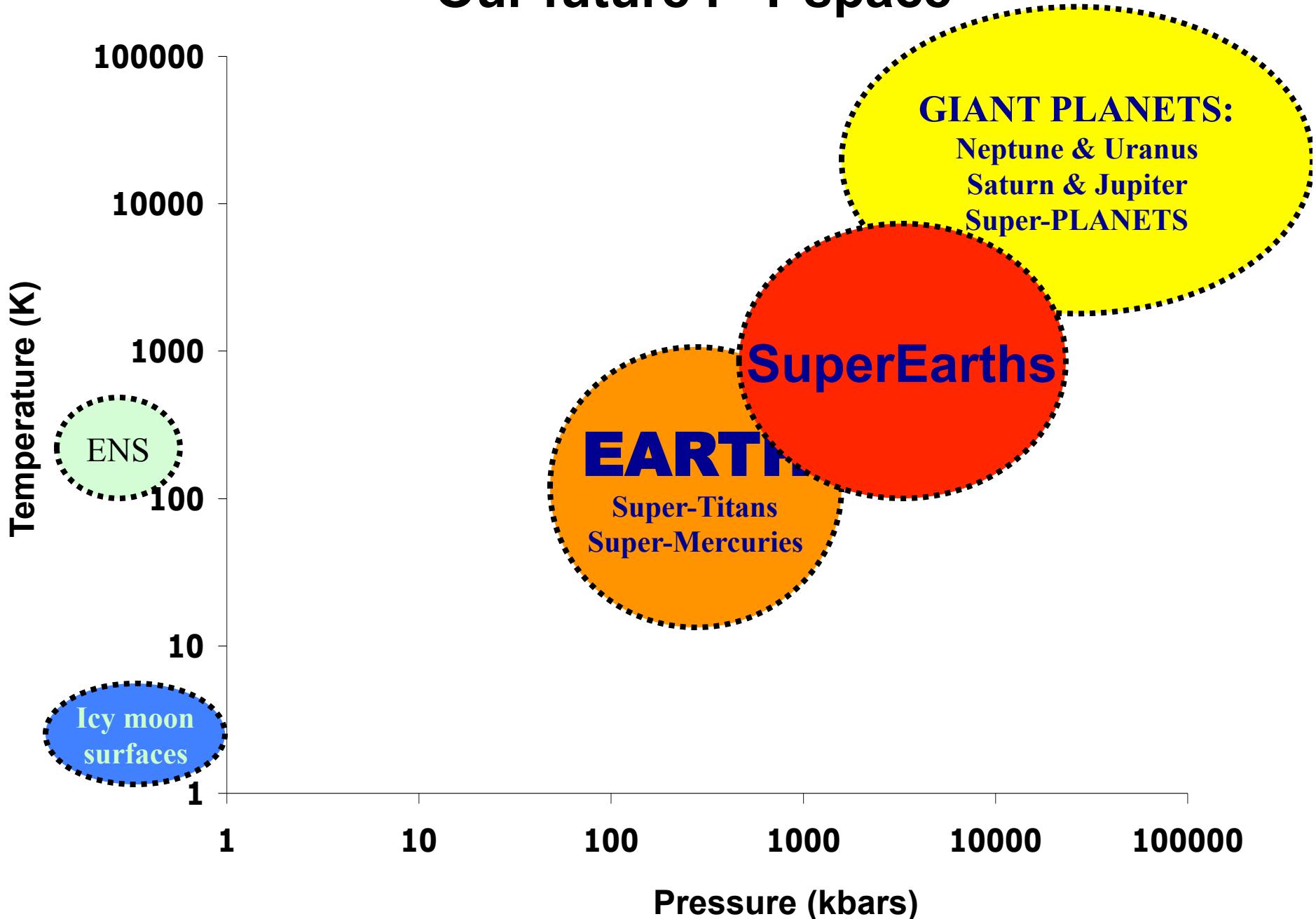
Current Potential Habitable Exoplanets

Compared with Earth and Mars and Ranked in Order of Similarity to Earth

Earth 1.00   Mars 0.66

	#1	#2	#3	#4	#5	#6	#7
Earth Similarity Index	0.92	0.85	0.81	0.79	0.77	0.72	0.72
	Gliese 581 g*	Gliese 667C c	Kepler-22 b	HD 40307 g*	HD 85512 b	Gliese 163 c	Gliese 581 d
Discovery Date	Sep 2010	Nov 2011	Dec 2011	Nov 2012	Sep 2011	Sep 2012	Apr 2007

*planet candidates

CREDIT: PHL @ UPR Arecibo (phl.upr.edu) Nov 19, 2012

Mass							
2.6	4.9	6.4	8.2	4.0	8.3	6.9	
Radius							
1.4	1.9	2.1	2.4	1.7	2.4	2.2	
Surface T °C							
10	27	31	6	78	61	-37	