Contribution of Geology Dept. to Mineralogy and Structure of the Earth’s Mantle

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MSU

Геологический факультет

N.V.Belov (1891-1982). President of IUCr (1966-1969). Head of the chair of crystallography and crystal chemistry (1962-1982).

N. Belov: “The scientist should live under the shadow of paradoxes. In other words to be “The Devil's Disciple” in his mind” (Shaw G.-B.- Nobel prizer)

This statement reflects our knowledge about the state of art in HP-crystallography and of the matter at extreme parameters.

- The problem regarding the composition, formation and structure of deep geospheres is a priority direction in geosciences. In particular, we note that more than 90% of matter in the Univers is under a pressure of more than 1 GPa.

- However the study of compounds which are anticipated as a constituents of the deep geospheres is more complicate as compared with cosmic investigations. In this connection I would like to emphazise that the deepest sample from the mantle available at the surface is a nodule from Lesoto kimberlite pipe, blasted out from about 250 km.

The deepest well in Kola peninsula (12262 m)

Temperature at this depth – 180°C but not 100°C, as it was expected. The rocks, erupted from the depths of less than 100 km, allow predicting only 0.02% of the Earth’s volume.

Estimates of elemental abundances (in atoms per 1atom Si): O,Si,Mg,Fe,Al ([a]estimates of Anders and Ebihara, 1989; [b]simple model based on cosmic abundances (Anderson, 1989); [c]recalculated from data of Anderson, 1989; [d]recalculated from (Ringwood, 1991).

Element	The Universe[a]	Whole Earth[b]	Earth's Crust[c]	Mantle (increase of depth)[c]	Pyrolitic Homo-geneous Mantle[d]
O	20.10	3.73	2.9	3.63 – 3.63	3.68
Na	0.06	0.06	0.12	0.03 - $2\cdot10^{-3}$	0.02
Mg	1.08	1.06	0.09	0.97 – 1.09	1.24
Al	0.08	0.09	0.36	0.17 – 0.06	0.12
Si	1	1	1	1	1
P	0.01	-	$4\cdot10^{-3}$	$6\cdot10^{-4}$ - $4\cdot10^{-5}$	$4\cdot10^{-4}$
S	0.52	-	$8\cdot10^{-4}$	$6\cdot10^{-4}$ - $5\cdot10^{-5}$	$2\cdot10^{-3}$
Ca	0.06	0.06	0.14	0.05	0.09
Cr	0.01	-	$1\cdot10^{-4}$	0.01	0.01
Fe	0.9	0.9	0.11	0.14	0.16
Ni	0.05	-	$3\cdot10^{-5}$	$4\cdot10^{-3}$	$3\cdot10^{-5}$

Bulk content of the rock-forming silicates in the continental crust

Feldspar minerals	64%		
Pyroxenes + amphibols	9%		
Qwartz	18%	Total	96.5%
Biotite	4%		
Olivine	1.5%		

It is only 0.6 wt.% in comparison with the total content of the silicates in the Earth. The first X-ray diffraction measurements on Mars also revealed the dominating role of silicates in its crust.

What’s the diference between the minerals of the Earth’s Crust and the mantle?

To answer this question I'll refer to the works of our researchers and graduators.

Minerals of the Earth's mantle
(4 series: silica polymorphs, perovskites, carbonates, garnets)

The leader of the Geochemical School in MSU academician A.P.Vinogradov and the Director of the Institute of HP-Physics academician S.M.Stishov

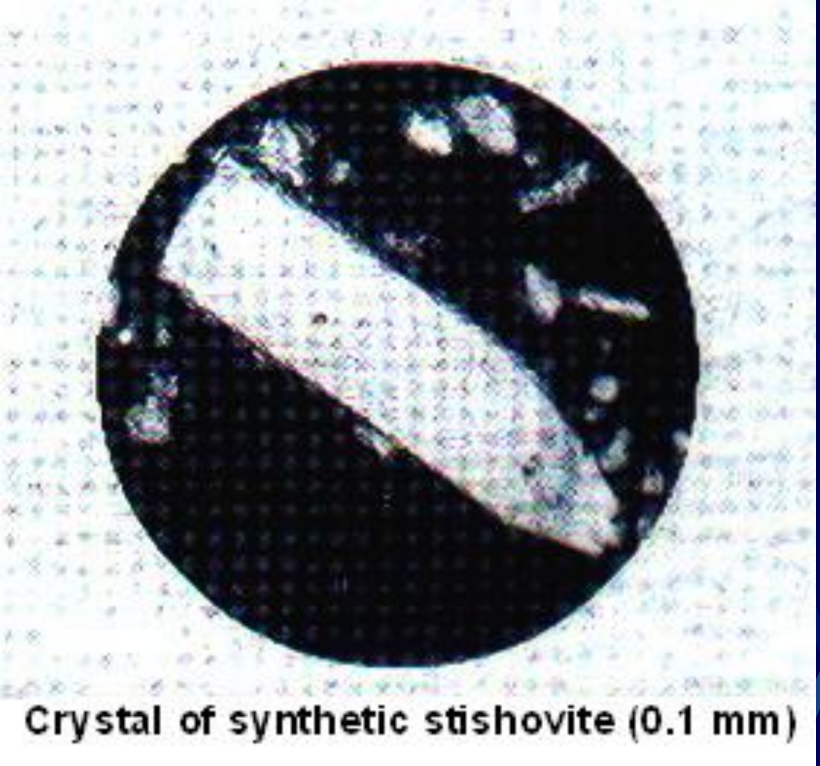
The discovery of stishovite in 1961 opened the new epoch in HP-mineralogy

Finaly Stishov and his supervisors decided to try the experiments on common rock-forming silicates at pressures up to 10 GPa. Thus S.M.Stishov started such investigation with SiO_2 and demonstrated its transition to the dense rutile-type structure with edge-sharing chains of silicate octahedra. The corresponding increase in density was more than 66% from 2.65 to 4.41 g/cm^3, in the pressure range between 0 and 8 GPa.

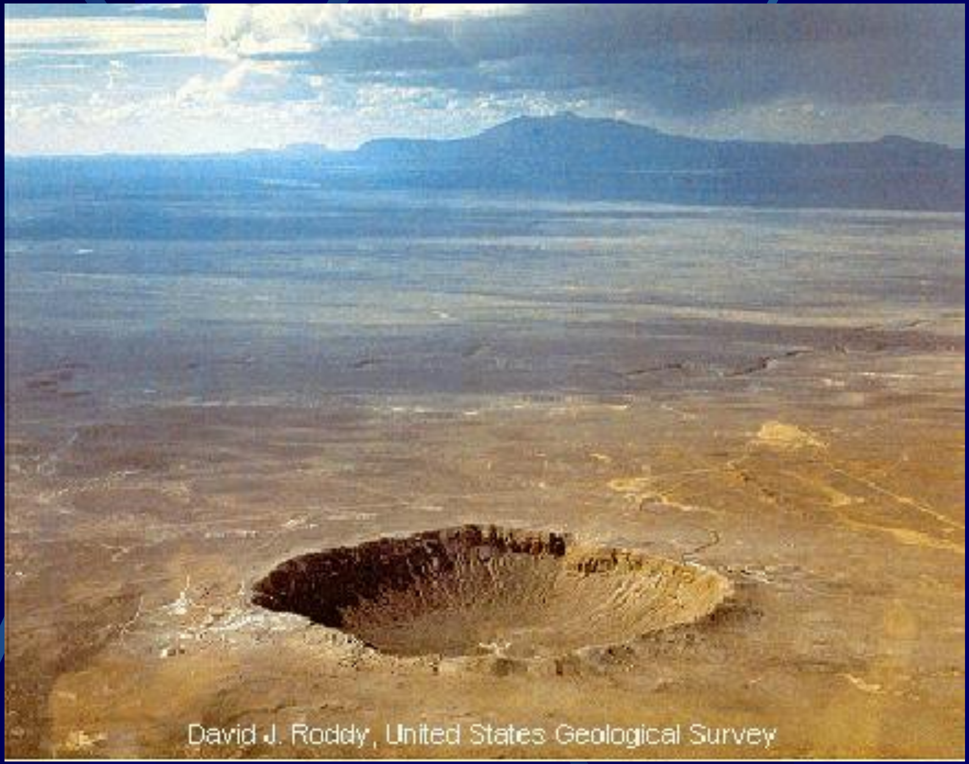
Since that time the crystal chemistry of six-coordinated Si is a key to understanding of the Earth's deep-seated geosphers.

One year later the rutile-like polymorph of SiO_2 was found in Arisona impact crater

Stishovite, SiO_2



Crystal of synthetic stishovite (0.1 mm)



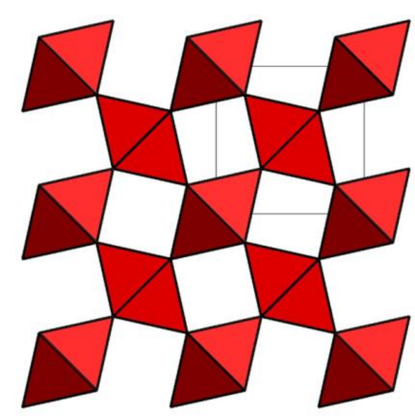
David J. Roddy, United States Geological Survey

Stishov & Popova (1961): Geochemistry, N10, 837)

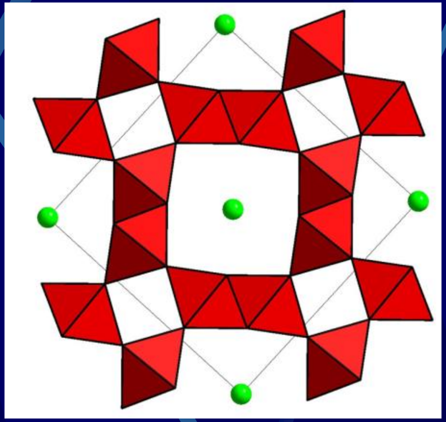
Chao *et al*. (1962): J.Geophys. Research, **67**, 419.

Stishovite in a lunar meteorite: Prof. Eiji Ohtani (PNAS, 2010); Despite countless impact craters on the Moon, high-pressure polymorphs have not been reported to date in returned Apollo samples. Discovery of stishovite in Apollo sample (Amer.Min., 2015)

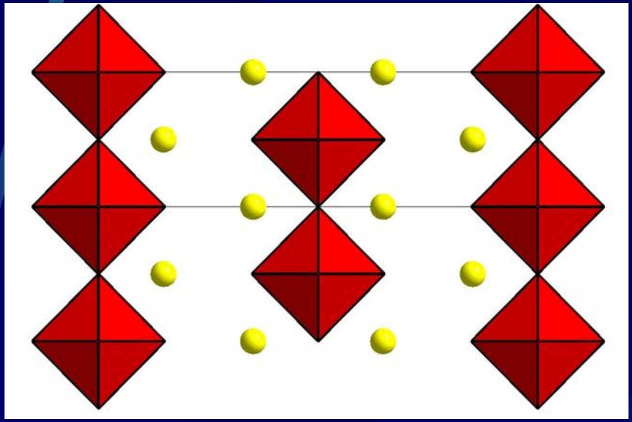
Structure types of stishovite (a), Ca_2SiO_4 (b), hollandite – $KAlSi_3O_8$ (c) and $CaFe_2O_4$ – $MgAl_2O_4$ (at P>25 GPa), $NaAlSiO_4$ (d)



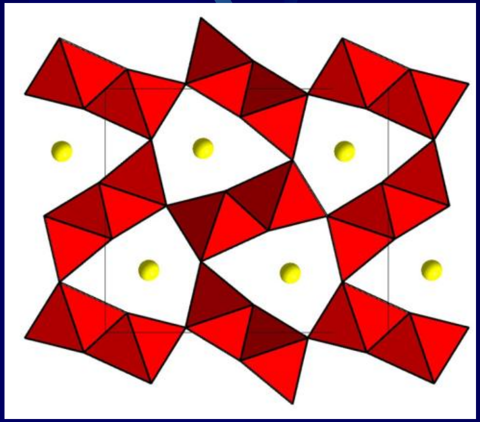
a



c



b



d

The transformation of Si-tetrahedra to Si-octahedra is accompanied by the decrease of O-O distances and by the decrease of molar volume for ~15%.

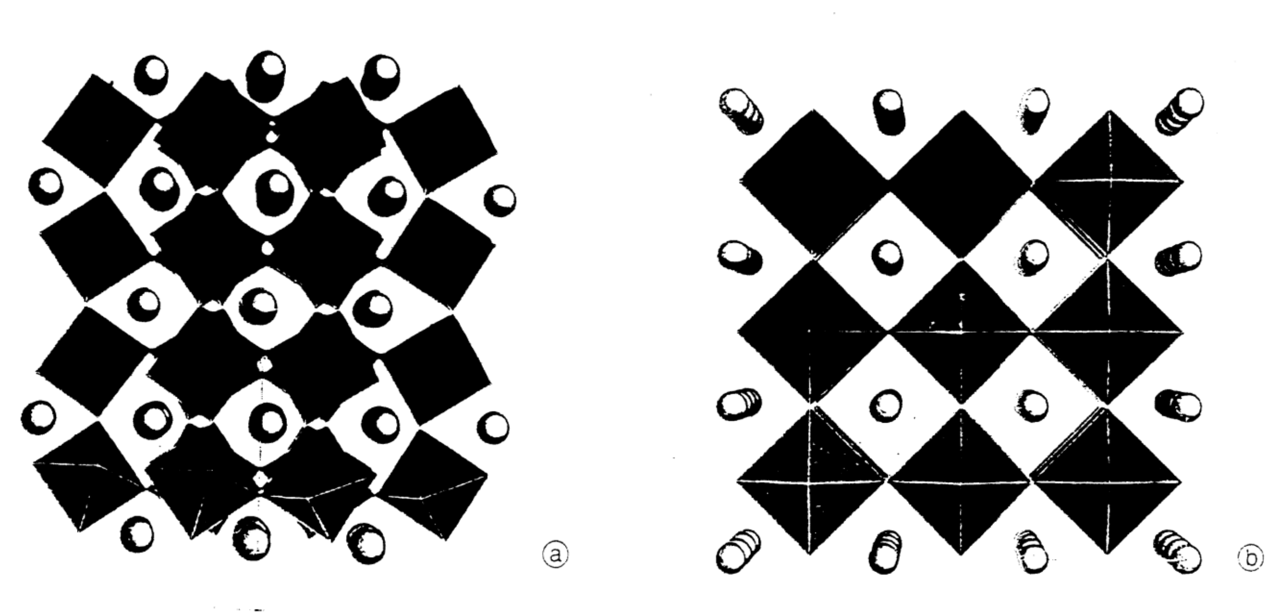
Prof. A.R.Oganov – our graduator – gives a talk in the faculty meeting

Low Mantle

70% - Perovskite-like (Mg,Fe)SiO_3 – phases (40% of the Earth's Volume

20% - Mg-wustite (Mg,Fe)O

5% - $CaSiO_3$

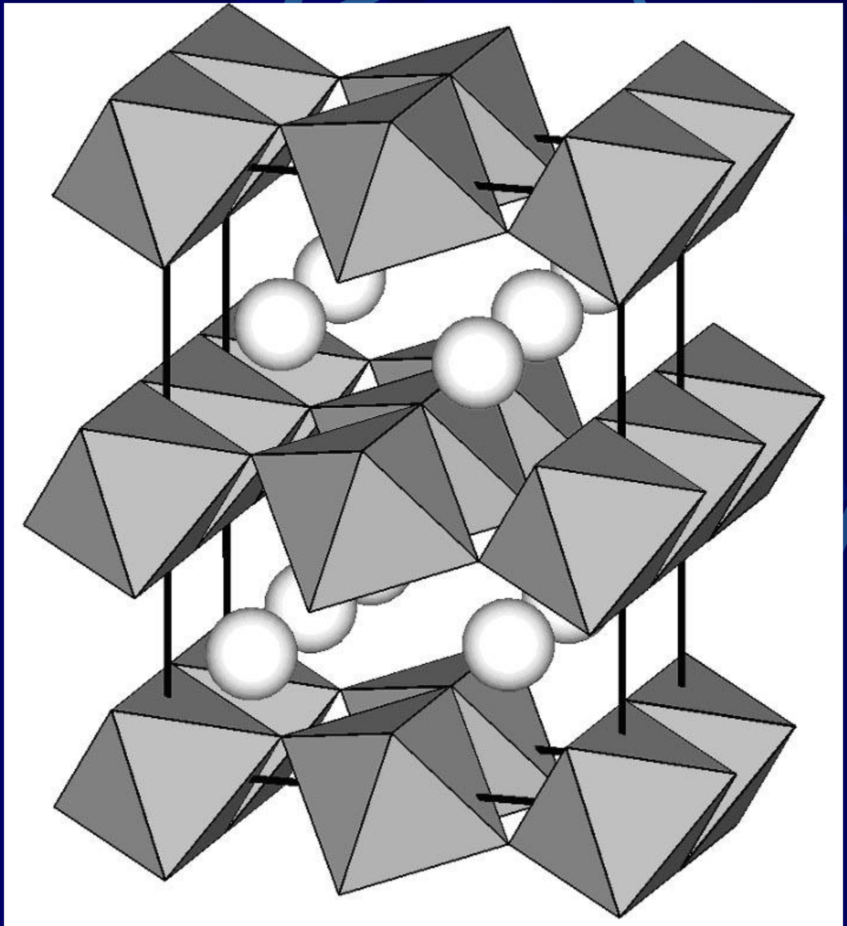


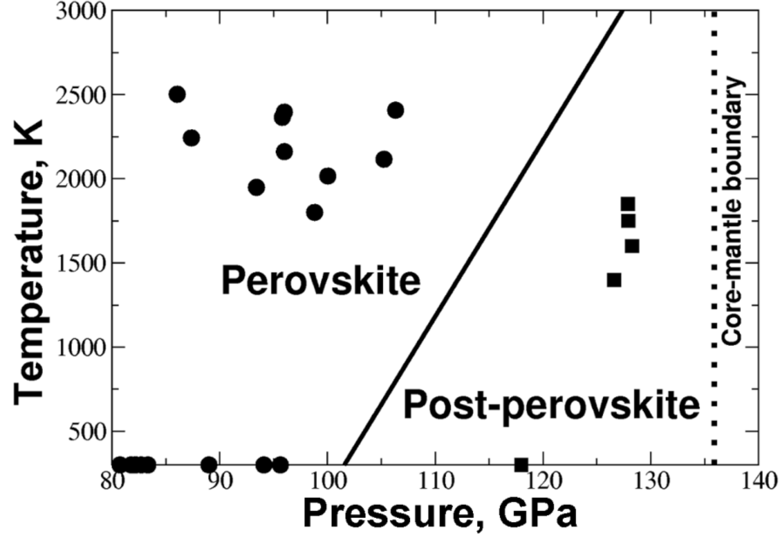
a) Orthorhombic structure of $MgSiO_3$;

b) Cubic structure of Prv

Post-perovskite phase $MgSiO_3$ (s.t. $CaIrO_3$):127 GPa, 3000 K (2740 km)

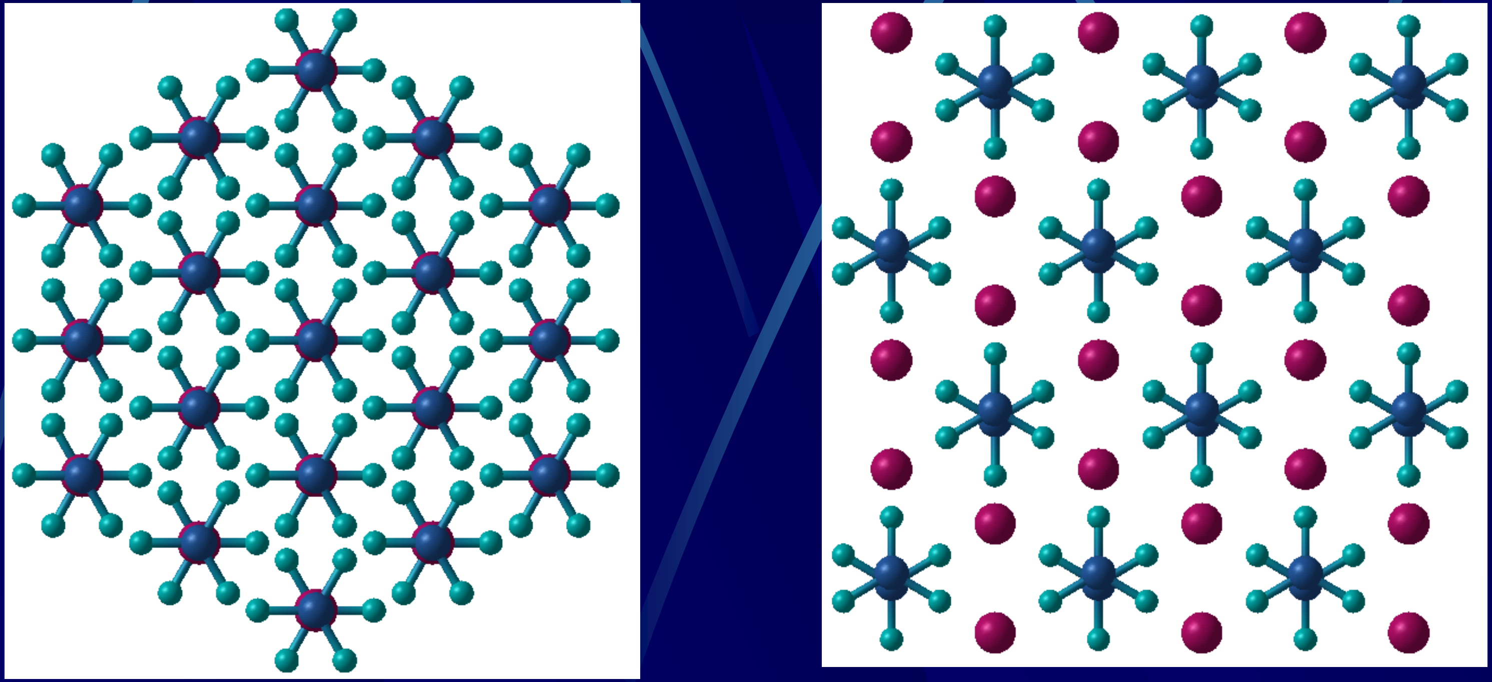
Oganov A.R., Ono S. // Nature. 2004. V. 430. P. 445.





Calcite (a) and aragonite (4-6 GPa) (b)

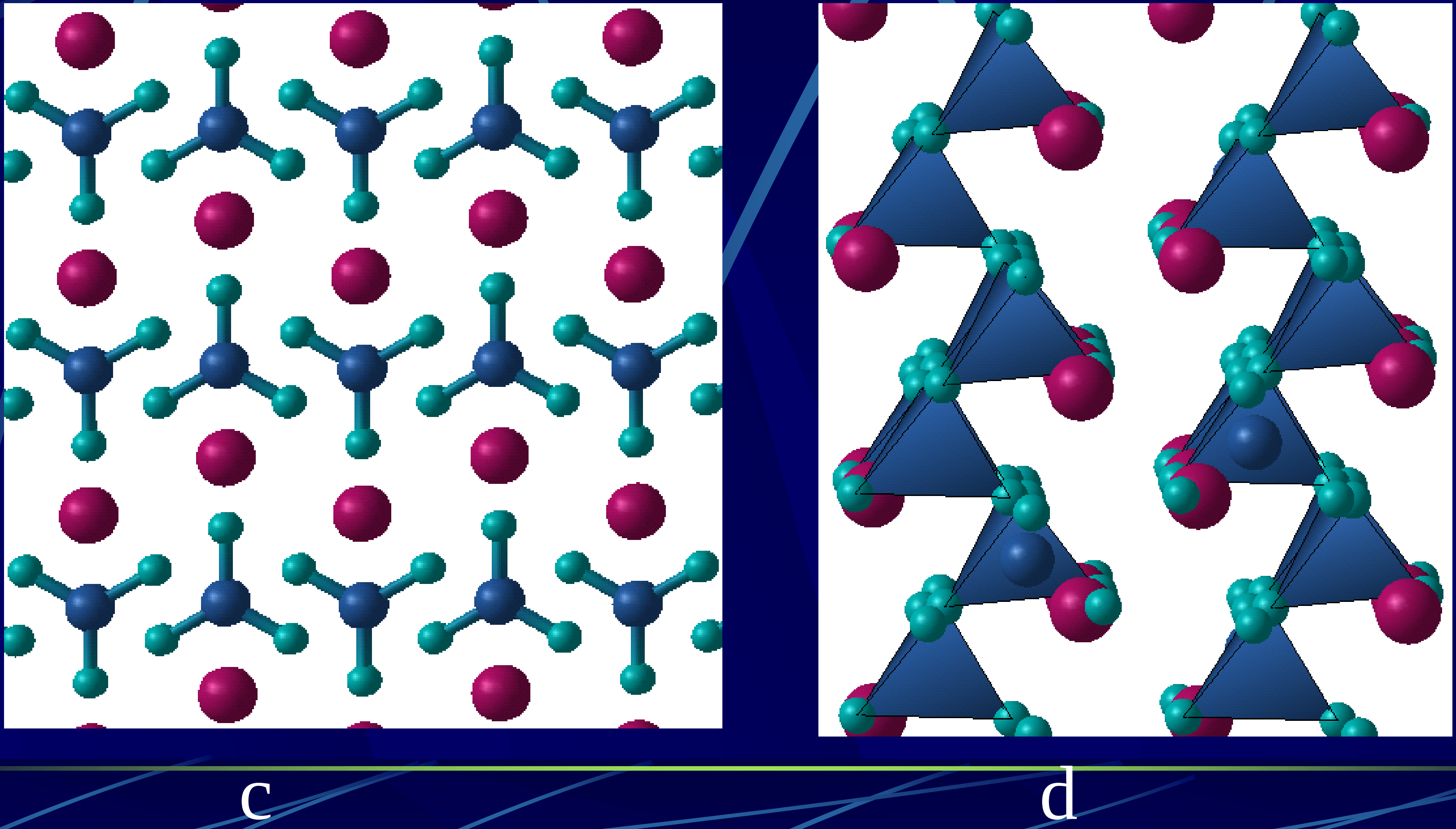
Only a small fraction of our planet’s total carbon is found at the surface. In fact, Earth’s mantle is thought to be the largest carbon reservoir. Three main carbonates exist at room conditions: calcite, $CaCO_3$, magnesite, $MgCO_3$, and dolomite, $(CaMg)(CO_3)_2$. In upper mantle: calcite → aragonite; dolomite → aragonite + magnesite



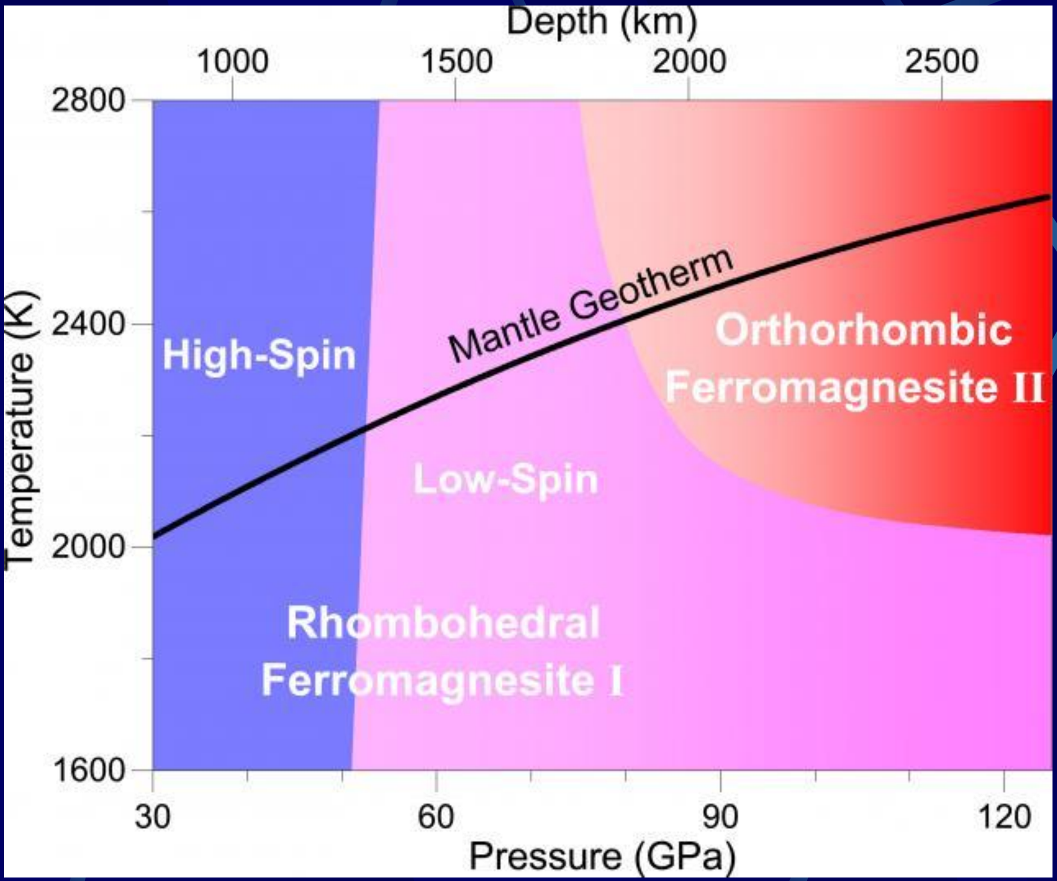
a b

Oganov A.R., Glass C.W., Ono S. **// Earth Planet. Sci. Lett. 2006. V. 241. P. 95.**

Structure of post-aragonite phase, stable at P > 42 GPa (1050 km) (c); pyroxene-like form of $CaCO_3$, stable at pressure > 137 GPa (d) (Oganov et al, EPSL, 2005); synthesized in 2006 (zone D”)



Carbonates [(Mg,Fe)CO_3 phases] at HP – new publications (2015)



HS→LS Transition

The experimental results show that the rhombohedral siderite (Phase I) transforms to an orthorhombic phase (Phase II with *Pmm*2 space group) at approximately **50 GPa and 1400 K**. **The structural transition is likely driven by the spin transition of iron accompanied by a volume collapse in the Fe-rich (Mg,Fe)CO_3 phases.**

The spin transition stabilizes the high-pressure orthorhombic phase II at much lower pressure conditions than its Mg-rich counterpart. It is conceivable that the low-spin ferromagnesite phase II becomes a major deep-carbon carrier at the deeper parts of the lower mantle below 1900 km in depth [**Liu J, Lin J-F, Prakapenka V.B. (2015) High-pressure orthorhombic ferromagnesite as a potential deep-mantle carbon carrier. Scientific Reports 5:7640**].

Tetrahedrally coordinated carbon in ferromagnesite at HP

With the combination of *in situ* **synchrotron infrared** spectroscopic measurements carried out at high pressure (80 GPa), and *ab initio* calculations on the **ferromagnesite** ((Mg,Fe)CO_3) structure, it was possible to identify a unique vibrational signature present only in the high-pressure phase, and thus a new carbon-oxygen bond forms in ferromagnesite under pressure. **The new vibrational signature is assigned to tetrahedrally coordinated carbon atoms with asymmetric C-O bonds.** **Ferromagnesite** represents an important rock-forming mineral, fundamentally distinct from silicates in Earth's crust.

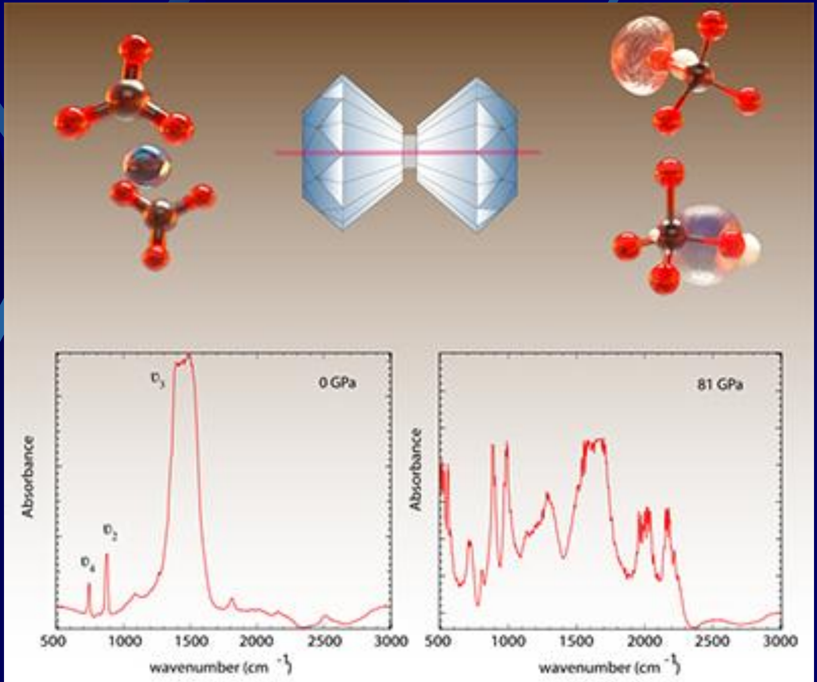
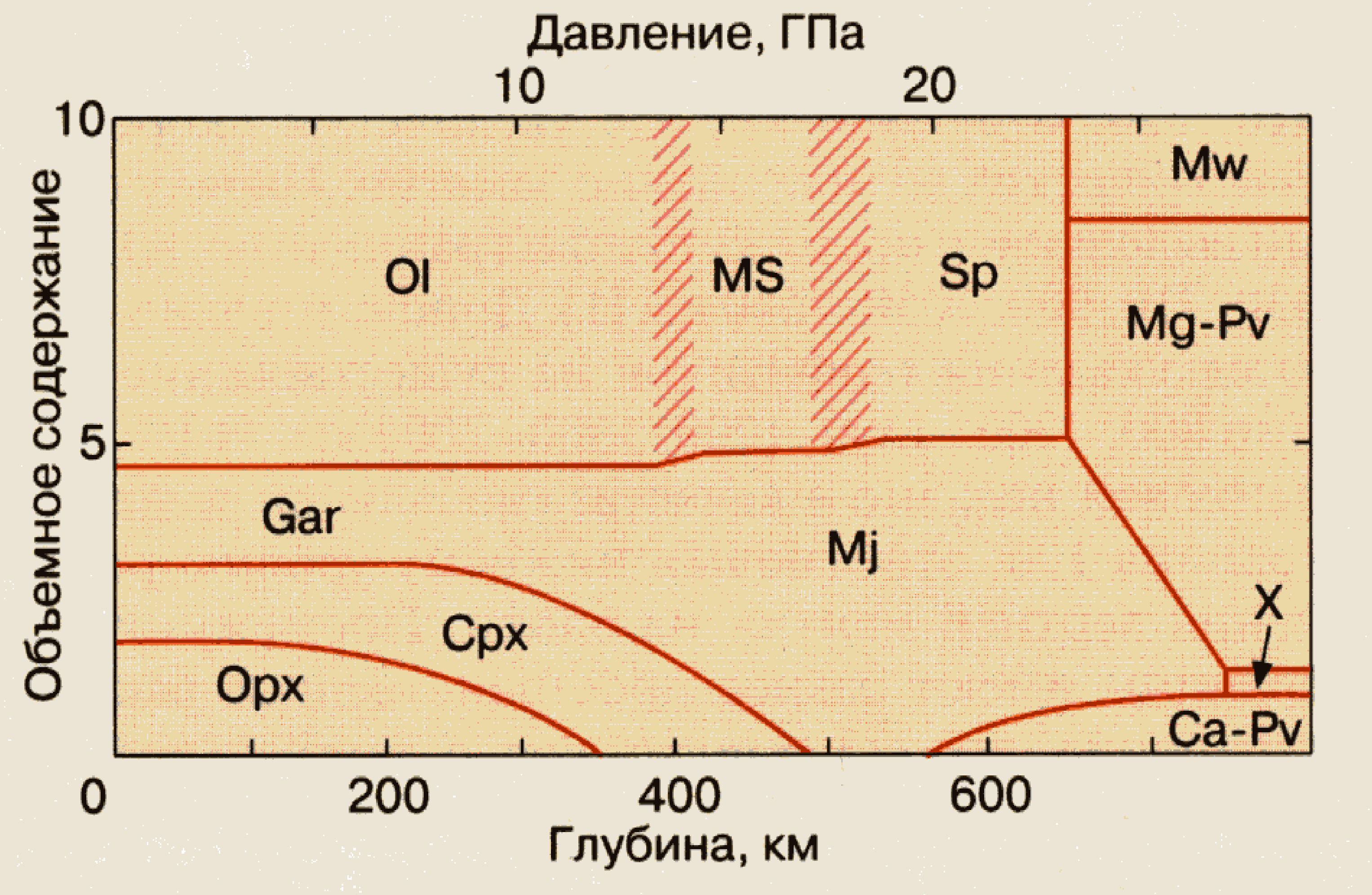


Figure 1. Carbon environment and associated in situ infrared spectra of ferromagnesite at ambient conditions (left) and at high pressure (right). At ambient conditions, carbon exists as the carbonate ion, CO_3^{2-}. At high pressure, carbon adopts tetrahedral coordination as CO_4^{4-}.

At low pressure, carbon bonds to three oxygen atoms, while silicon bonds to four. Tetrahedrally coordinated carbonates likely exhibit dramatically different behavior compared to three-fold coordinated carbonates, including ***altered reactivity*** with other mantle phases and changes in chemical melt properties. This bonding behavior could therefore have significant implications for carbon reservoirs and fluxes, as well as for our understanding of the global geodynamic carbon cycle [E. Boulard et al., **Tetrahedrally coordinated carbonates in Earth's lower mantle.** [***Nature Comm.*** (2015)].

Volumetric proportions of minerals in upper mantle *versus* the pressure (depth), after Ringwood, 1991; Akaogi, 1997; Frost, 2008



Scientific group: Ekaterina Sirotkina, Leyla Ismailova, Anastasia Tamarova, Aleksandra Bendeliani

Cooperation: Yuriy Litvin, Tetsuo Irifune, Leonid Dubrovinsky, Victor Garanin

Andrey Bobrov, Professor
Department of Petrology,
Geological Faculty,
Moscow State University

Research:

- Mantle xenoliths and diamondiferous rocks;
- Diamond synthesis at high pressures and temperatures;
- Experimental study of phase relations in the model and multicomponent systems of the Earth's mantle;
- High-pressure components

A.M.Dymshits: 1) Na-majorite, $Na_2MgSi_5O_{12}$, was primarily synthesized in a wide range of temperatures (1500-2100°C) and pressures (11-20 GPa). **2) Na- majorite can be considered as a main Na-constituent of the transition zone in the depth's interval 410 – 670 km**

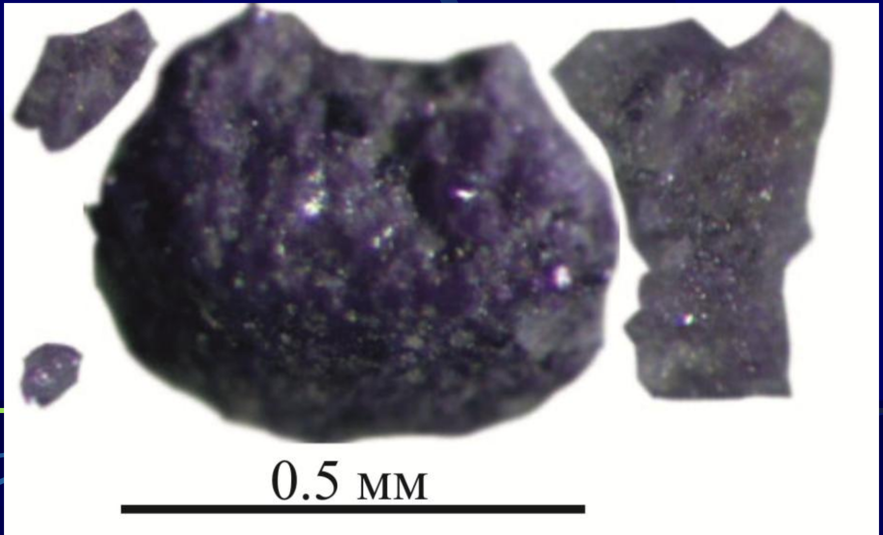
Impurities: influence on the main mantle equilibrium

E.A.Sirotkina: 1) Phase relations in the system majorite $Mg_4Si_4O_{12}$– knorringite $Mg_3Cr_2Si_3O_{12}$ were studied at 10–24 GPa and 1600 °C. 2) Results of HP-experiments revealed that Cr can be concentrated in garnet and some other minerals found as inclusions in peridotitic diamonds. Thus the ideas related with composition of the primitive mantle were extended.

Prof. Luca Bindi, University of Florence

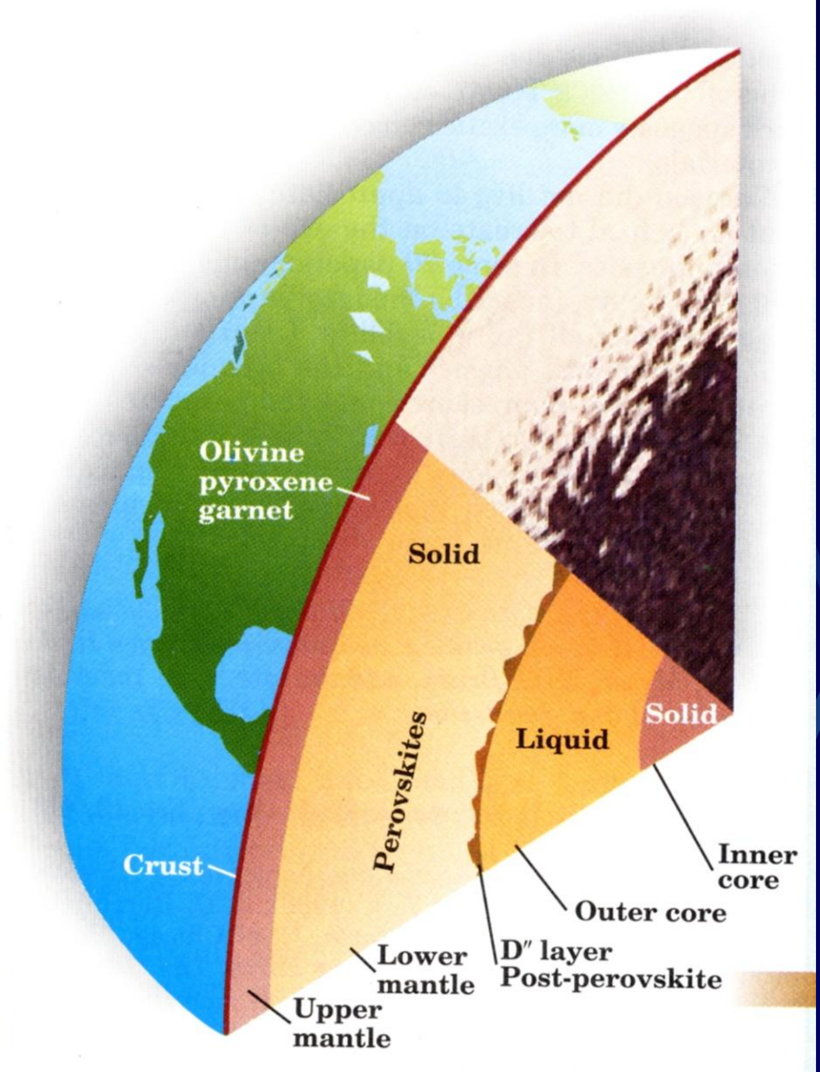
Prof. Tetsuo Irifune
Ehime-University

Knr-Maj Grt



The structure of deep geospheres: new ideas and emerging opportunities

Schematic model of Earth's deep interior (after Williamson and Adams, 1st half of XX centuary)



An English crystallographer, J.Bernal (Bernal, 1936) was the first to suggest that, in the mantle, conventional olivine become stable in the form of a polymorphic modification with a spinel structure whose density is 9% higher.

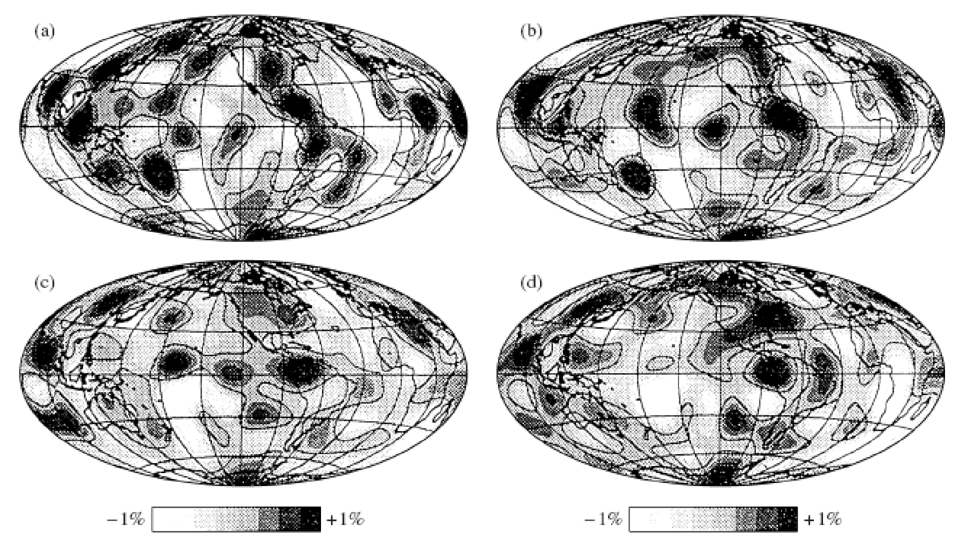
1909 –**Mohorovichich boundary**

1936 – **boundary between outer and inner core** (I.Lehmann)

Middle of XX century – upper and lower mantle; transition zones (K.E.Bullen)

Illustration of the lateral mantle nonhomogenity

The temperature deviation on the same depth varies from 500^{o} in the upper mantle till 2000^{o} in the low mantle



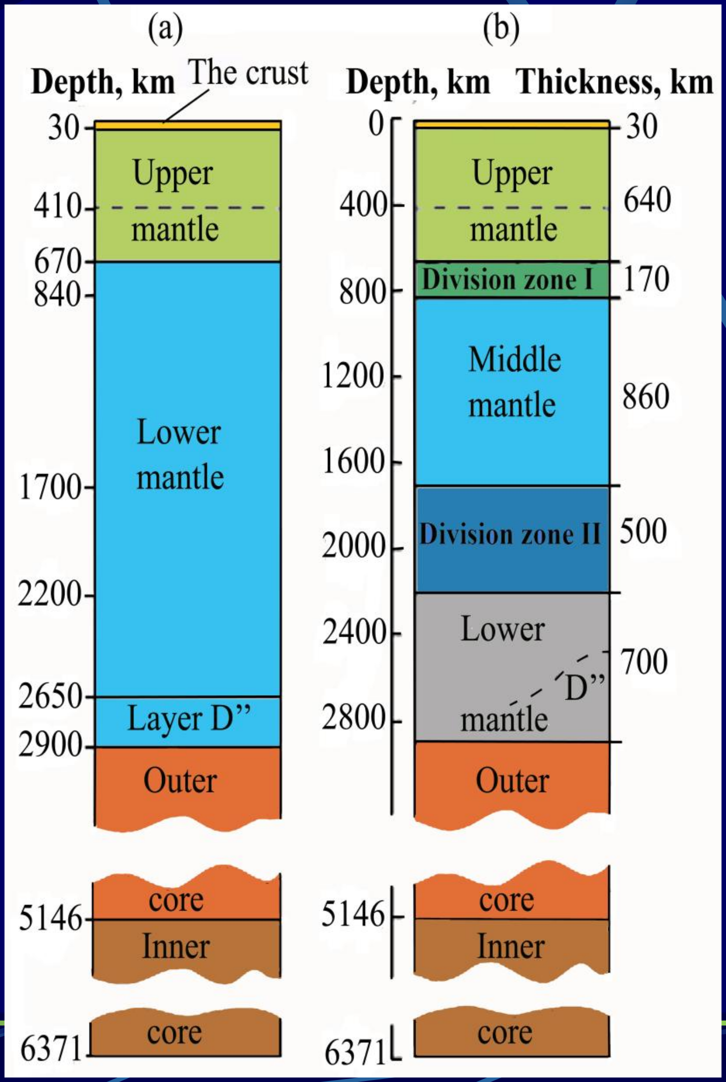
Seismic heterogenities in the middle mantle of the Pacific sector of the Earth for the depths of 900 (a), 1150 (b), 1450 (c) and 1750 km (d). The scale indicates positive and negative seismic wave velocity deviation from mean values, % (Su et al., 1994). The middle mantle differs from other geospheres by grater dimensions of seismic heterogenities (low- and medium-velocity domains). In contrast to the upper and lower mantle, where the Pacific ocean is imprinted distinctly, its manifestation in the middle mantle is somewhat uncertain.

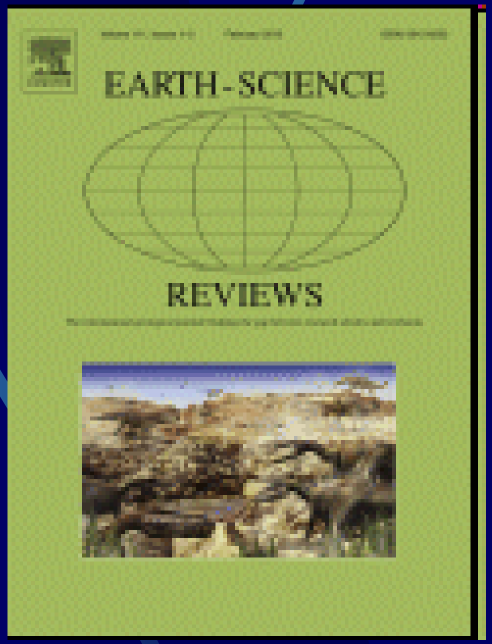
The recognition of middle mantle between 850 and 1700 km

Global seismic boundaries:

Mohorovichich discontinuity, 410, 520 (traceable beneath the oceans), 670, 900 (Semenov, 1998), 1700 (Su et al., 1994), 2900 (core-mantle), 5146 (outer-inner core)

Regional seismic discontinuities (transitional – Ringwood, 1994) in low mantle: 800, 1200-1300, 1900-2000.

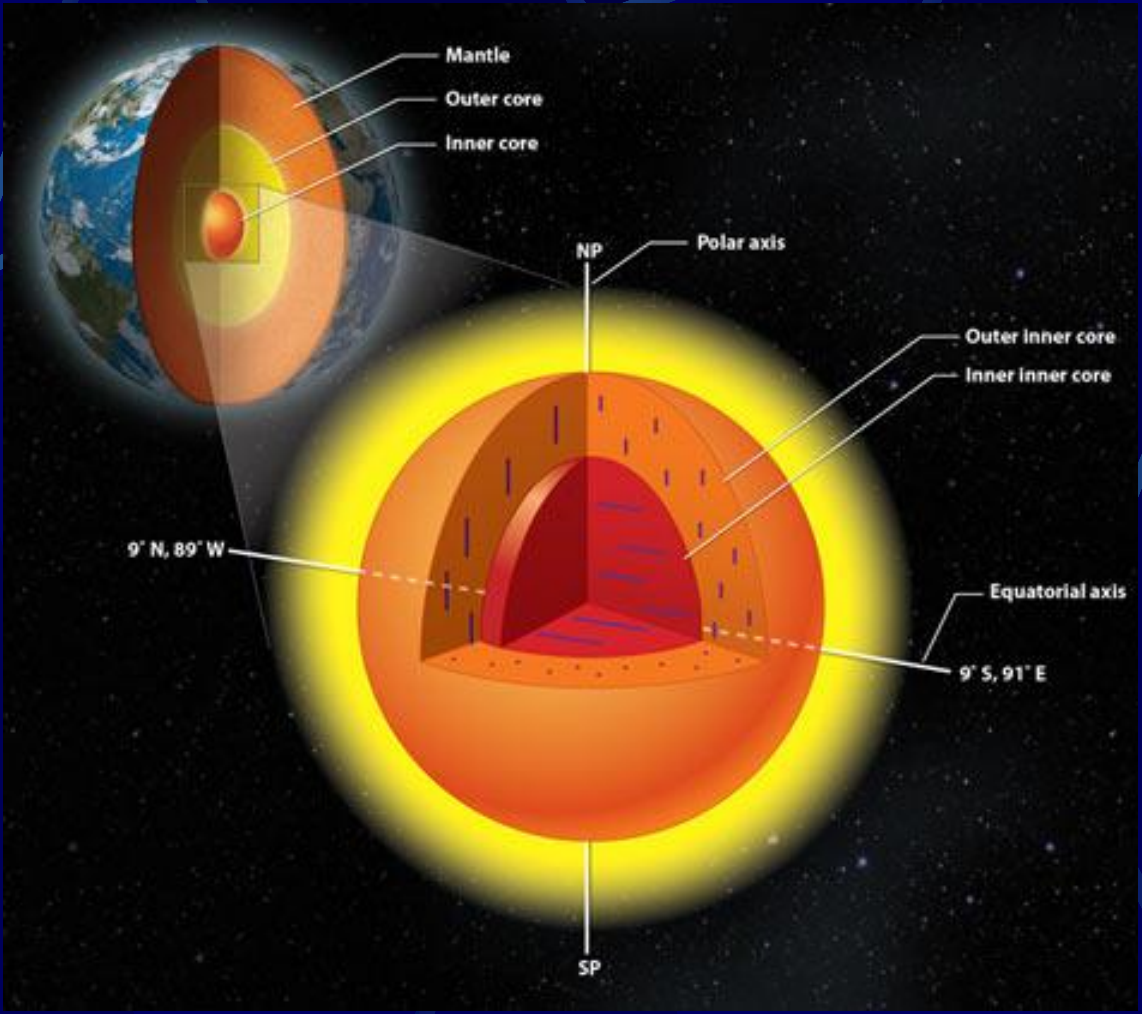



EARTH-SCIENCE

REVIEWS

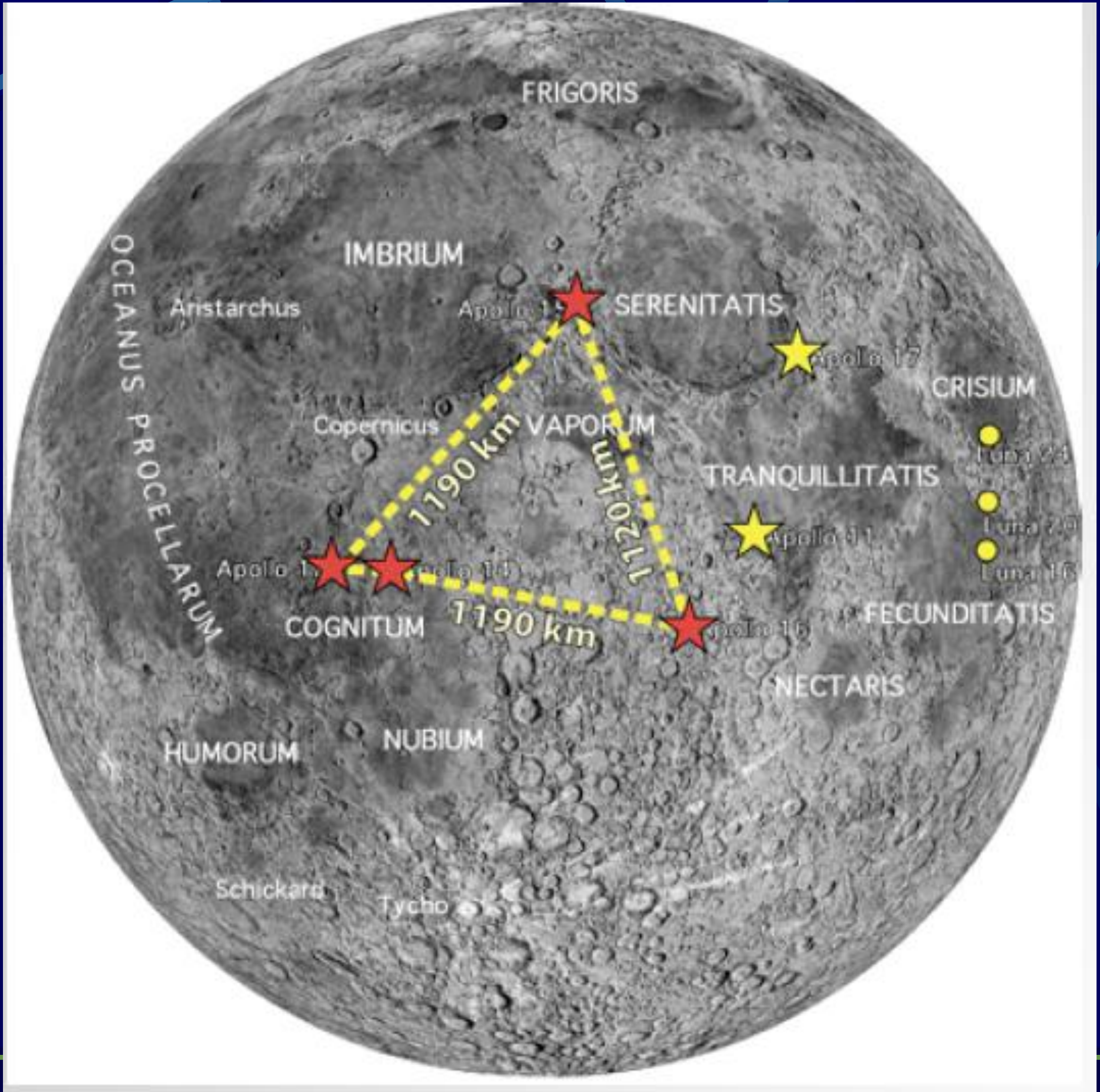
Pushcharovsky D., Pushcharovsky Yu. «The Mineralogy and the Origin of Deep Geospheres: A Review» Earth-Science Reviews, 2012, 113, N2, 94-109

Earth's Inner Core Found To Have A Core Of Its Own

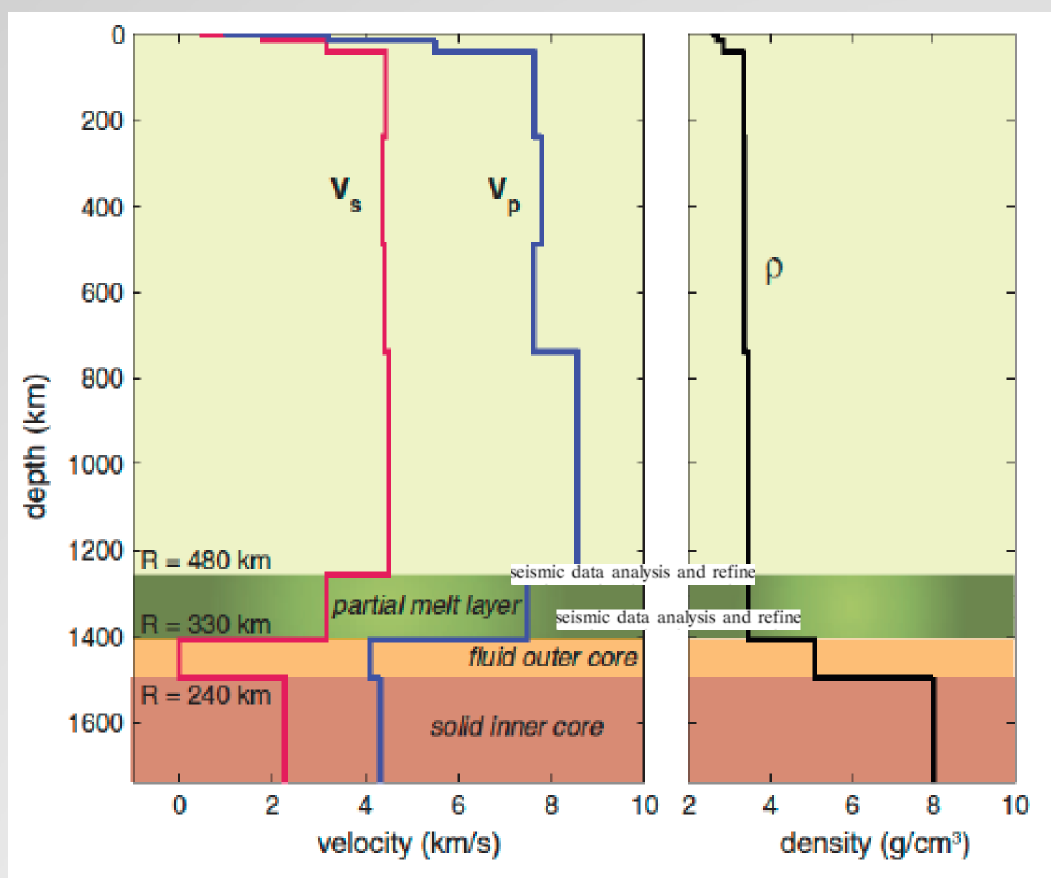


The Earth’s core : the inner metallic core (radius 1300 km), composed mostly of iron with crystals (hcp) aligned in a different direction. Thus it has double-layered structure. The thickness of outer core – 2200 km (Tao Wang, Xiaodong Song & Han H. Xia. Nature Geoscience, 8, 224–227, 2015).

The receivers of seismic waves on the Moon surface. The Moon is the only other terrestrial body besides Earth on which multiple seismic observations have been made from the Apollo missions



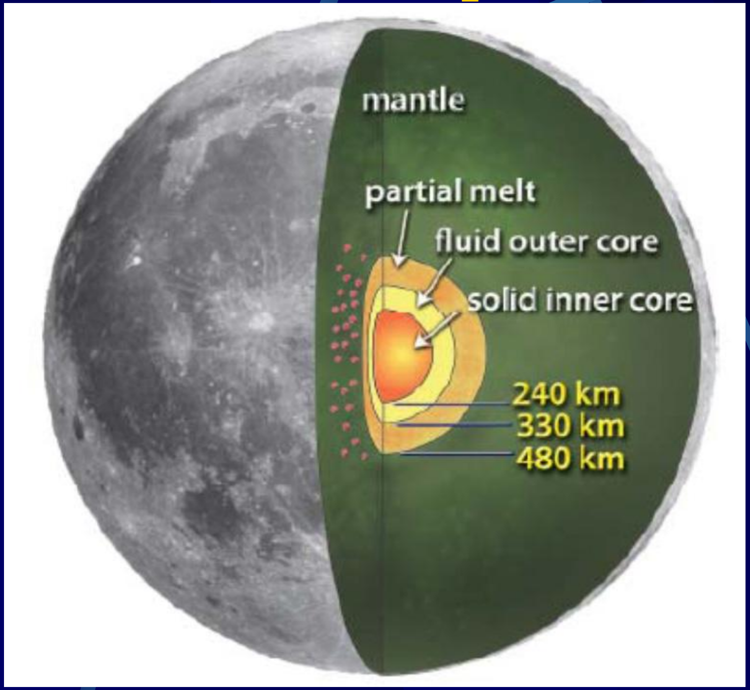
Profile of the longitudinal (V_p) and transverse (V_s) seismic wave velocities in the Moon (left). The variation of density – right.

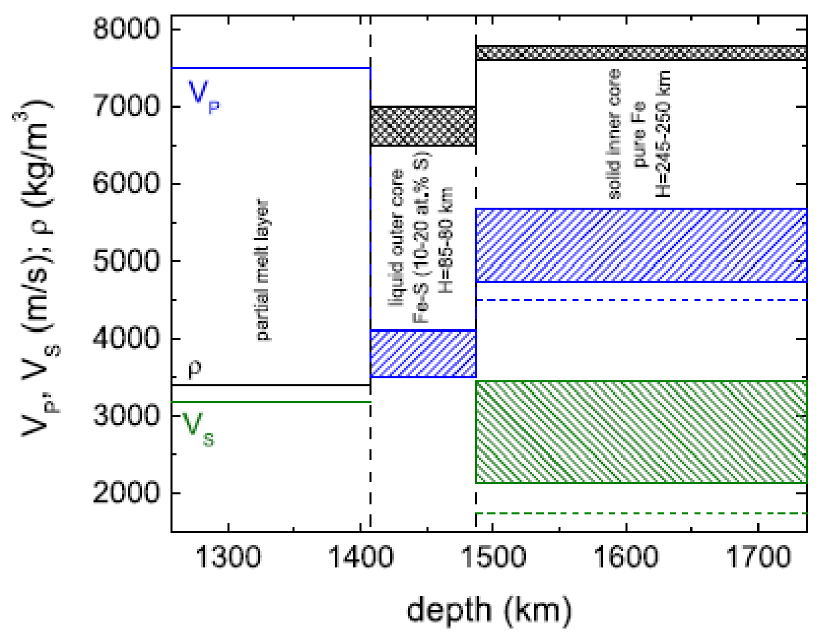


Seismic data analysis and refinements of the lunar moment of inertia require the Moon to have an inner solid core and an outer liquid core.

Radius of Moon – 1740 km. Mantle – to 1240 km. In the interval 1240 – 1410 km – partial melt layer. 1410 – 1500 km – outer core (fluid). 1500 – 1740 km –solid inner core. Max. density – 7.6 – 7.8 g/cm^3 (Antonangeli et al., PNAS, 2015)

Improving Models of the Moon's Core: measurements of the sound velocity through fcc γ-iron under high pressures (to 19 GPa) and temperatures, ranging from 300 to 1150K





ICB – Inner Core Boundary:
5 GPa, 1700 – 1900 K

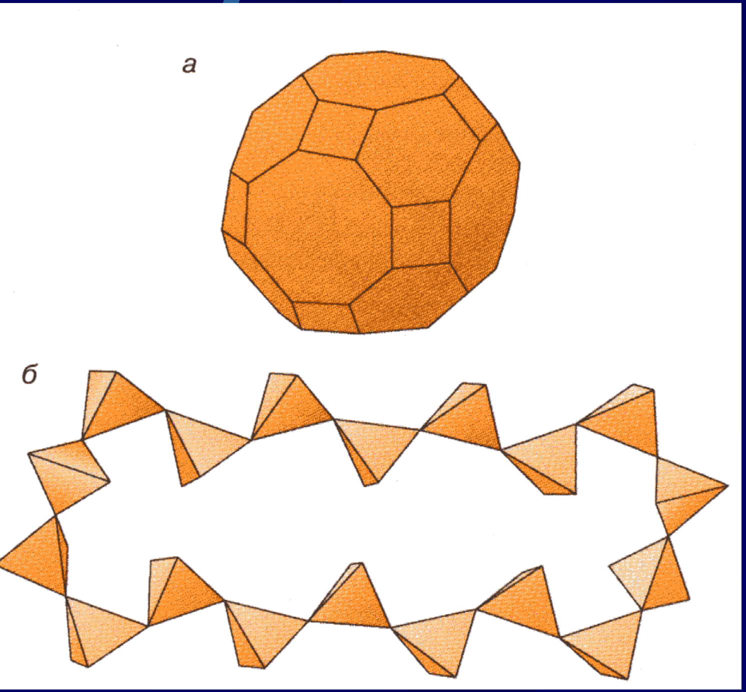
Moon's inner core is incompatible with that of pure solid iron.

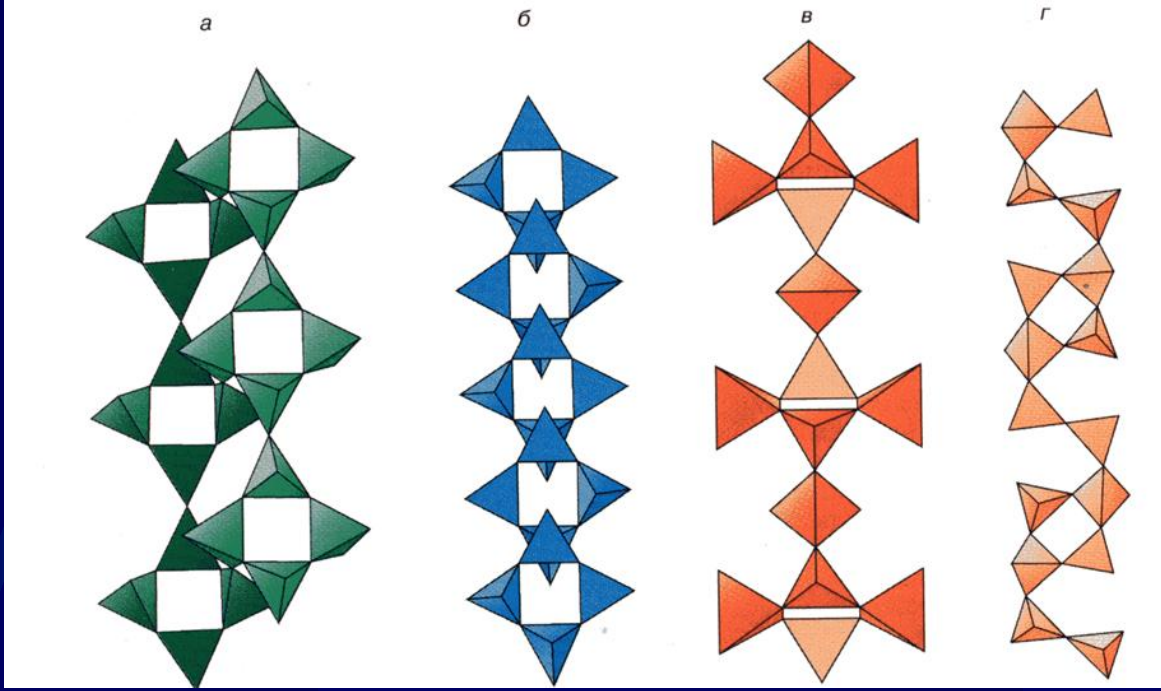
In the Earth's core, iron is stable with ε-form. Considering the Moon's interior points to the Fe-FeS system as the most probable. The total amount of S in the Moon's core 3-6 wt% (in outer core – 6-11 wt%): Antonangeli et al. *PNAS, 2015.*

General conclusion: step by step we extend our knowledge about the formation, evolution, composition and the structure of our planet.

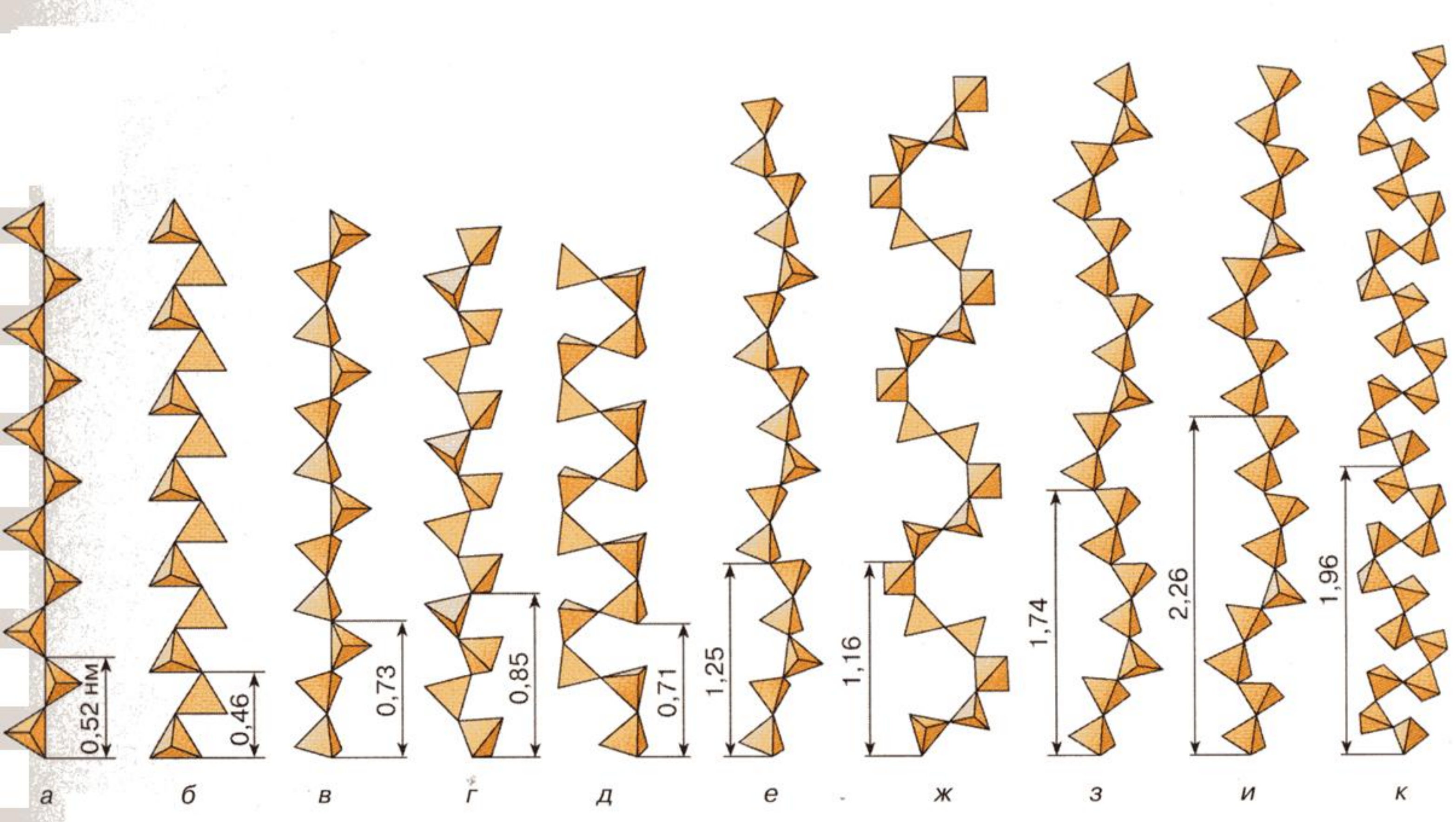
Thank you for your attention!

The unique isolated complexes (left) and the bands formed by four-membered rings (right) in silicate structures

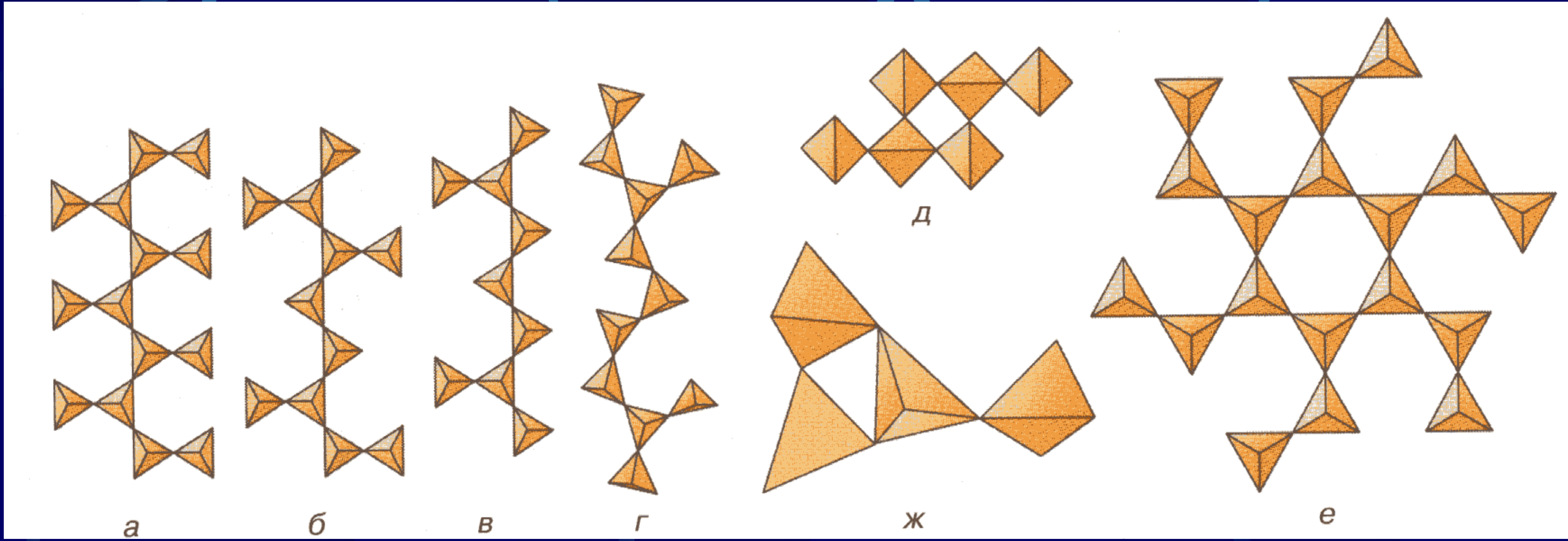




Different types of silicate chains

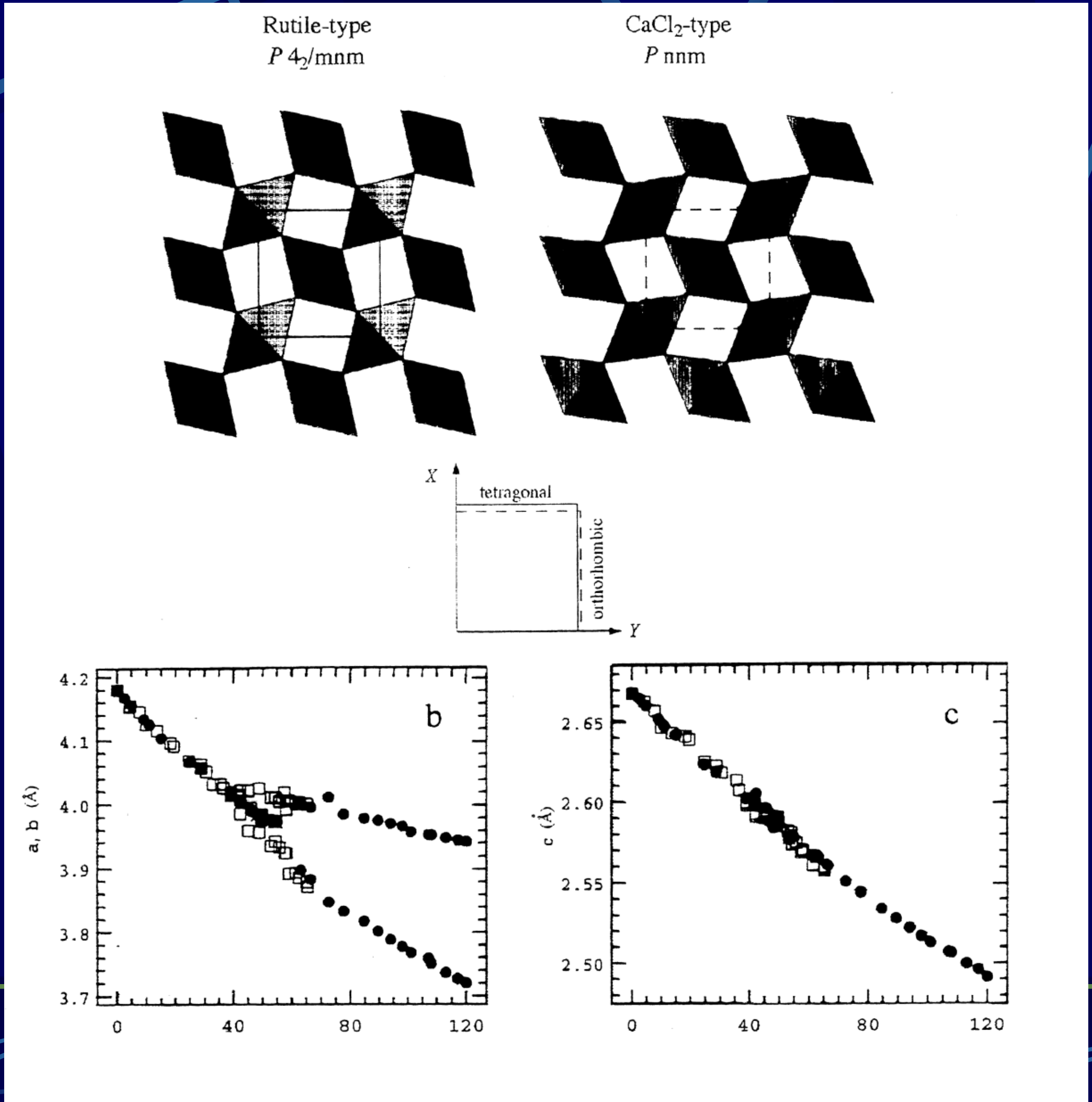


Branched (Si,O) complexes in silicate structures



Considering the most specific features of silicate comlexes formed by tetrahedra their number actually exceeded 100.

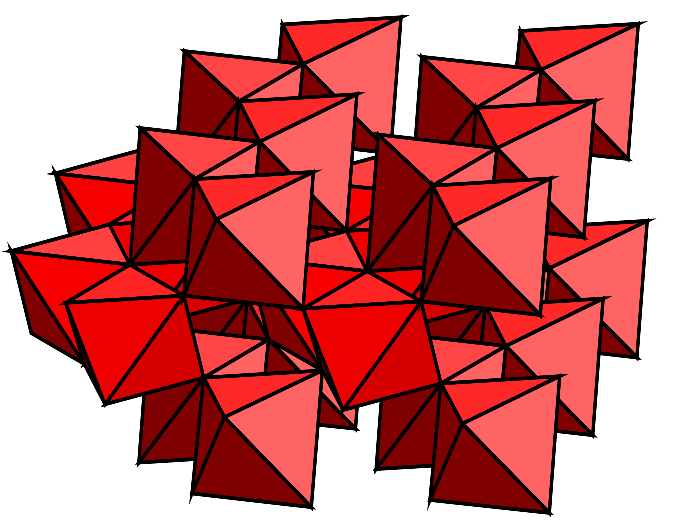
SiO_2 polymorphs: SiO_2 with s.t. $CaCl_2$ 50 – 120 Gpa (Andrault et al., 1998). Assuming the temperature in the mantle, 50 GPa corresponds to the depth ~1500 km



At 100 GPa (2200 km) – s.t. α-PbO_2 (Dubrovinsky et al., 1997). Density difference – 1.5%. At 200 GPa – s.t. pyrite (Kuwayama Y. et al., 2005)

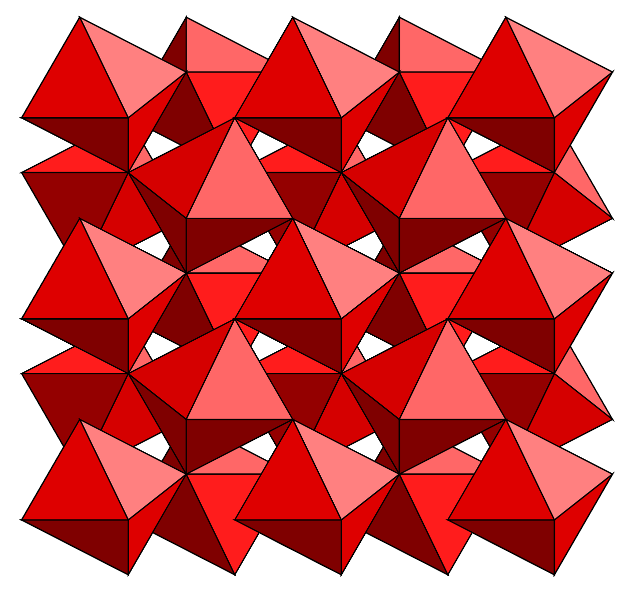
SiO_2 with s.t. α-PbO_2

Seifertite

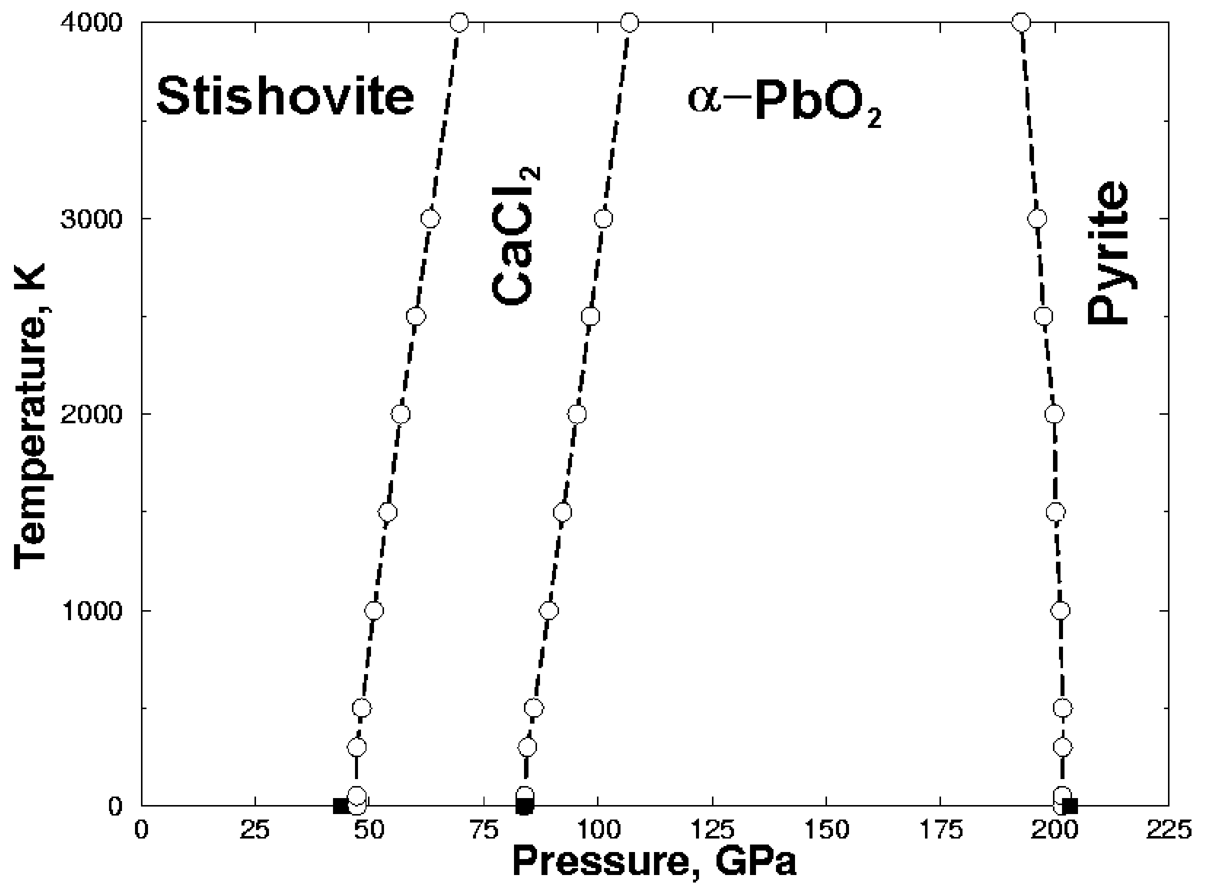


found in Martian and Lunar meteorites

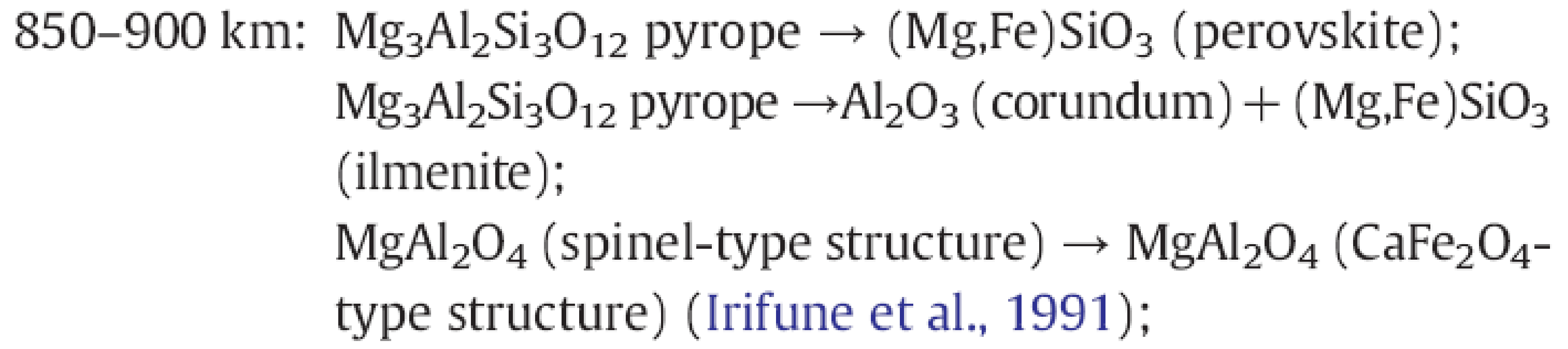
SiO_2 with s.t. pyrite



High-pressure phase diagram of SiO_2 (from Oganov et al., 2005; Ohtani & Sakai, 2008): anion close packing disappears at > 200 GPa.



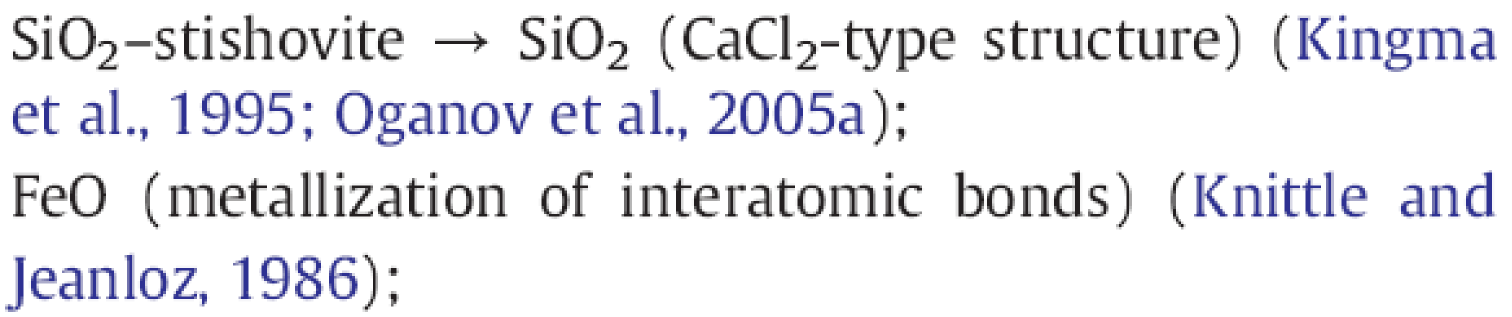
New global seismic boundaries and corresponding mineral transformations



850–900 km: $Mg_3Al_2Si_3O_{12}$ pyrope → $(Mg,Fe)SiO_3$ (perovskite);
$Mg_3Al_2Si_3O_{12}$ pyrope → Al_2O_3 (corundum) + $(Mg,Fe)SiO_3$ (ilmenite);
$MgAl_2O_4$ (spinel-type structure) → $MgAl_2O_4$ ($CaFe_2O_4$-type structure) (Irifune et al., 1991);

1200 km: $MgAl_2O_4 \rightarrow MgAl_2O_4$ ($CaTi_2O_4$- type structure)

1700 km



SiO_2–stishovite → SiO_2 ($CaCl_2$-type structure) (Kingma et al., 1995; Oganov et al., 2005a);
FeO (metallization of interatomic bonds) (Knittle and Jeanloz, 1986);

2300 km: SiO_2 ($CaCl_2$) - SiO_2 (PbO_2 str.type) - *Seifertite*