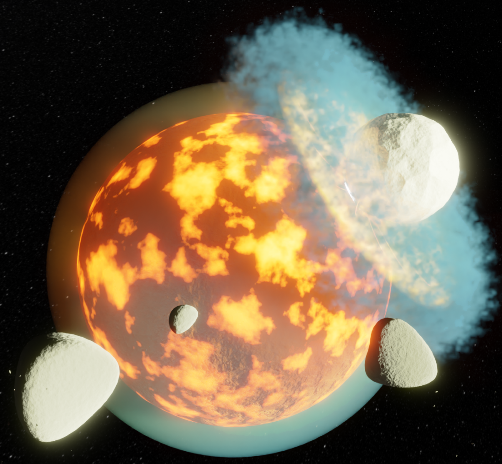
Solving the missing Xe paradox:

What does that tell us about planetary formation ?



Chrystèle SANLOUP
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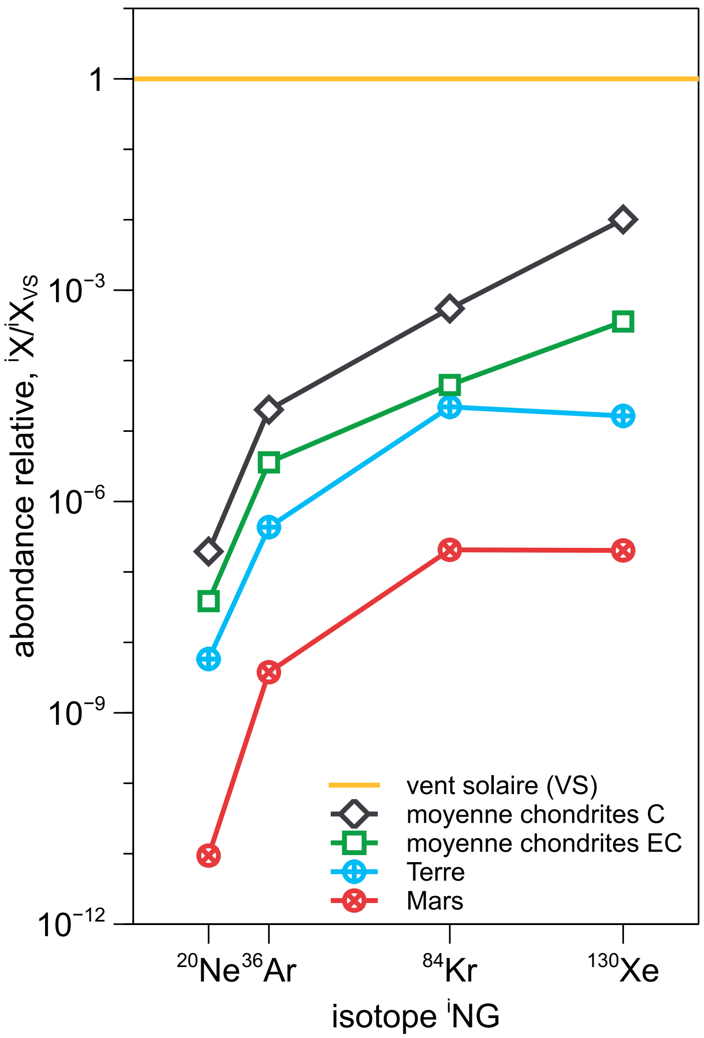
Collaborators for noble gas spectrometry:
D. HORLAIT and E. GILABERT, LP2i@Bordeaux

SORBONNE UNIVERSITÉ

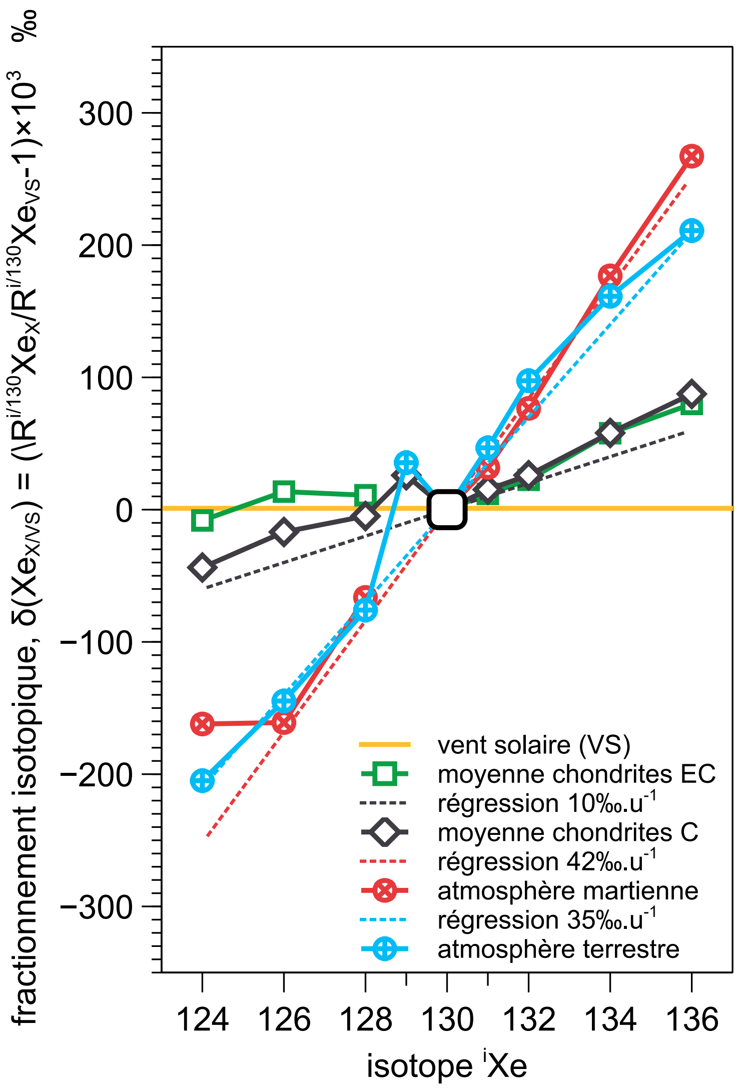
Missing Xe problem



90% of primordial Xe is missing

Ozima&Podosek, *J. Geophys. Res.*, 1999

Anders & Owen, *Science* 1977



Strong depletion in light isotopes

Krummenacher et al., *Geochim. Cosmochim. Acta* 1962

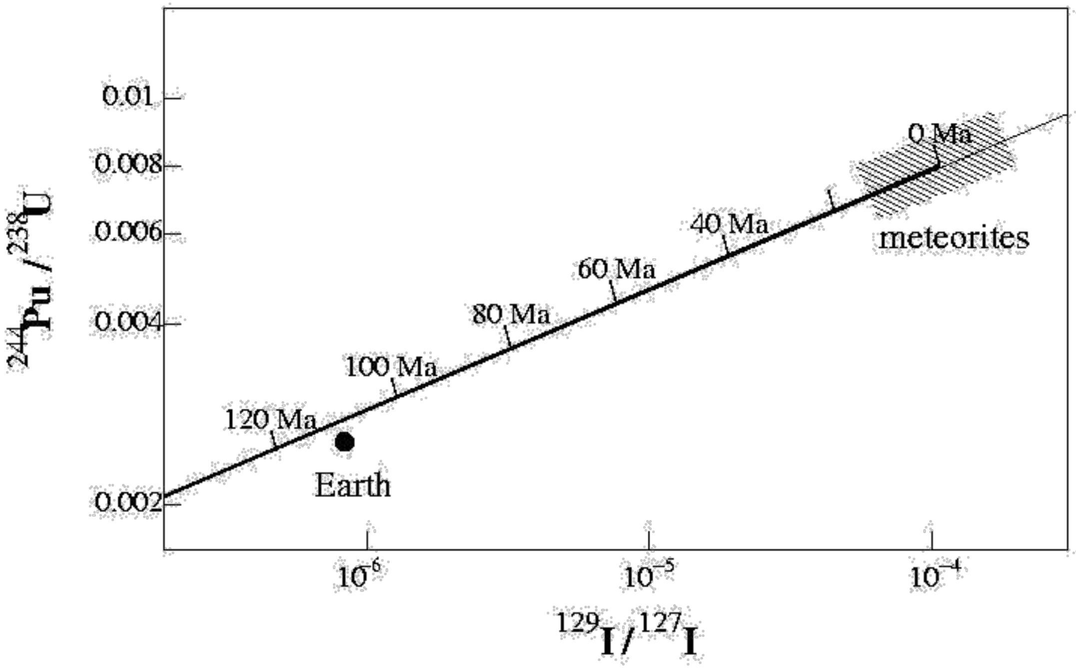
Xenon isotopes: tracers of atmosphere formation

→ timing of atmosphere formation
→ timing of Earth's formation

Allègre et al. *EPSL* 1986,
Tolstikhin et Marty *Science* 1998, Pepin *EPSL* 2006

$^{129}I \rightarrow ^{129}Xe$, $T_{1/2}$=15.7 My

$^{244}Pu \rightarrow ^{136}Xe$, $T_{1/2}$=82 My



Earth formation
in 110 Ma

Ozima & Podosek, *JGR*, 1999

Xenon isotopes: tracers of atmosphere formation

→ timing of atmosphere formation
→ timing of Earth's formation

Allègre et al. *EPSL* 1986,
Tolstikhin et Marty *Science* 1998, Pepin *EPSL* 2006

$^{129}I \rightarrow ^{129}Xe$, $T_{1/2}$=15.7 My

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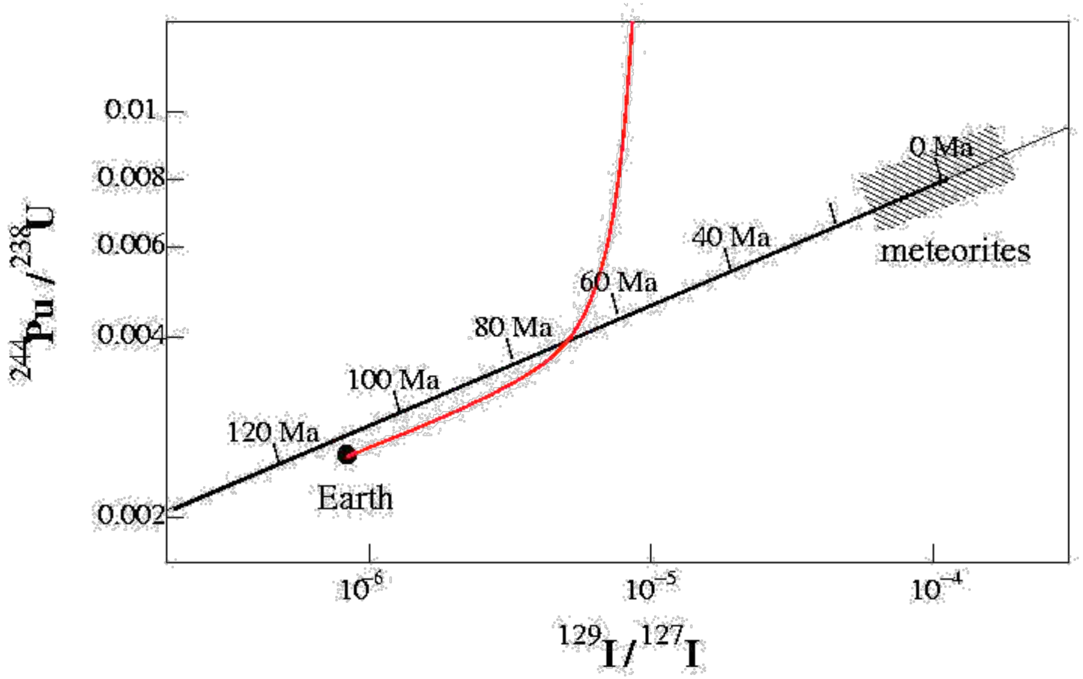


Ozima & Podosek, *JGR*, 1999

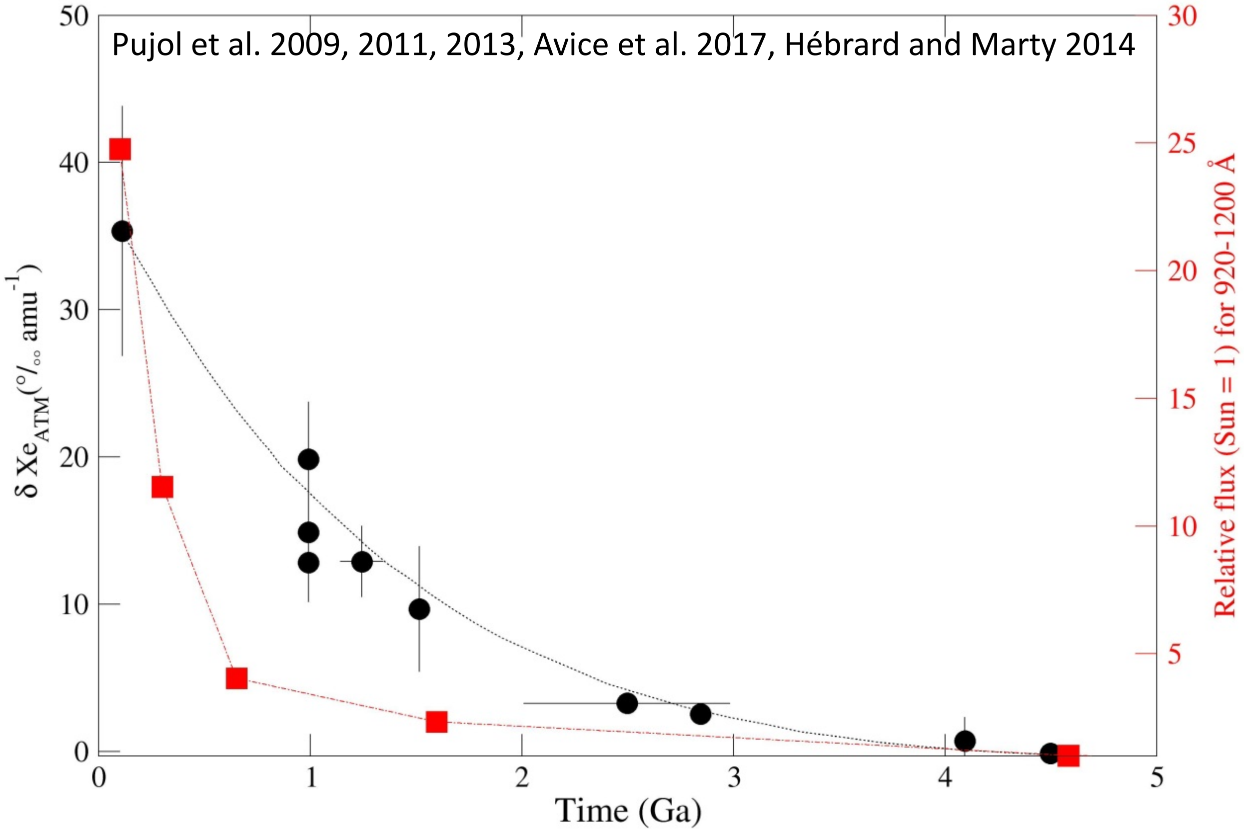
If 90% of primordial Xe
is missing:

Earth formation
in less than 70 Ma

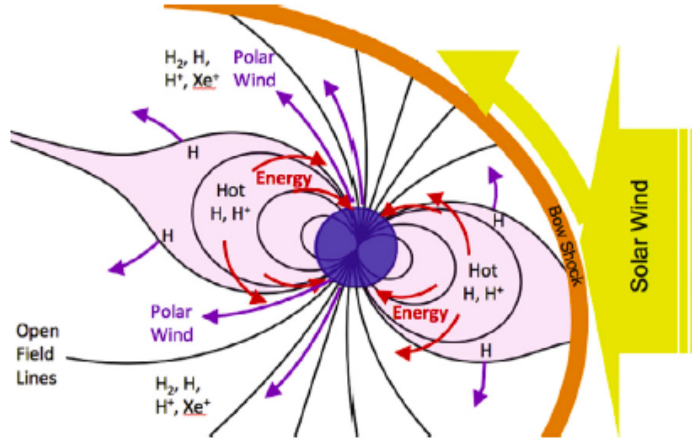
Xenon isotopes: tracers of atmosphere formation

Hypothesis: ionization and atmospheric escape

either UV photoionisation:



or H+ entrainment:



Zhanle et al. *GCA* 2019

Pb: requires unlikely large amounts of water during the Archean to produce H+

Problems: 1) asynchronicity between high UV flux and Xe isotopic evolution
2) Xe too heavy to be lifted through the atmosphere

Is Xe in planetary interiors?

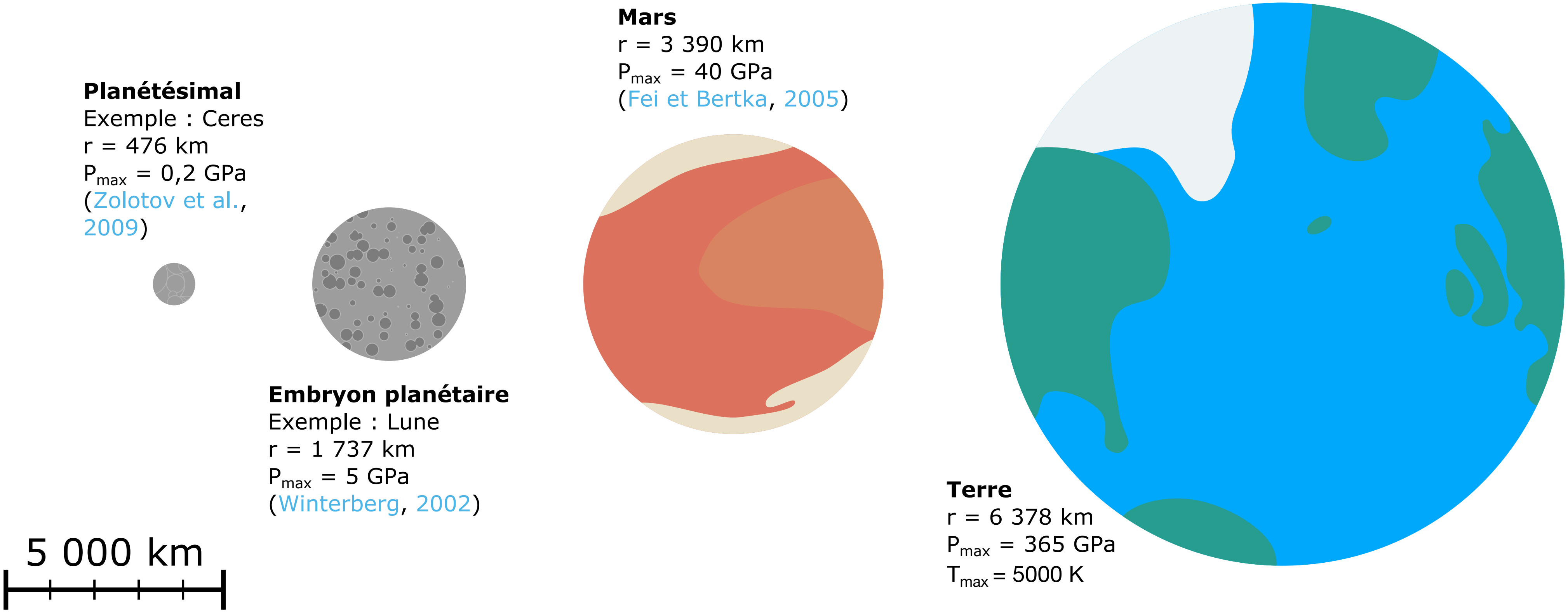
Podosek et al. *Geochim. Cosmochim. Acta* 1980

« [Xe could be missing because] *the total terrestrial inventory is, i.e. that* ***Xe*** *has been nearly quantitatively* ***retained in the solid earth*** *while the lighter gases have been nearly quantitatively out-gassed.* »

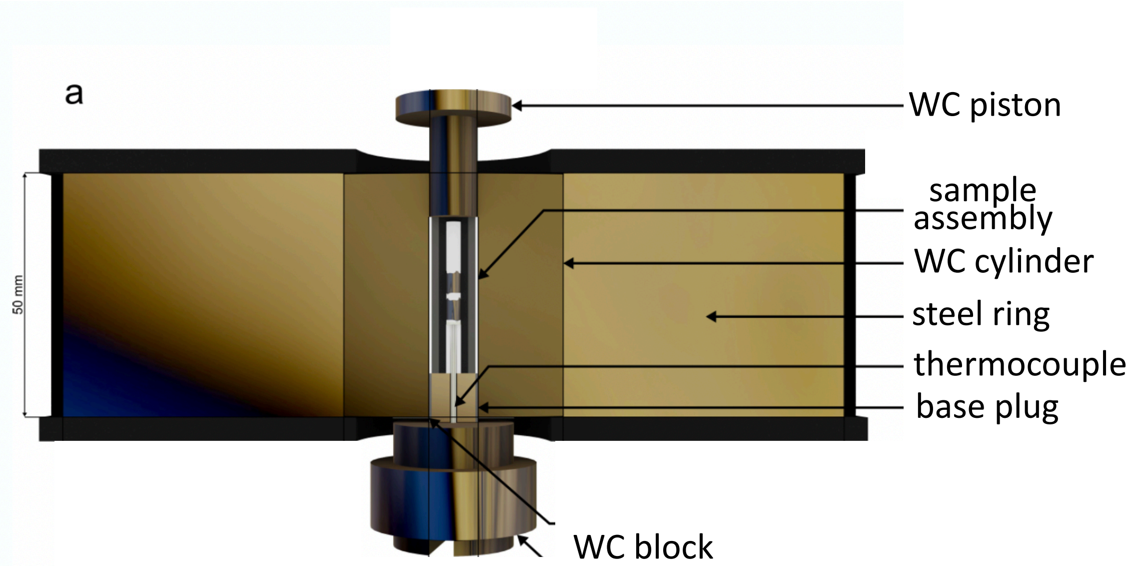
Pepin *Icarus* 1991

« *Consequently the model demands that most of this* ***Xe be retained within the solid planets****, presumably by preferential partitioning into iron-rich mineral phases under conditions of high pressure.* ***The small size of Mars dictates that this behavior must occur at pressures not exceeding a few hundred kilobars*** [few tens GPa, n.d.a.]. *Thus the model, at least in its present form, will stand or fall on the results of laboratory investigations of Xe partitioning in this pressure range.* »

Planetary interiors: extreme pressures and high temperatures

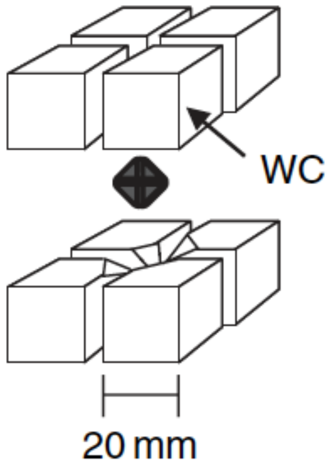


Generating extreme pressures and high temperatures in the lab



Piston-cylinder press

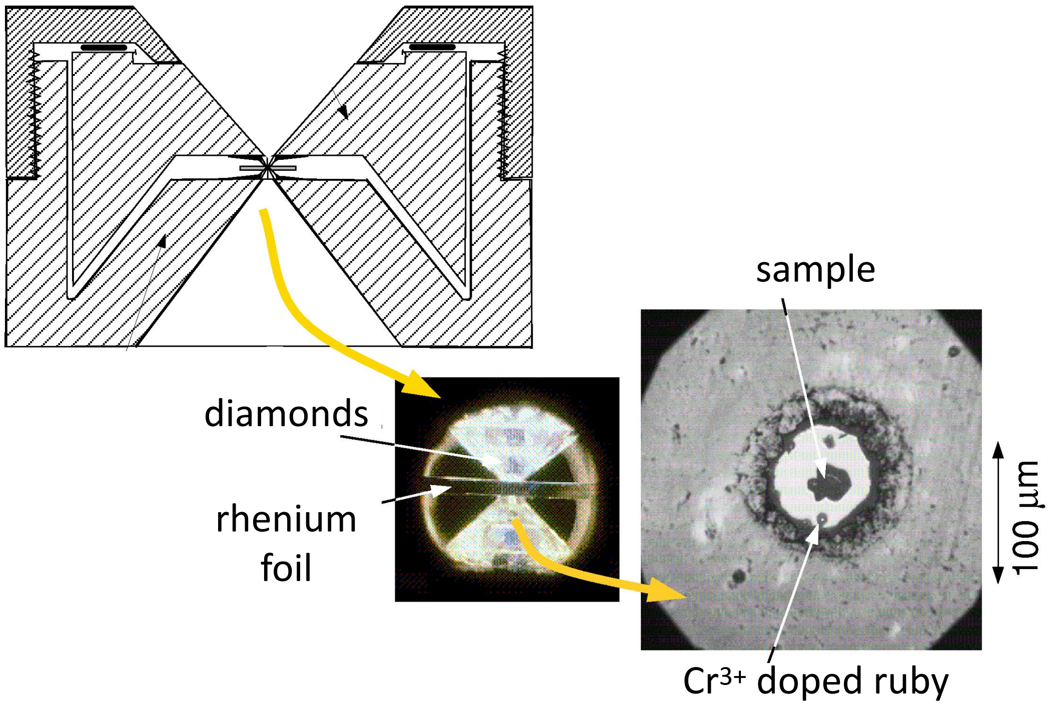
“large volume” samples:
1 mm^3-1 cm^3



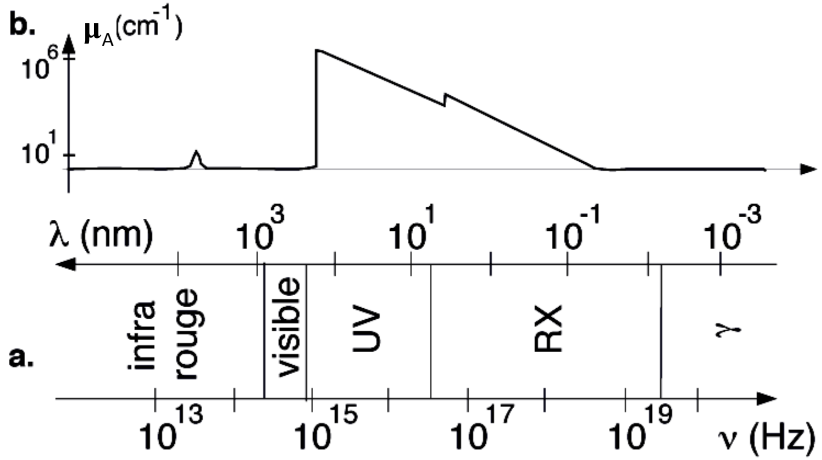
Multi-anvil press

Generating extreme pressures and high temperatures in the lab

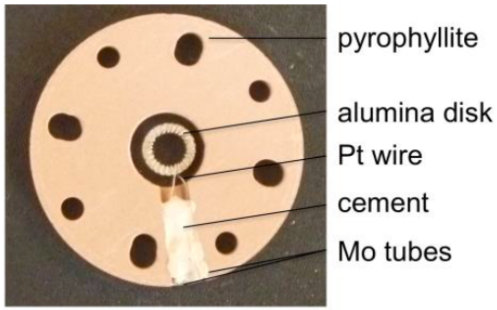
Diamond-anvil cells



Diamond absorption:

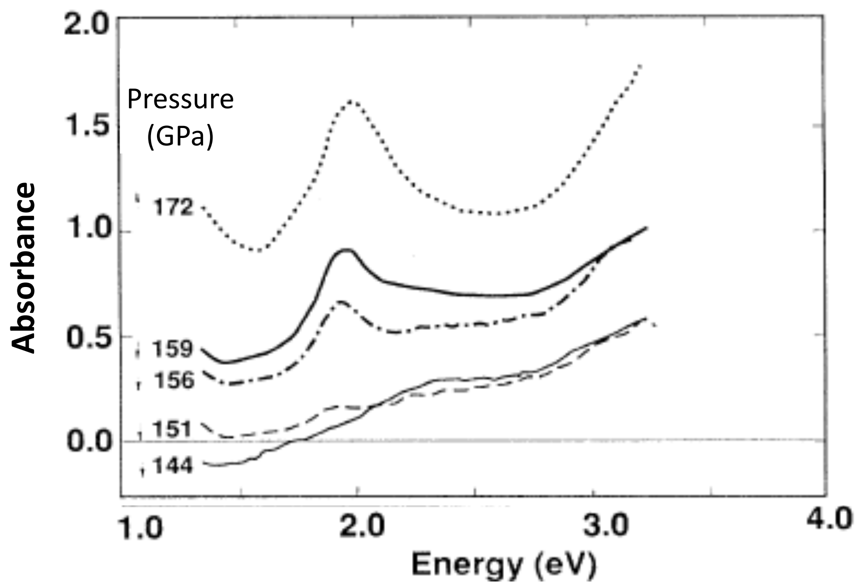


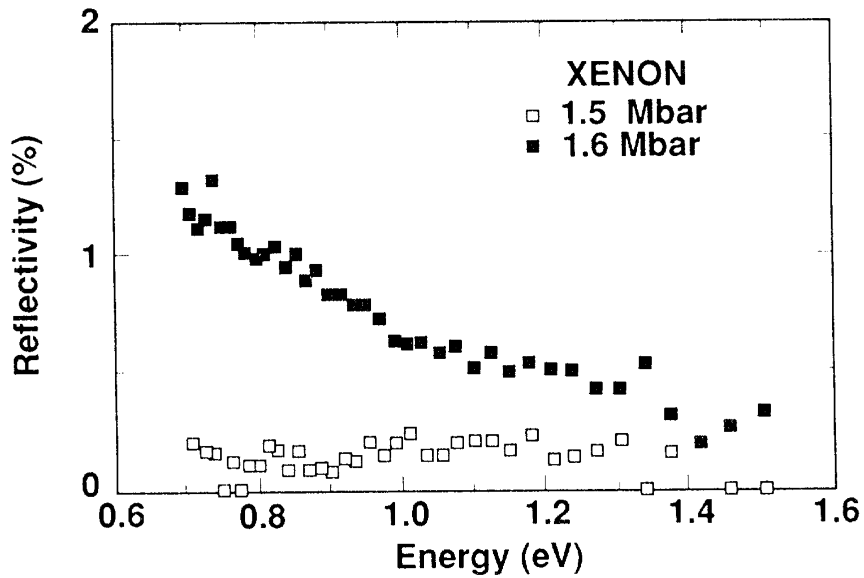
Heating: resistive wire (1500 K max) or IR laser (>5000 K)



Xenon under extreme pressures

Metallic xenon



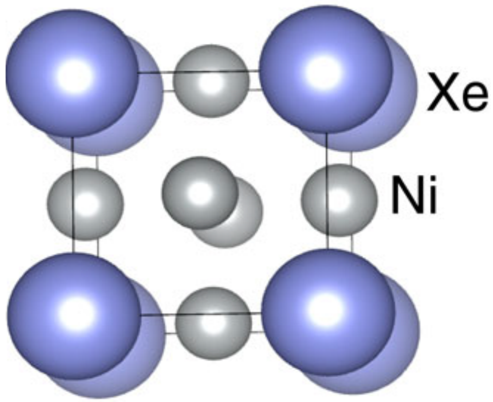


Reichlin et al. *PRL* 1989; Goettel et al. *PRL* 1989; Eremets et al., *PRL* 2000.

Reactivity of Xe in planetary interiors

Core materials

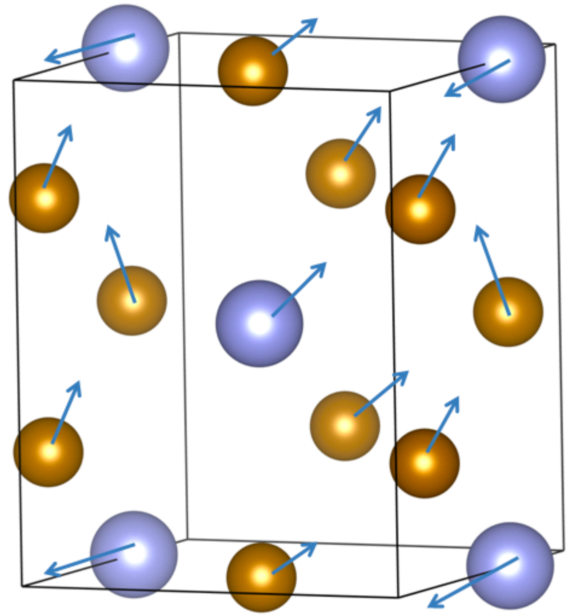
Synthesis in laser-heated diamond-anvil cells



$XeNi_3$

P>150 GPa

Dewaele et al. *High Pressure Research* 2016



$XeFe_3$

P>200 GPa

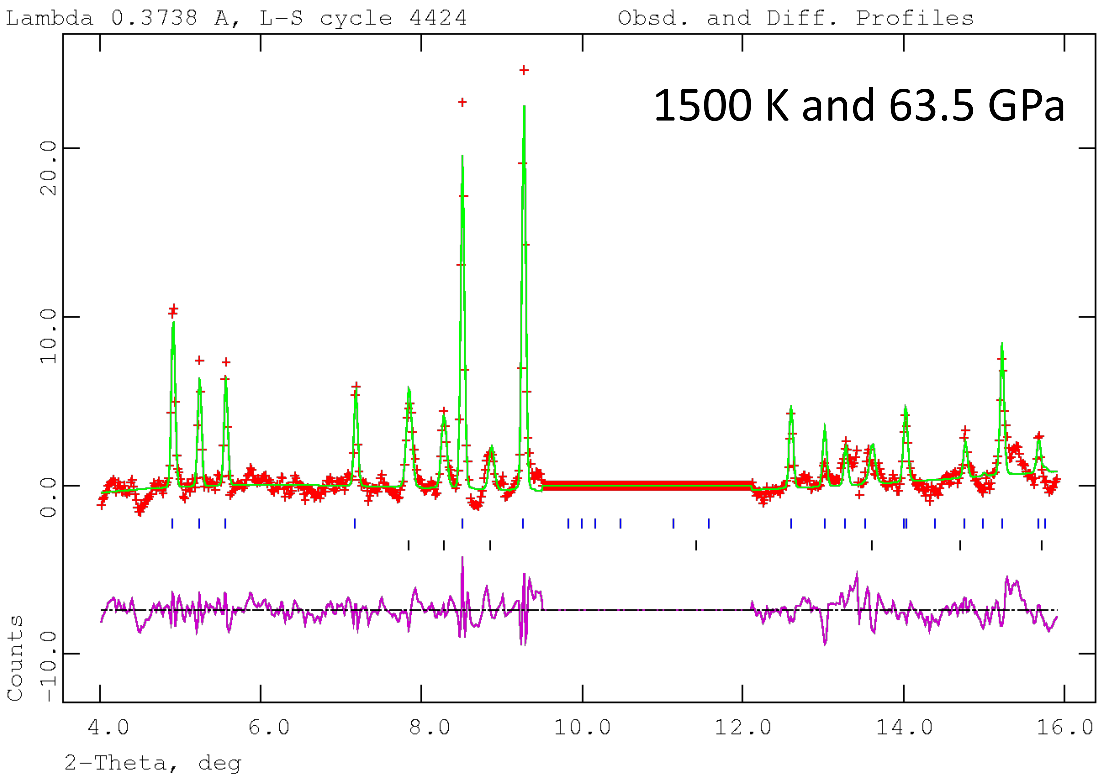
Stavrou et al. *PRL* 2018

Very interesting P-induced chemistry, but stoichiometric compounds likely not relevant to store Xe as a trace element

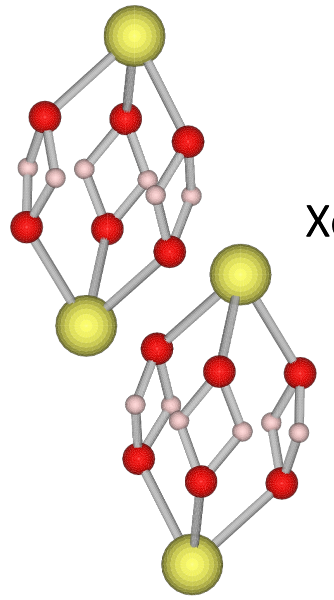
Reactivity of Xe in planetary interiors

High pressure xenon oxides

Synthesis in laser-heated diamond-anvil cells



Xe+H_2O at P>50 GPa



$Xe_2O_6H_6$

Rietveld fit (Xe, O) + MD calculations (varying H)

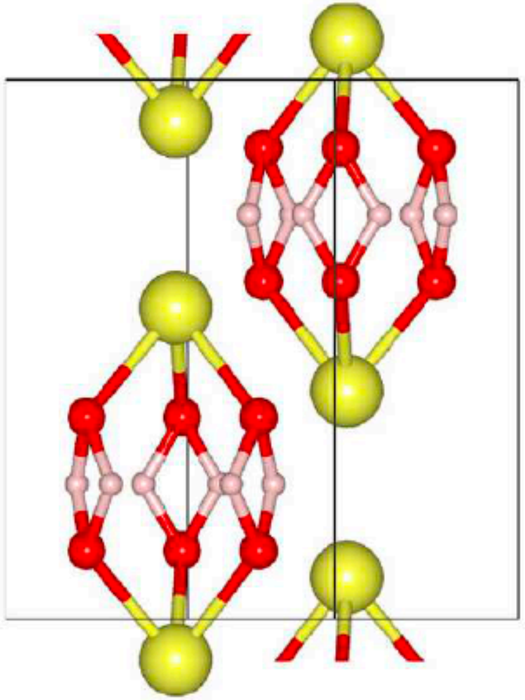
Good match with experimental data within 1% (a,c)

Sanloup et al. *PRL* 2013

Reactivity of Xe in planetary interiors

High pressure xenon oxides

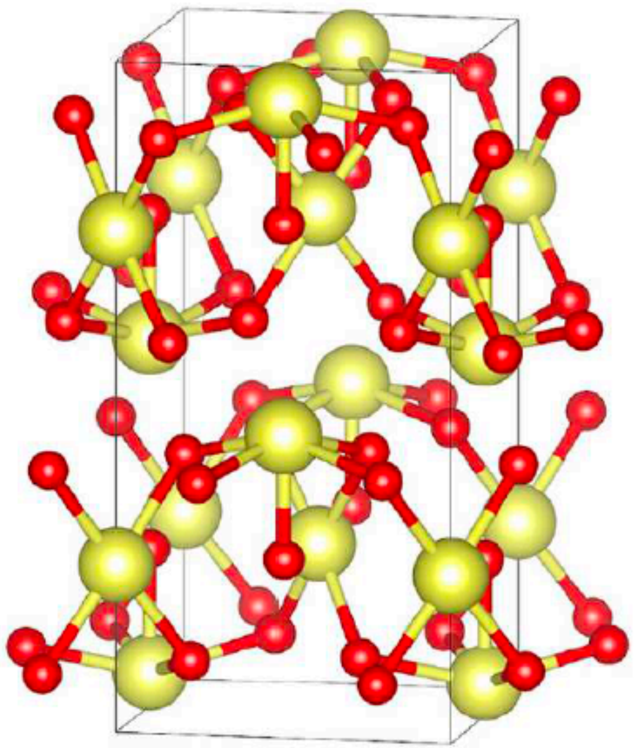
Synthesis in laser-heated diamond-anvil cells



$Xe_2O_6H_6$

$Xe+H_2O$ P>50 GPa

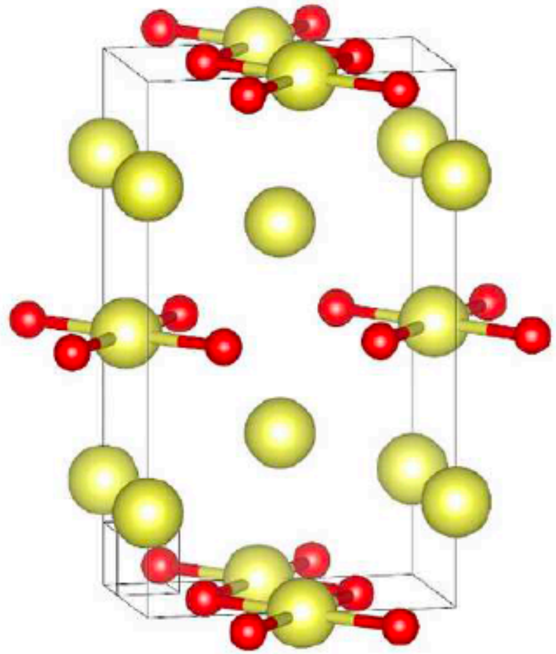
Sanloup et al. *PRL* 2013



Xe_2O_5

$Xe+O_2$ P>87 GPa

Dewaele et al. *Nat. Chem.* 2016



Xe_2O_3

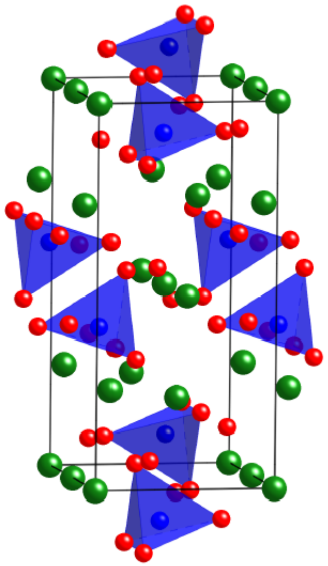
$Xe+O_2$ P>83 GPa

Dewaele et al. *Nat. Chem.* 2016

Major minerals on Earth

Mantle rock: peridotite

Photo: Damien Mollex, lithothèque ENS Lyon

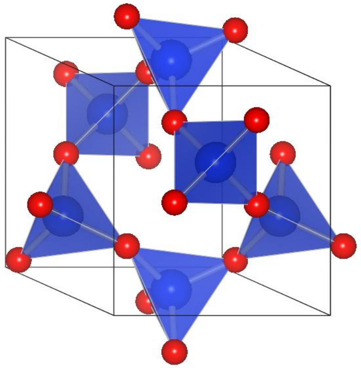


Olivine
$(Mg,Fe)_2SiO_4$

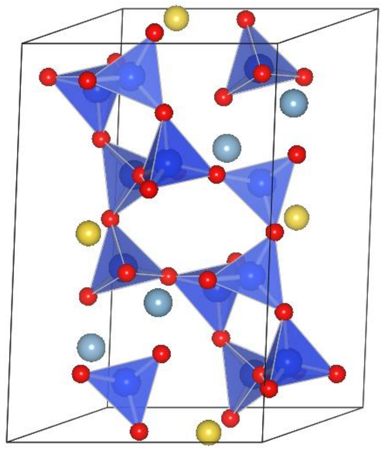
O
Si
Mg,Fe

Continental crust rock: granite

Photo: Tourisme en Bretagne website (Ploumanac'h)



Quartz
SiO_2

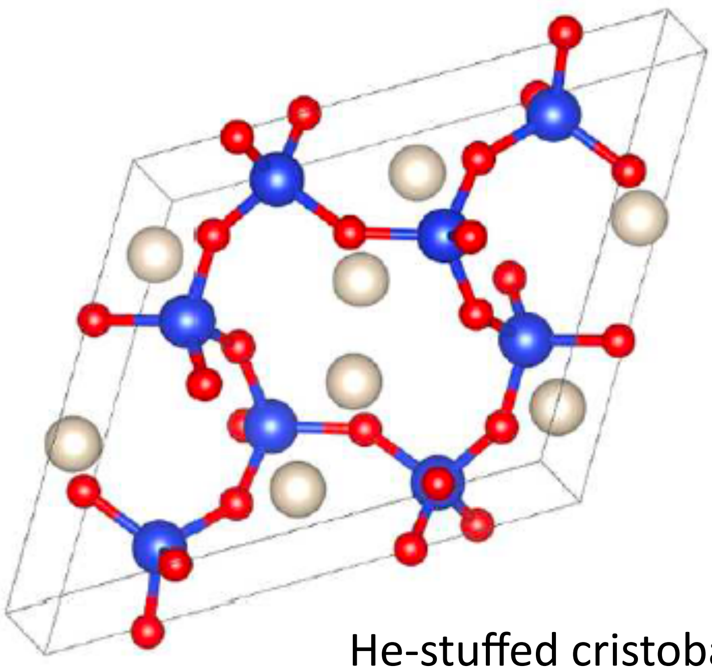


Feldspars
$(Na,K)AlSi_3O_8$

Natural conditions: Xe chemistry as a trace element

Can xenon react with silicates?

- ✓ Starting with SiO_2 cristobalite (cages)
- ✓ Cryogenic loading of Xe in diamond-anvil cells

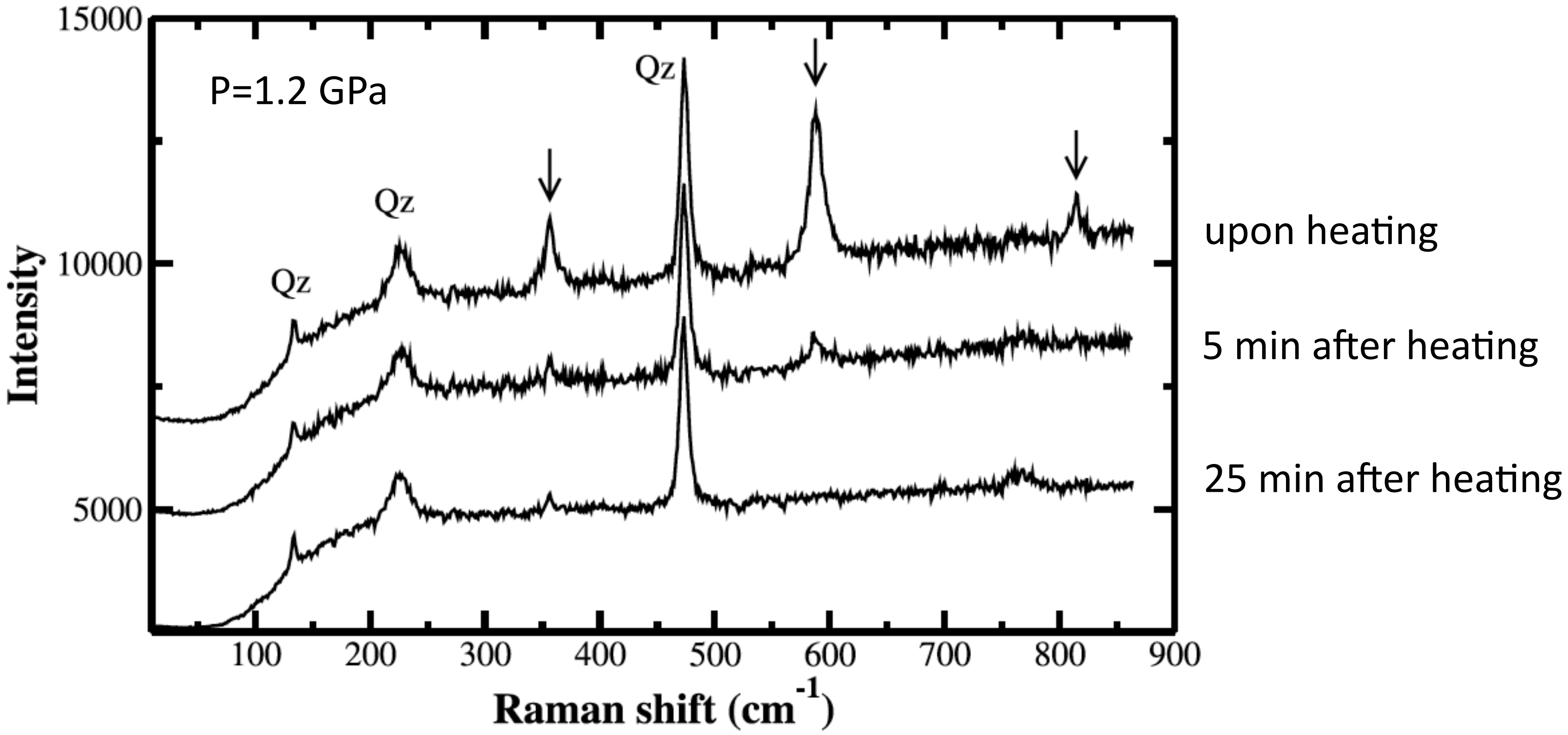


He-stuffed cristobalite

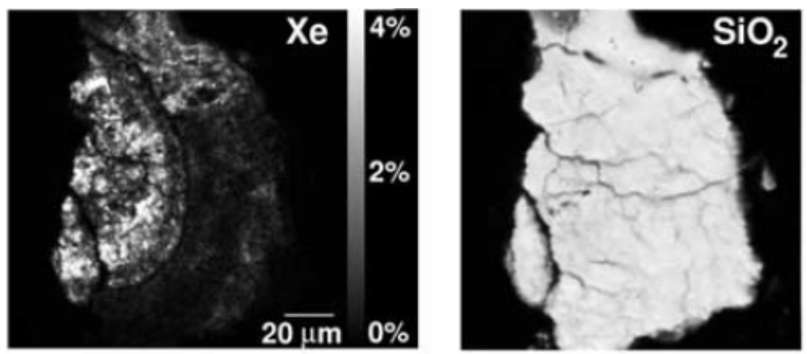
Matsui et al., *Amer. Mineral.* 2014

It all started at the Geophysical Lab (2000-2001)...

Raman spectroscopy



Electron microprobe maps

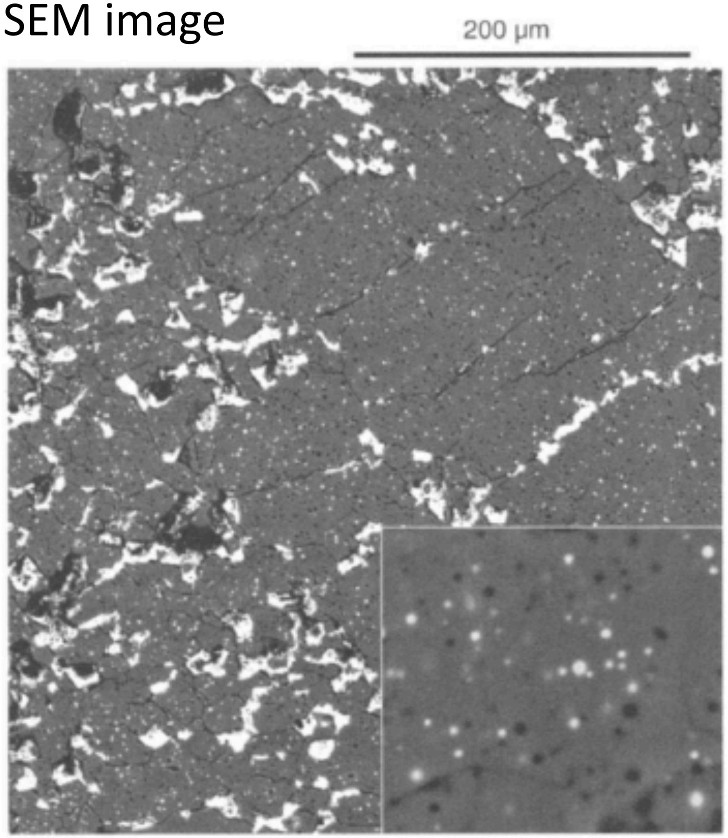


Sanloup et al. *Geophysical Res. Lett.* 2002

Chemical analyses of quenched samples

Xe + SiO_2

SEM image



EDX spectra

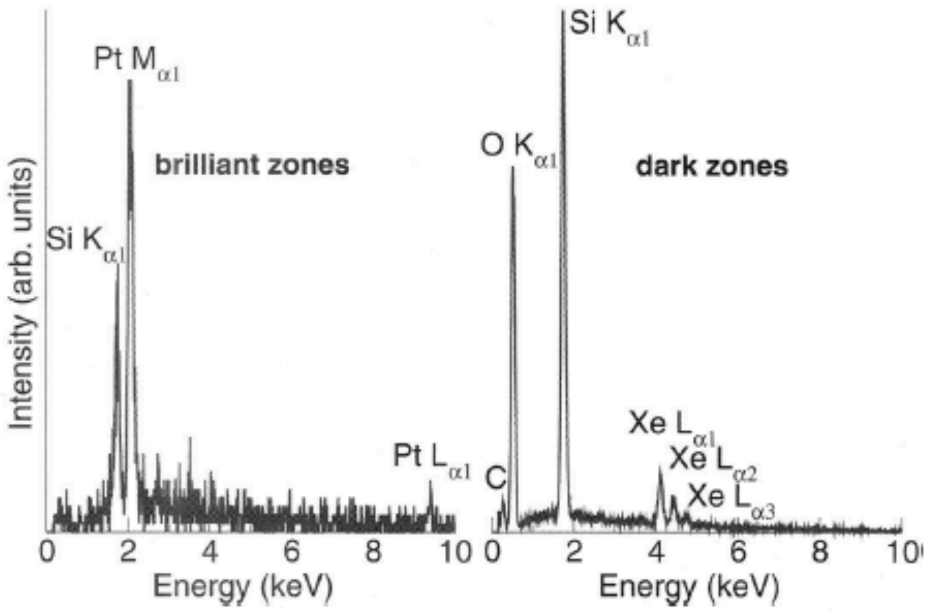


Fig. 3. Scanning electron microprobe image of a 10 GPa and 2273 K run. **(A)** Pt-Si areas are bright and 1 to 10 µm wide. Xe-filled bubbles are bright, submicrometer to micrometer sized, and located inside coesite crystals. (Inset) Zoom on a Pt-Si–free zone. **(B)** Energy dispersive x-ray analysis spectra.

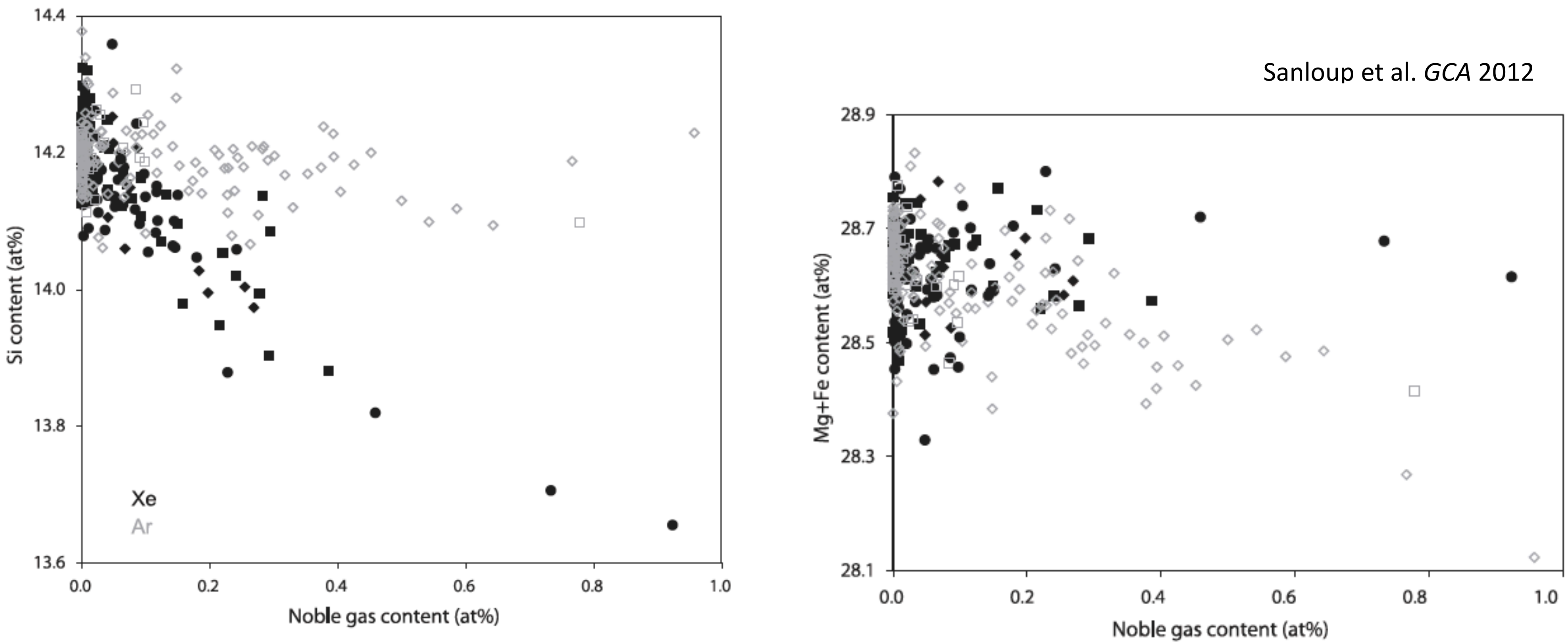
Sanloup et al. *Science* 2005

Explanation of Pt_3Si: reduction of Si by oxidation of Xe

$$SiO_2 + xXe + yPt = yPt_3Si + (Xe_x,Si_{1-x})O_2$$

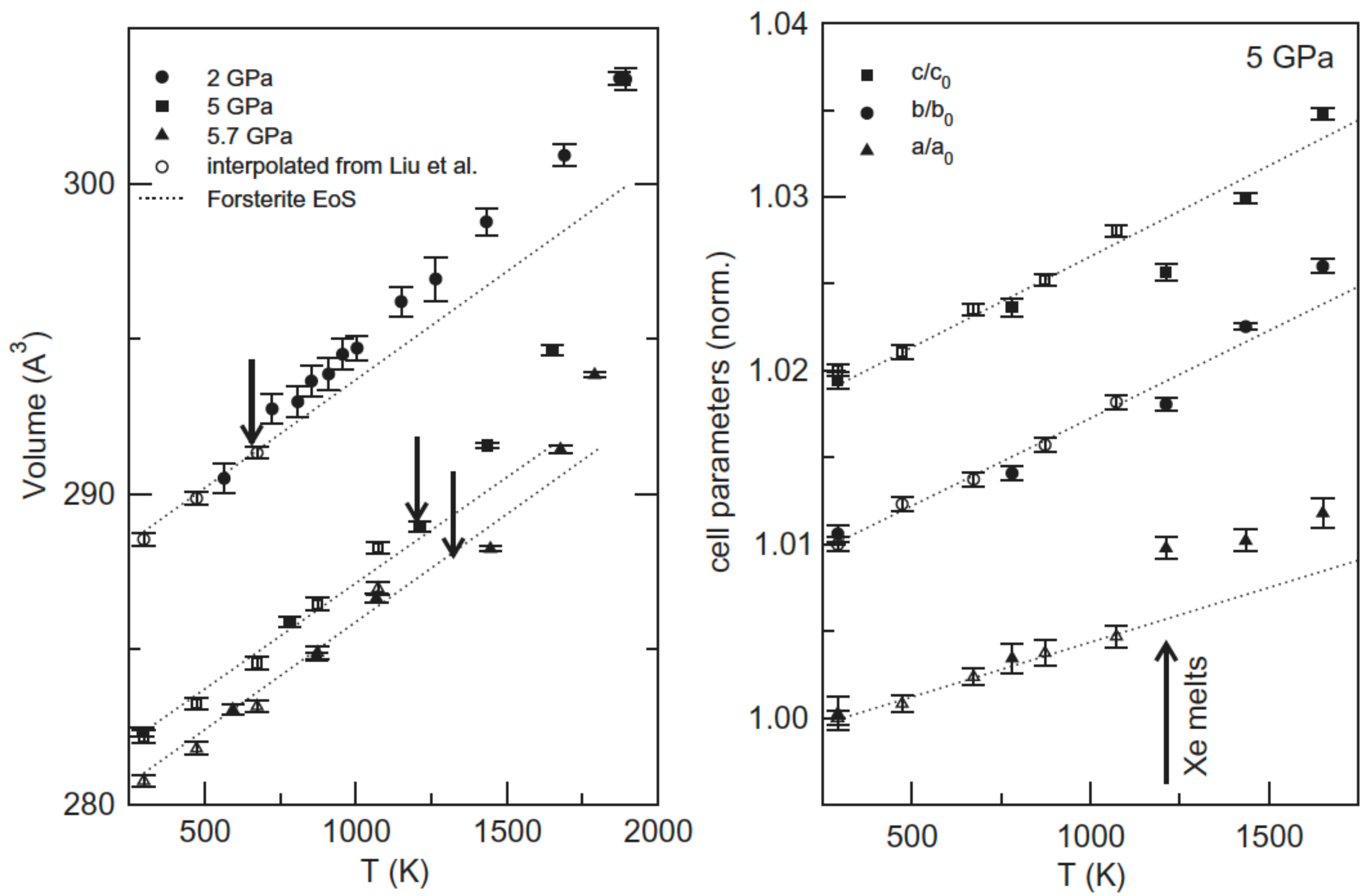
Chemical analyses of quenched samples

Sanloup et al. *GCA* 2012



Xe to Si substitution confirmed in Xe-doped olivine $(Mg,Fe)_2SiO_4$

In situ x-ray diffraction data on Xe-doped olivine

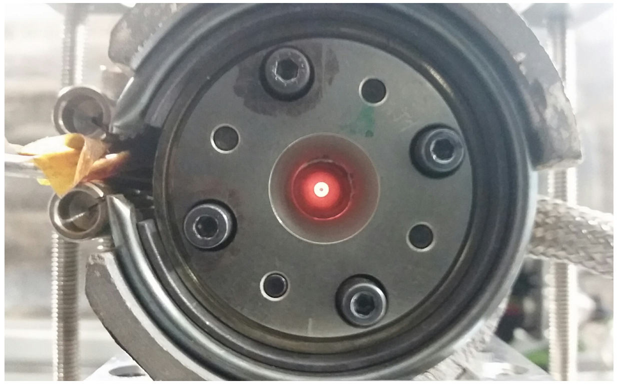


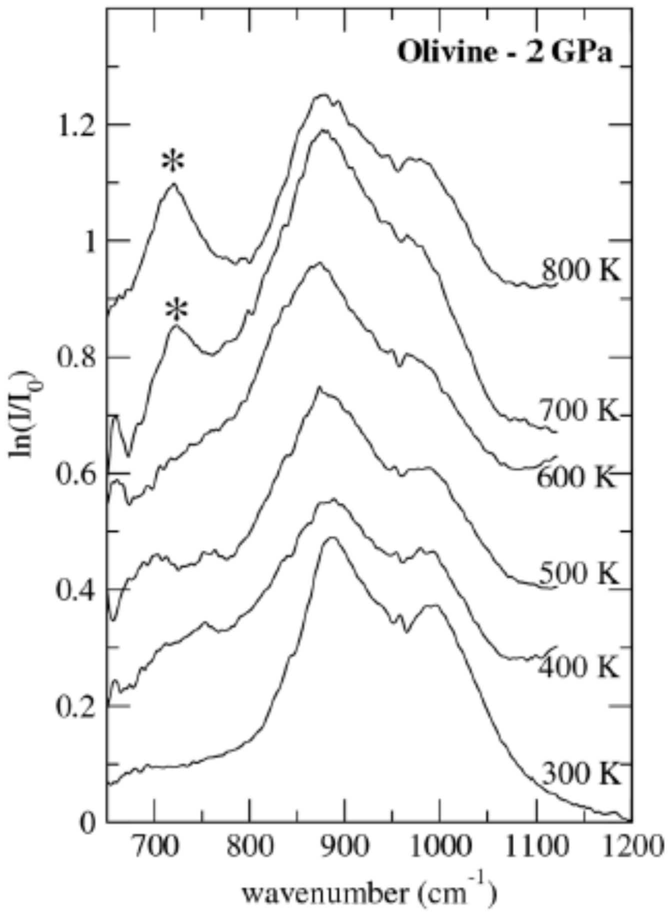
Xe oxidation induced by volume reduction

Infrared spectroscopy data

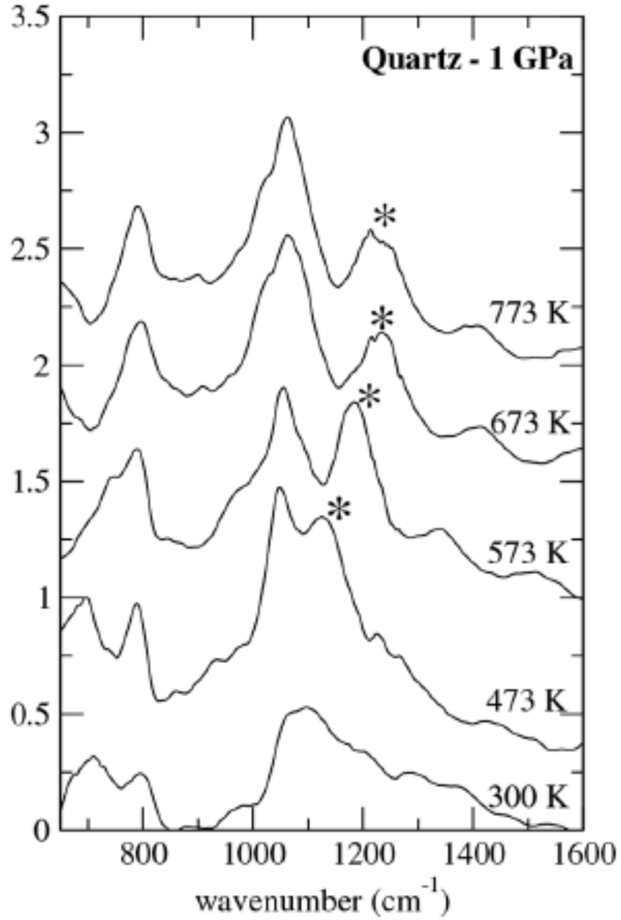
SMIS beamline @Soleil

Resistive-heating diamond-anvil cells





Sanloup *Frontiers in Physics* 2020



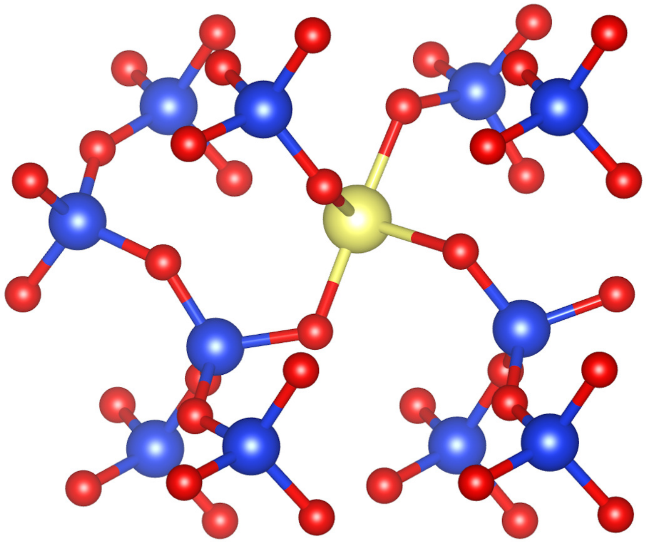
Crépisson et al. *G3* 2019

New vibrational modes observed upon heating

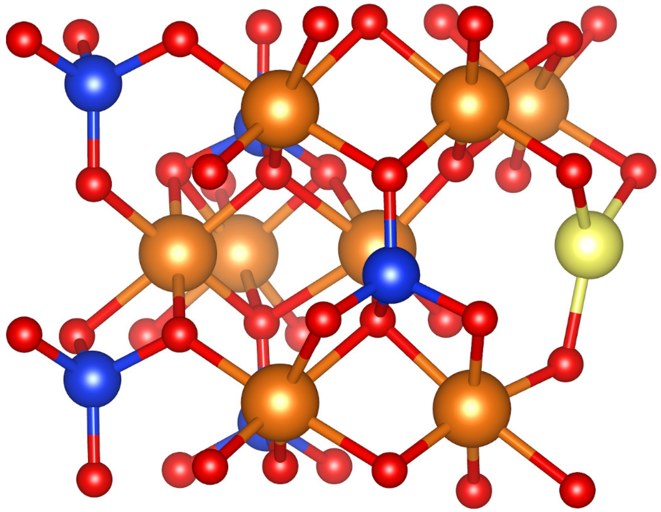
… and Xe crystal chemistry in silicates solved in 2018-2019

ab initio calculations (DFT)
up to 3x3x3 supercells for quartz (0.4 at% Xe)
up to 4x2x4 supercells for olivine (0.1 at% Xe)

Si
O
Mg
Xe



Quartz
Crépisson et al. *G3* 2019



d_{Xe-O}=2.0 Å
Z=+2.9

Olivine
Crépisson et al. *Geochim. Cosmochim. Acta* 2018

⇒ Xe as a minor/trace element oxidizes at much lower P than in stoichiometric compounds

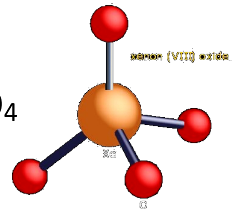
Ambient pressure Xe chemistry

First Xe compound: $XePtF_6$

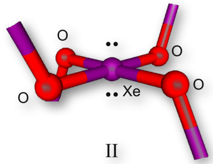
Bartlett, *Nature* 1967.

Xenon oxides:

XeO_4

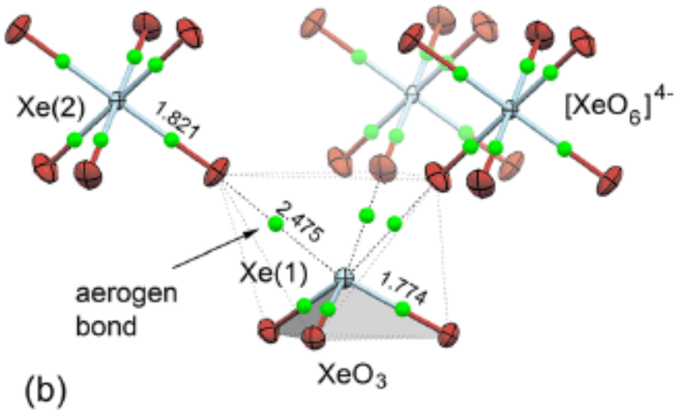


XeO_2



Brock & Schrobilgen, *JACS* 2011

Xe perovskites: $K_4Xe_3O_{12}$



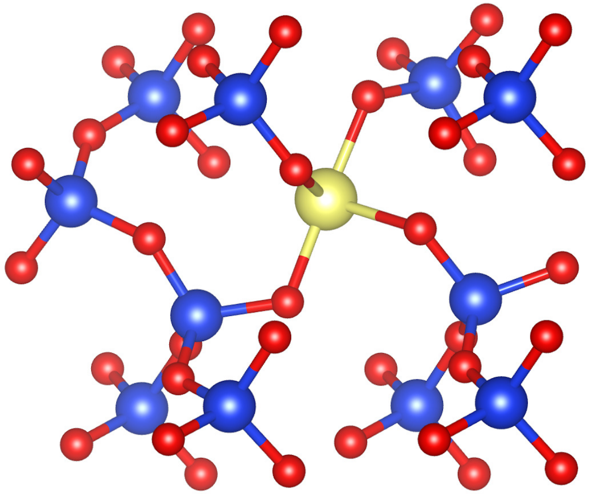
Britvin et al. *JACS* 2016

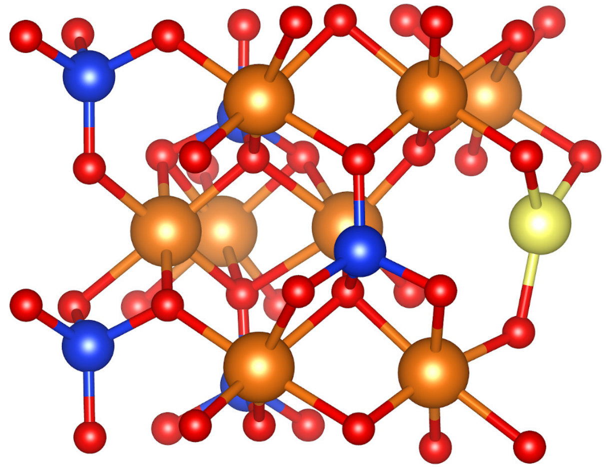
2022: >100 Xe compounds synthesised by UV synthesis, aqueous chemistry

High-energy compounds, explosives

Magma/crystals Xe partitioning

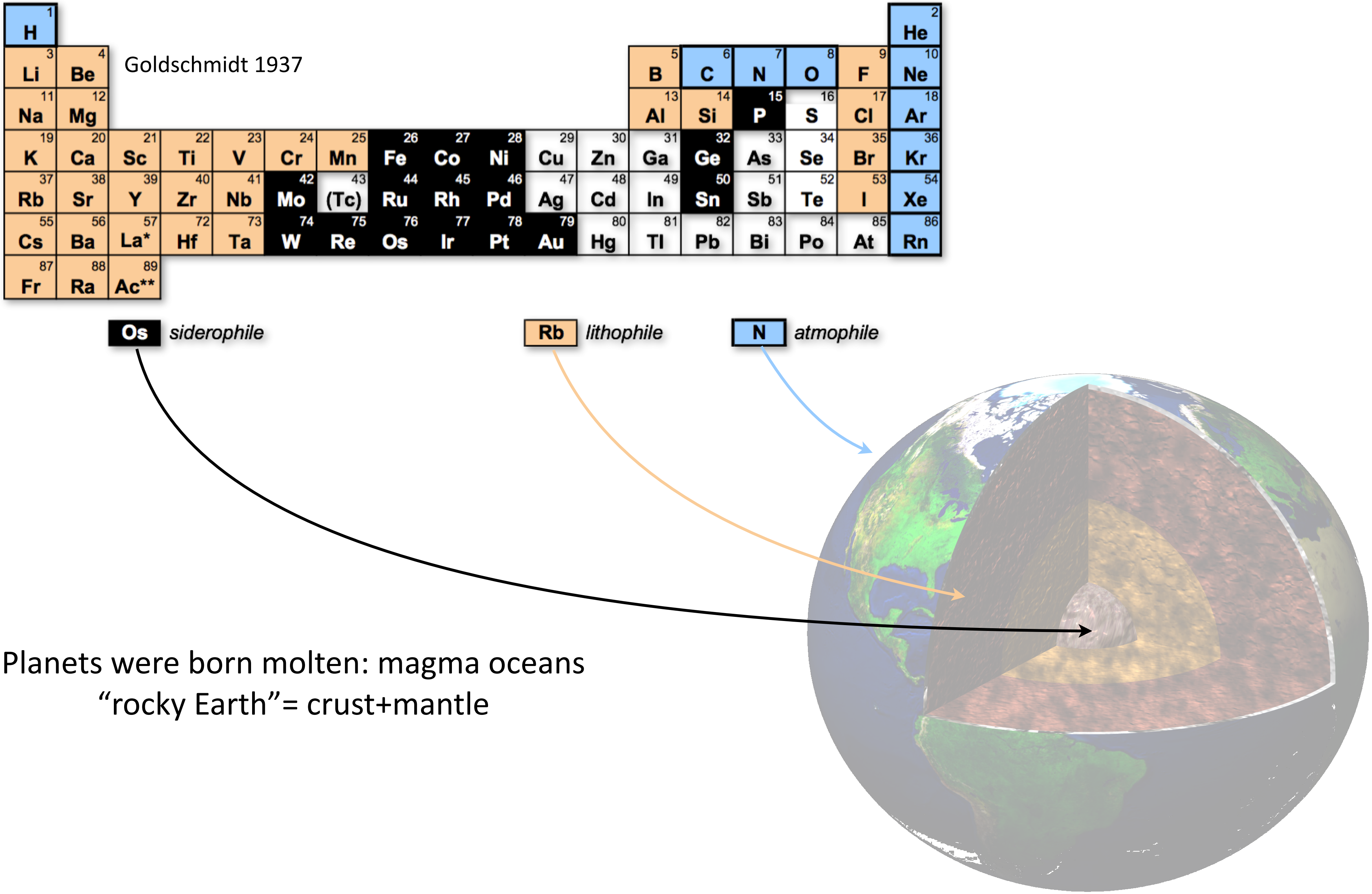
Xe oxidation is systematic in tetrahedral crystalline silicates by substitution to Si at high P-T





⇒ Impacts on Xe magma/crystal partitioning?

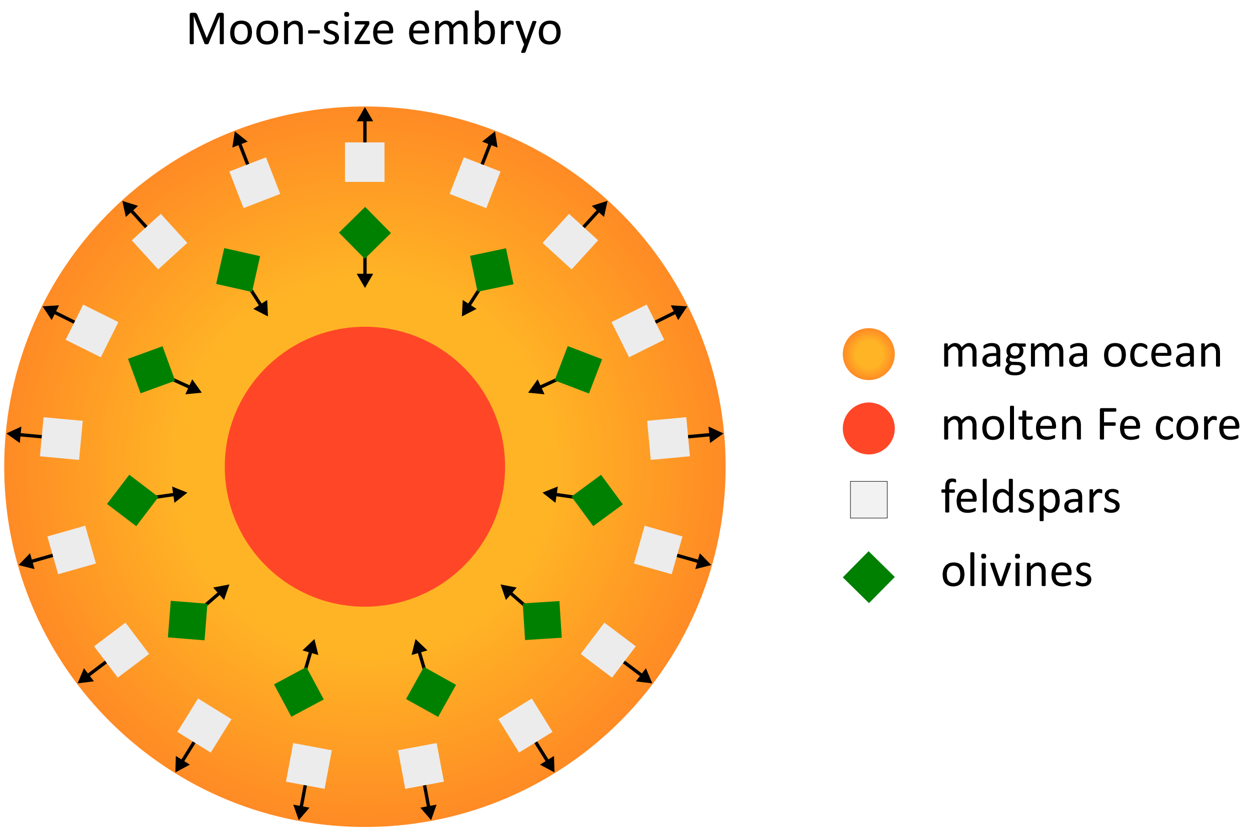
Earth's differentiation:
Chemical composition of terrestrial enveloppes



Planets were born molten: magma oceans
"rocky Earth"= crust+mantle

Magma ocean on a planetary embryo

Silicates grow at depth:
- feldspars at 0.6 GPa
- olivines at 3.9 GPa

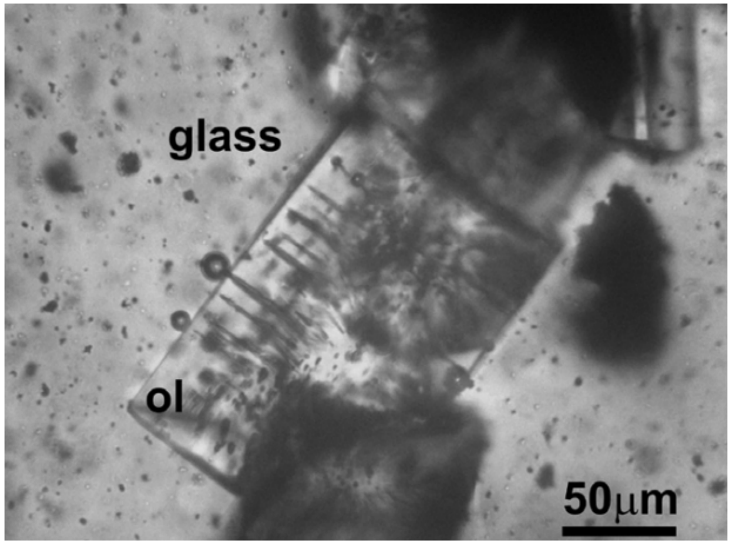


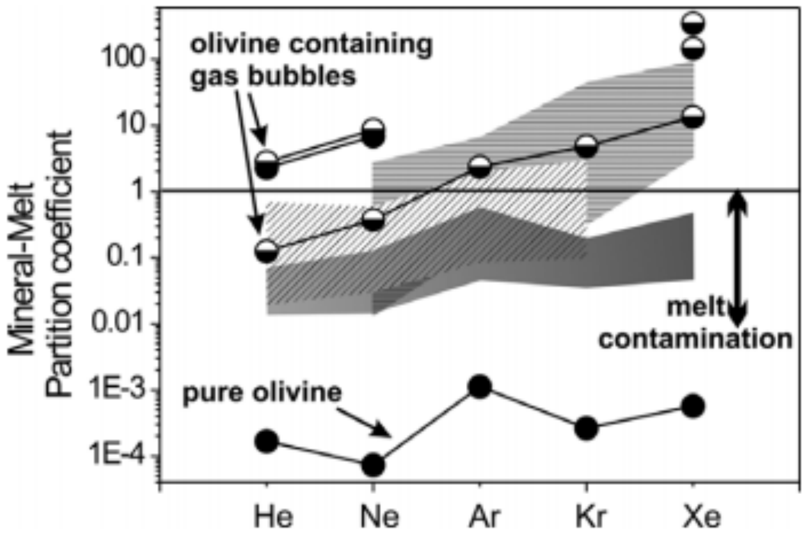
How Xe behaved in magma oceans?
How Xe partitions between magma and crystals?

Existing data on mineral-magma Xe partitioning

Partition coefficient: $D_{cristal/melt} = \frac{[Xe]_{cristal}}{[Xe]_{melt}}$

Heber et al. *Chem. Geol.* 2007



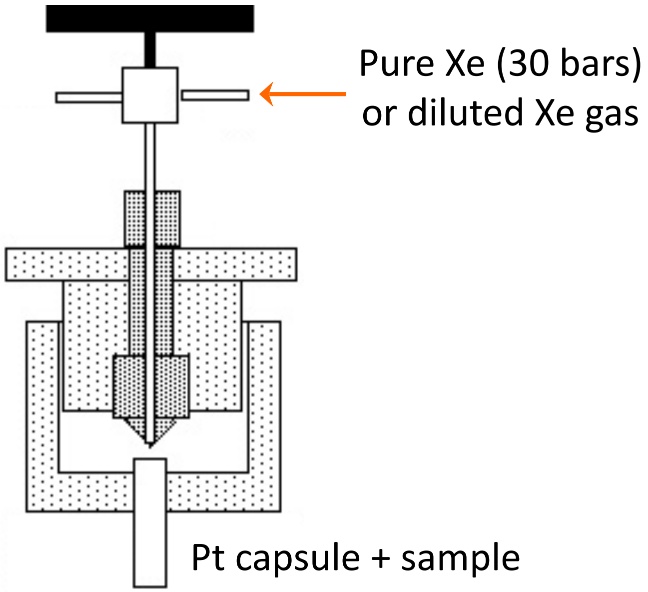


$D_{olivine/melt}$: over 6 orders of magnitude range due to contamination by melt and gas bubbles

But are gas bubbles at equilibrium ?

⇒ **Crucial need of *in situ* high P-T measurements**

High pressure Xe doping of silicates



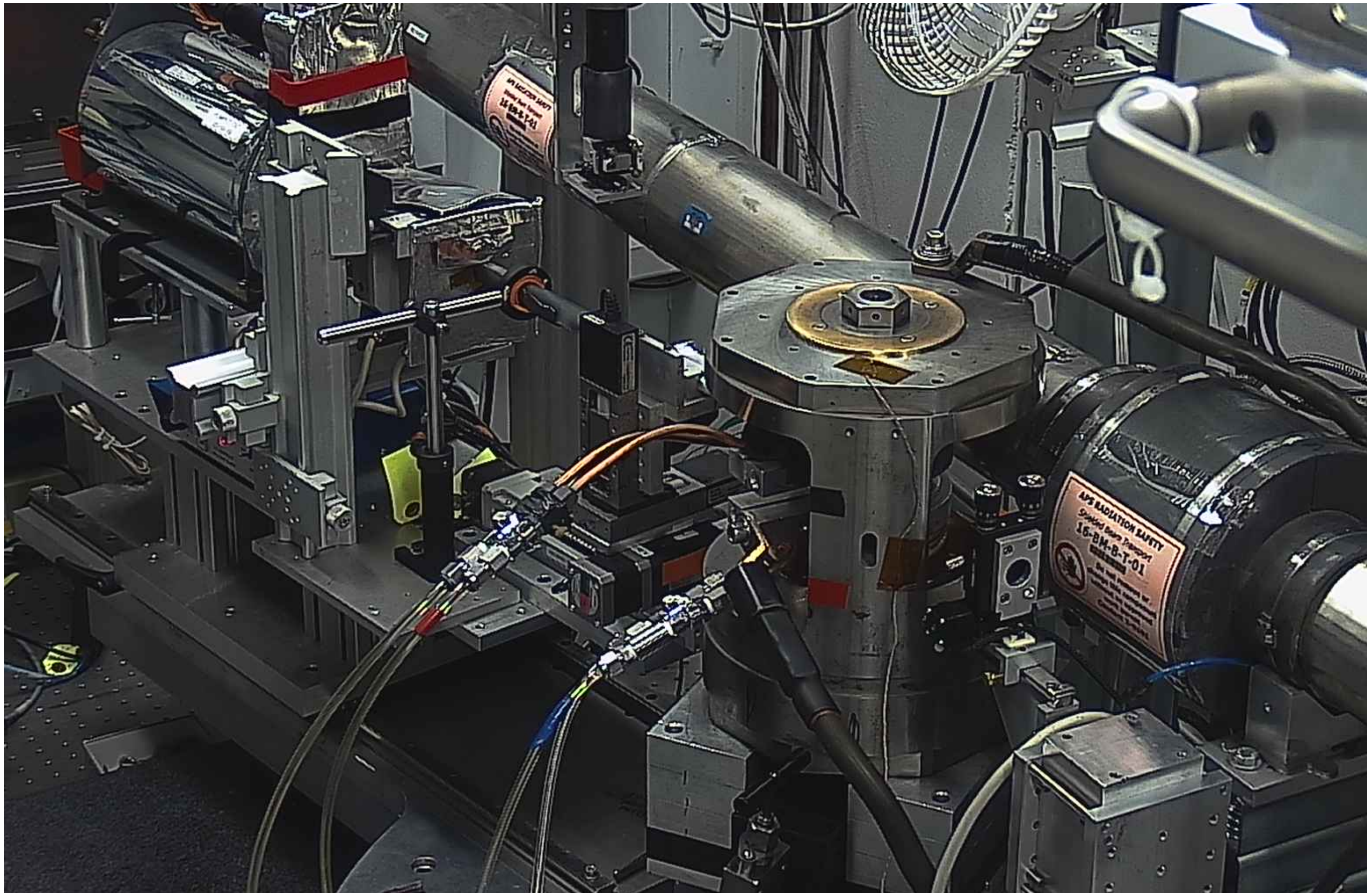
Montana et al., *Amer. Mineral.* 1989.

High P-T synthesis, piston-cylinder press

⇒ Better control of the Xe doping level in starting materials

Crystals/basaltic magma Xe partitioning

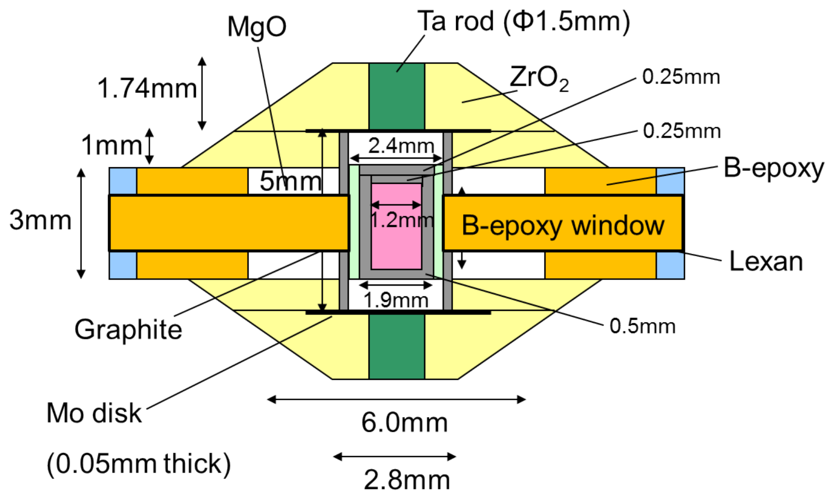
Energy-dispersive x-ray diffraction @HPCAT, Advanced Photon Source (Chicago)
Paris-Edinburgh press
Fully remote-mode operation



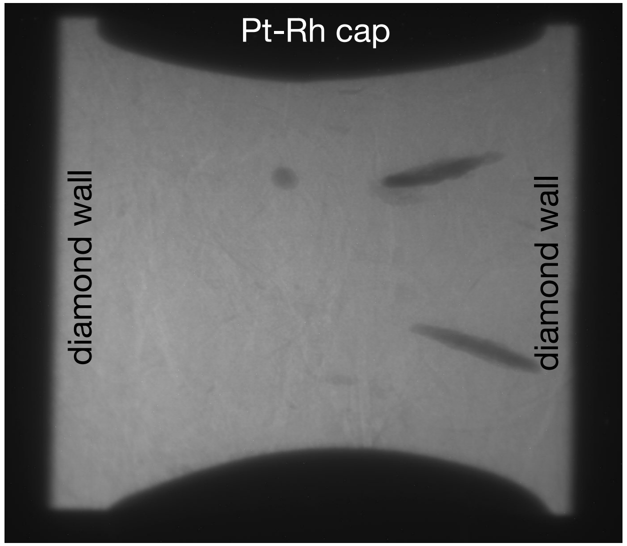
Feldspar/basalt Xe partitioning

Cell-assembly
Sample in diamond capsule
sealed by Pt-Rh caps

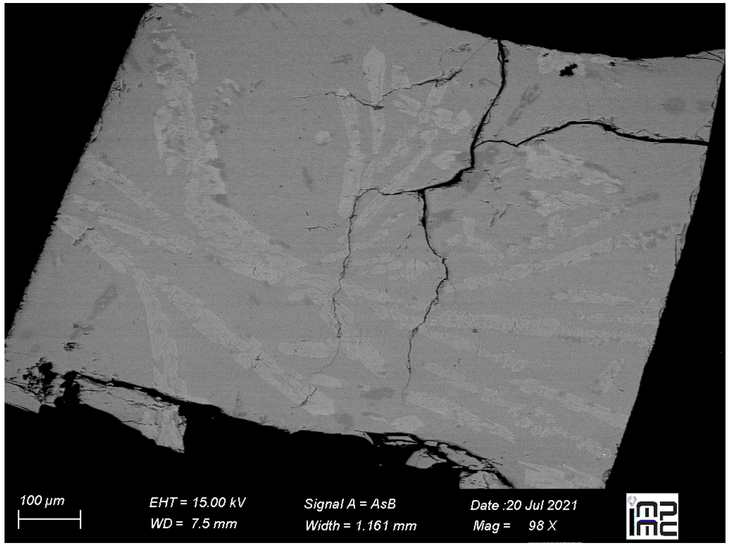
Qi CHEN, PhD Thesis



in situ X-ray radiography
at high P and T

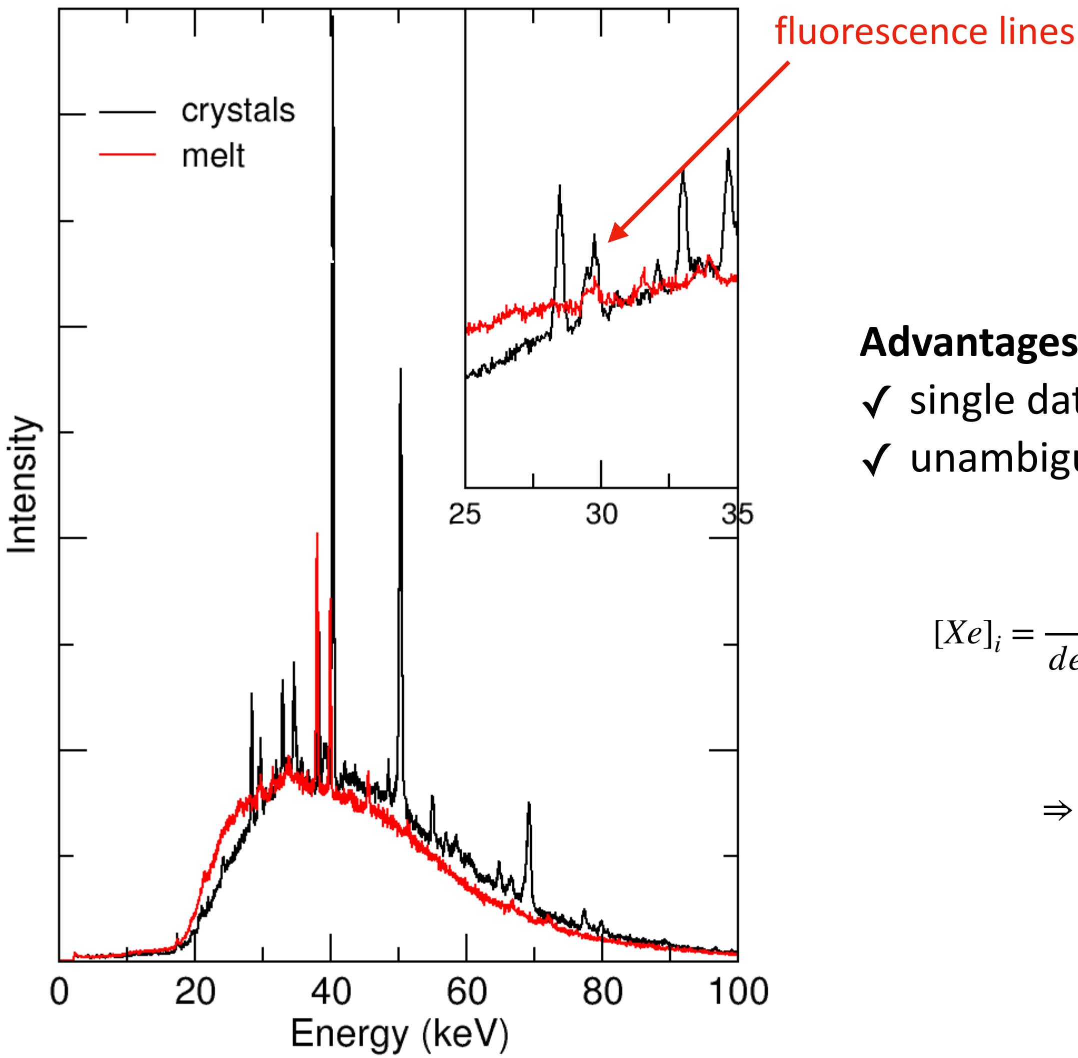


Electronic microscope (SEM)
image on recovered sample



Feldspar/basalt Xe partitioning

energy dispersive x-ray diffraction



$[Xe]_{starting\ glass}$=0.1 wt%

⇒ $D^{feldspar/basalt}$**=2.4** at 1.1 GPa-1500 K

Advantages of using EDX for partitioning measurements:

✓ single data-set for fluorescence and diffraction

✓ unambiguous phase determination from diffraction peaks

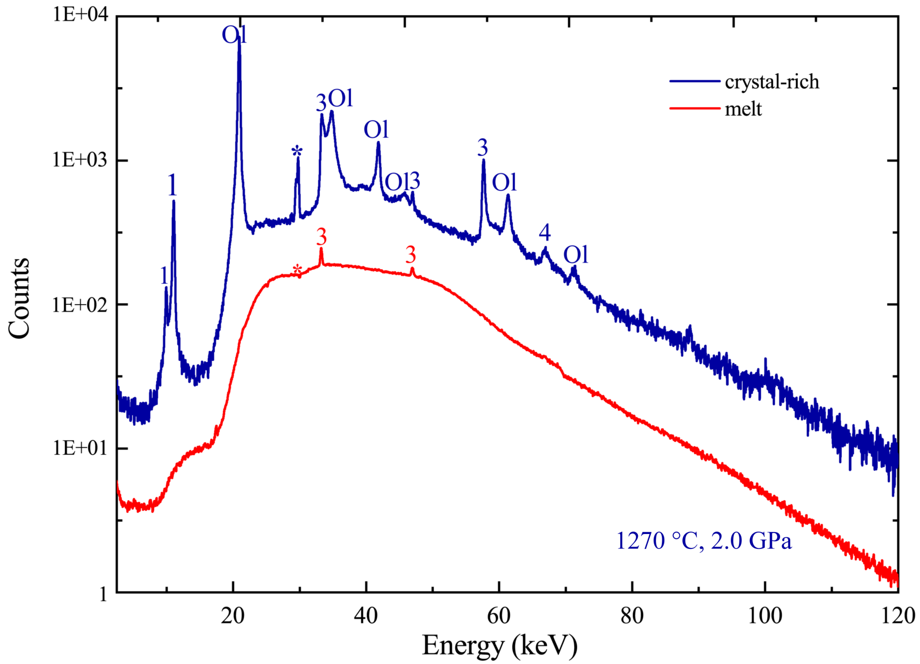
$$[Xe]_i = \frac{Fluo.Intensity}{density \times thickness \times Detec.sensitivity \times absorption}$$

$$\Rightarrow D_{Xe}^{crystal/melt} = \frac{crystals \quad Xe \quad Fluo.Intensity}{melt \quad Xe \quad Fluo.Intensity}$$

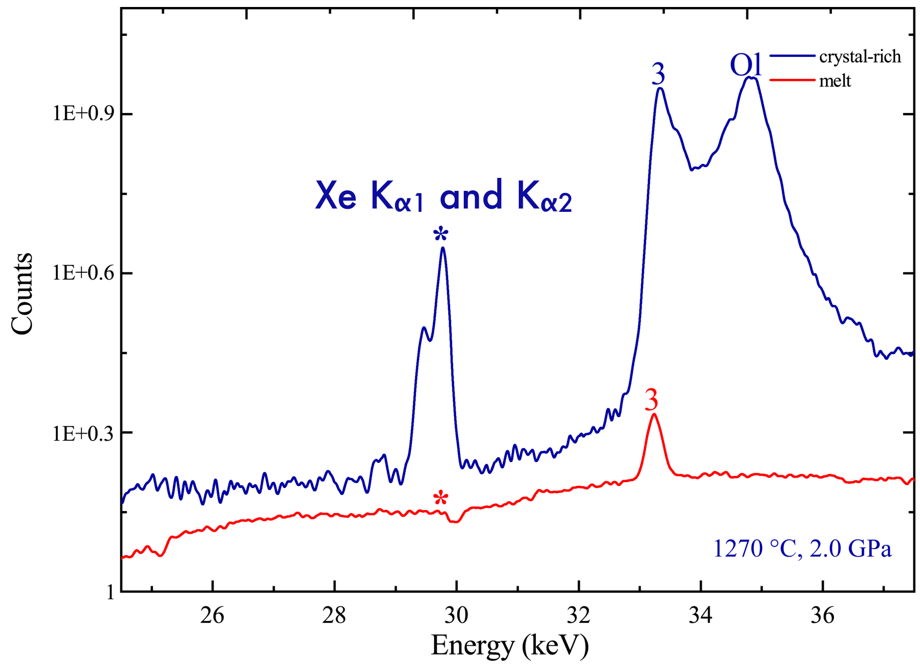
Qi CHEN, PhD Thesis

Olivine/basalt Xe partitioning

Energy-dispersive x-ray diffraction



Zoom on Xe fluorescence peaks



Xe fluorescence signal not detected in molten basalt in equilibrium with olivine

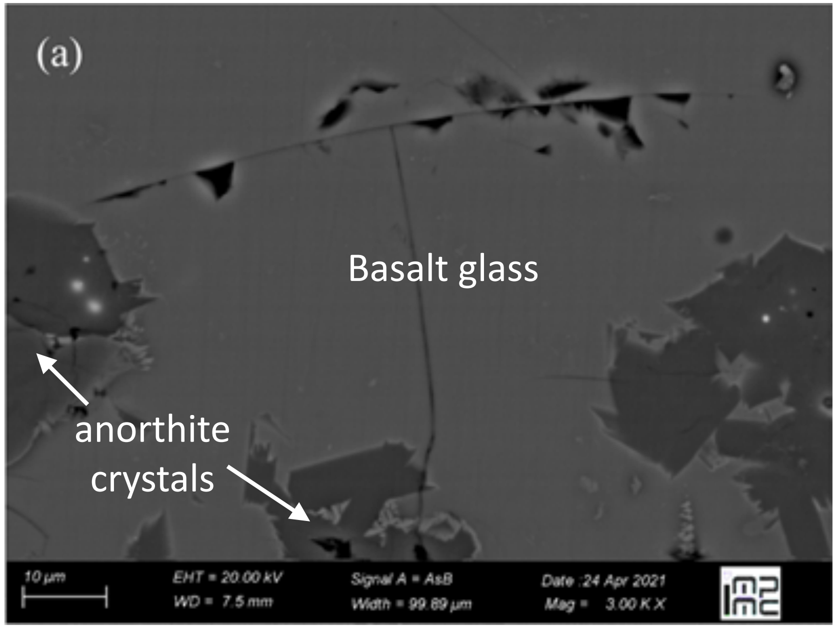
$\Rightarrow$ **$D^{olivine/basalt}$ > 12** at 1.1 GPa-1500 K

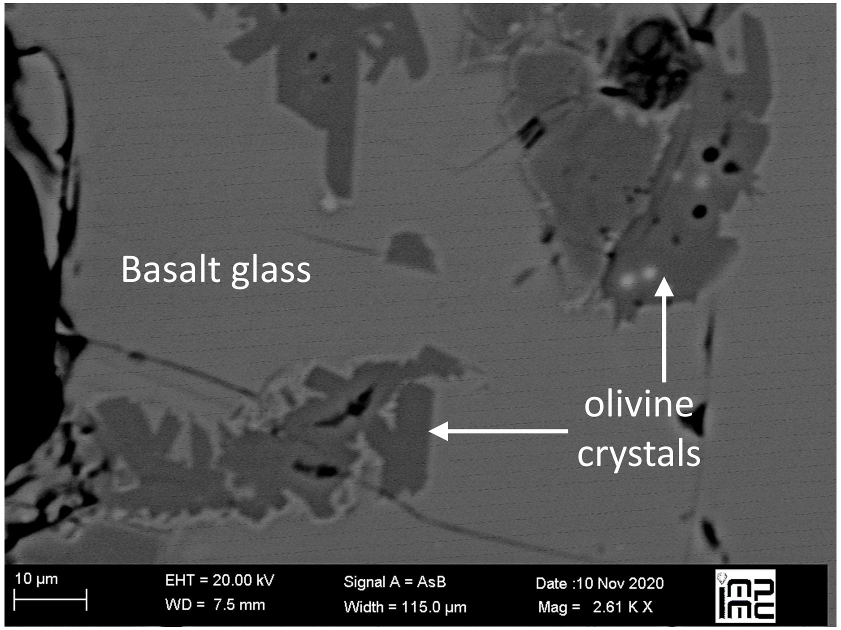
Additional mass spectrometry analyses on recovered quenched glass

$\Rightarrow$ **$D^{olivine/basalt}$ =60-140**

Crystals/basalt Xe partitioning

SEM images on additional samples
(higher Xe content)



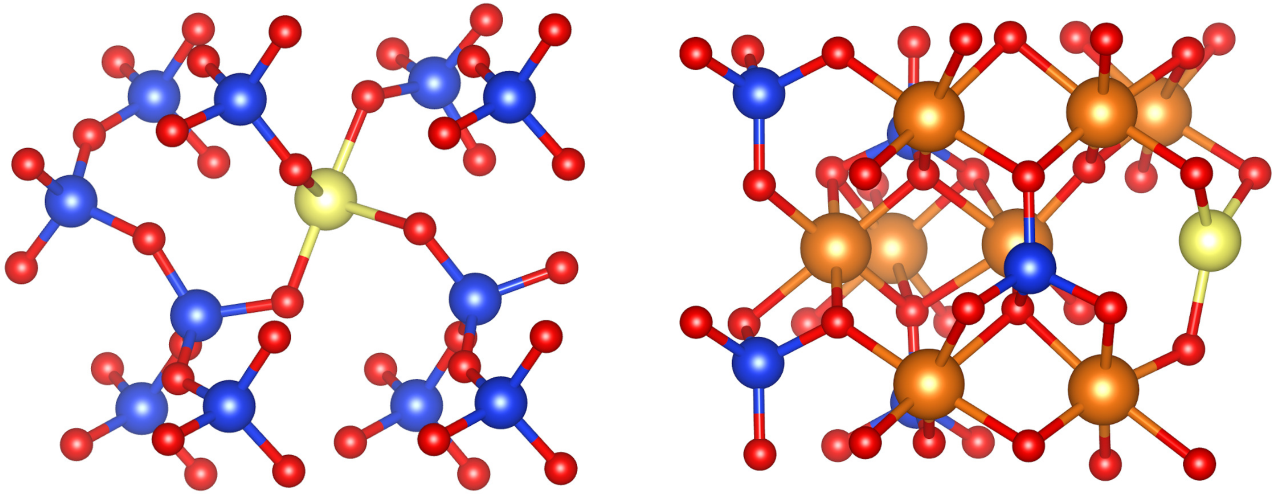


Xe bubbles in crystals only

⇒ Xenon is trapped in crystals growing at depth in magmas

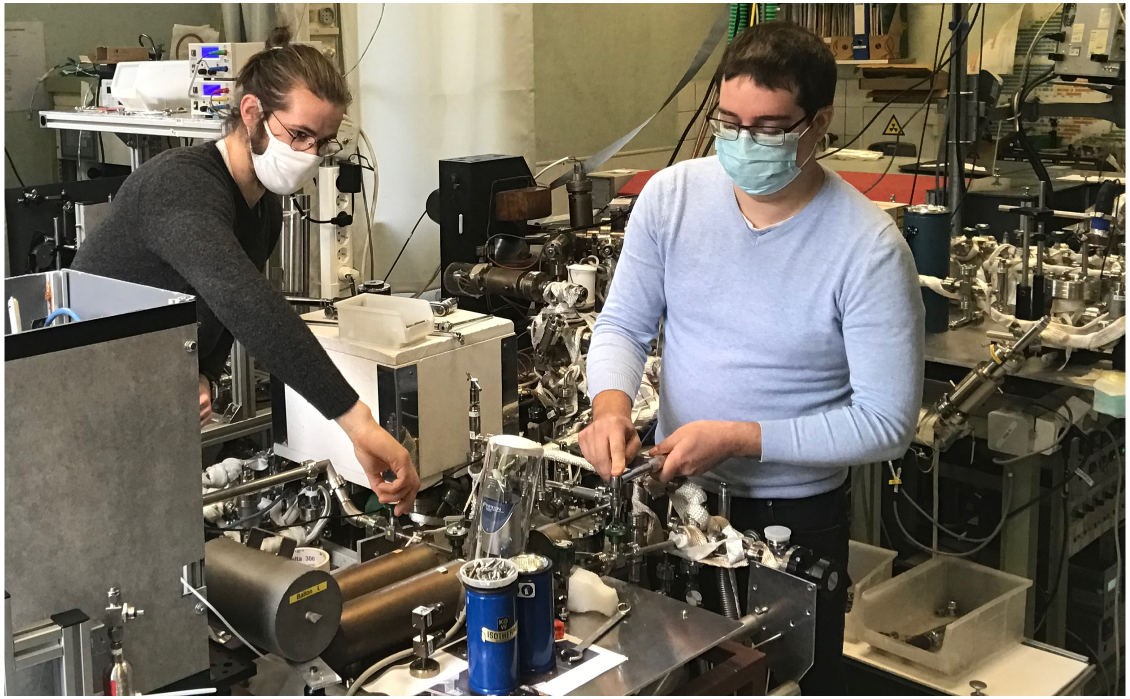
Xenon isotopic fractionation

Xe oxidation is systematic in tetrahedral crystalline silicates by substitution to Si at high P-T



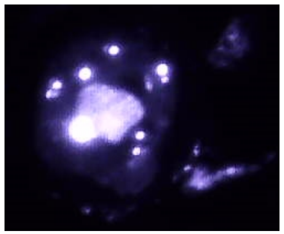
⇒ Impacts on Xe isotopes partitioning?

Xenon isotopic fractionation

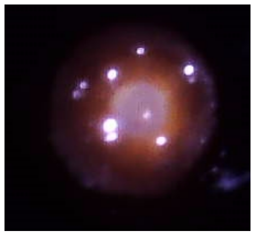


Noble gas mass spectrometry at LP2i@Bordeaux

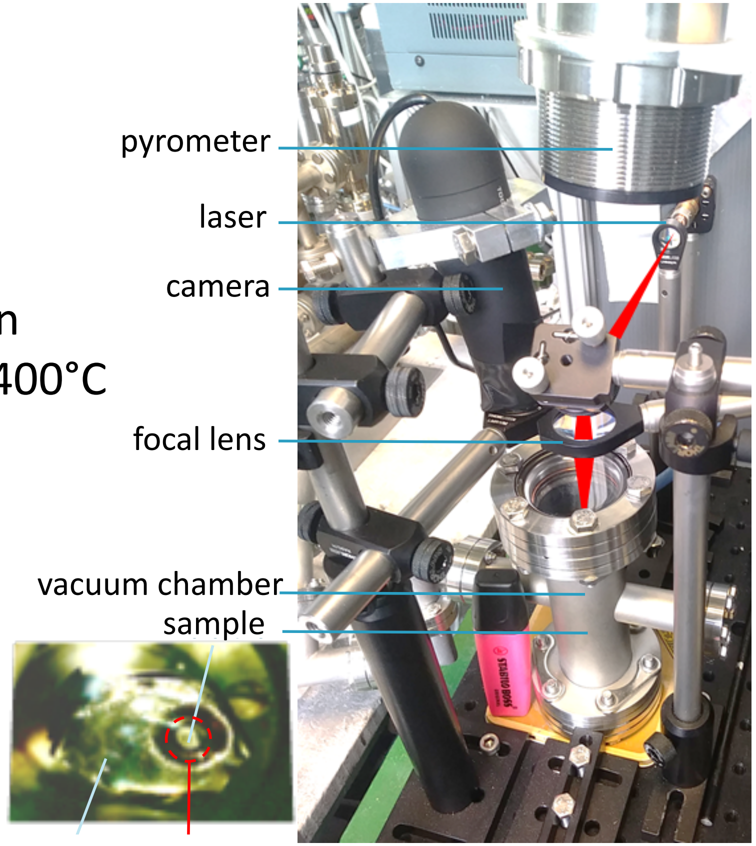
- ✓ Samples: feldspar or olivine + diluted Xe-Kr (1 ‰ or 1%) in either air or N_2 brought at 3.5 GPa and T from 800°C to 1400°C
- ✓ Analyses on bulk sample melted by laser heating



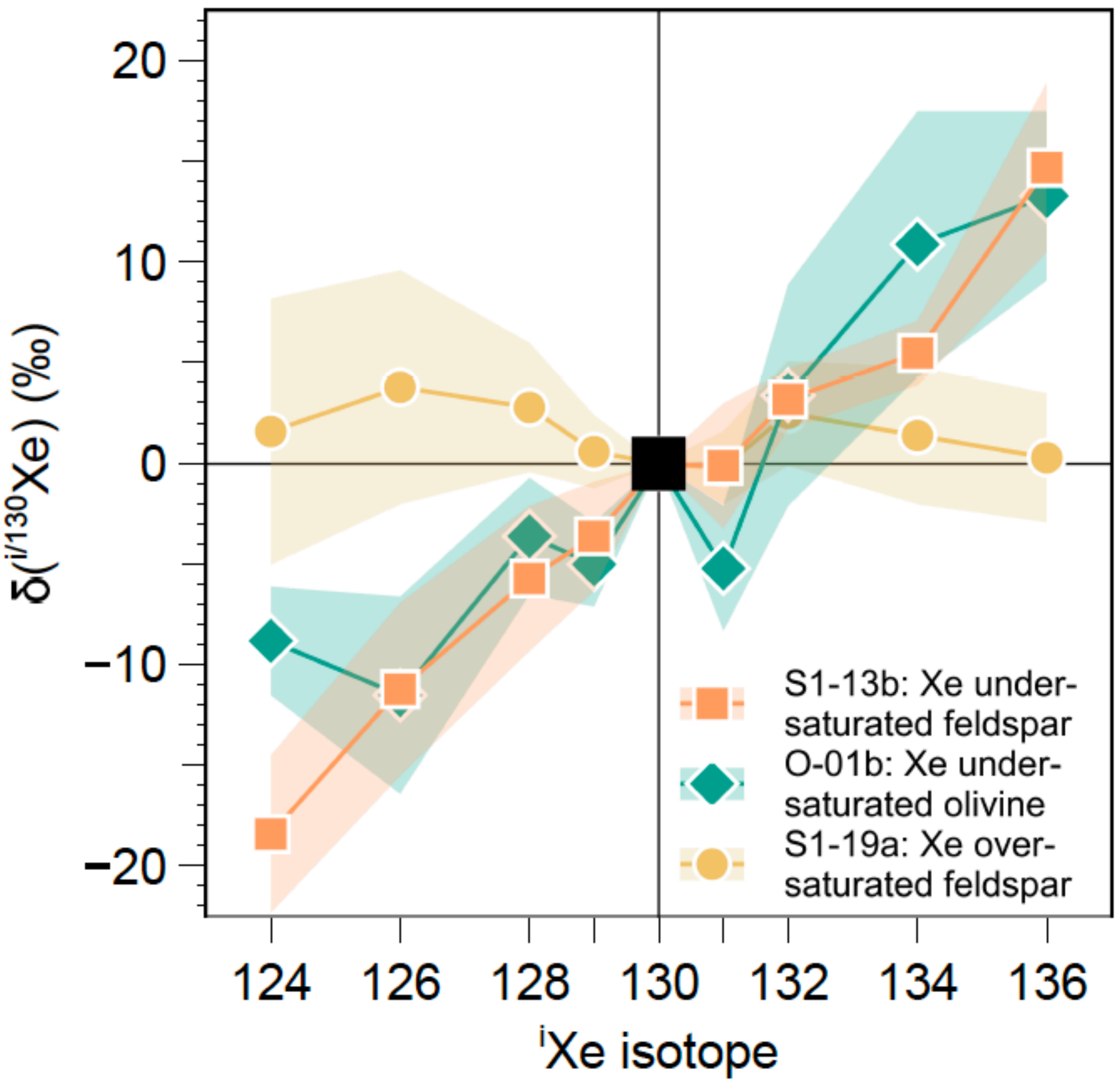
slice of sample



fully molten sample



Xenon isotopic fractionation

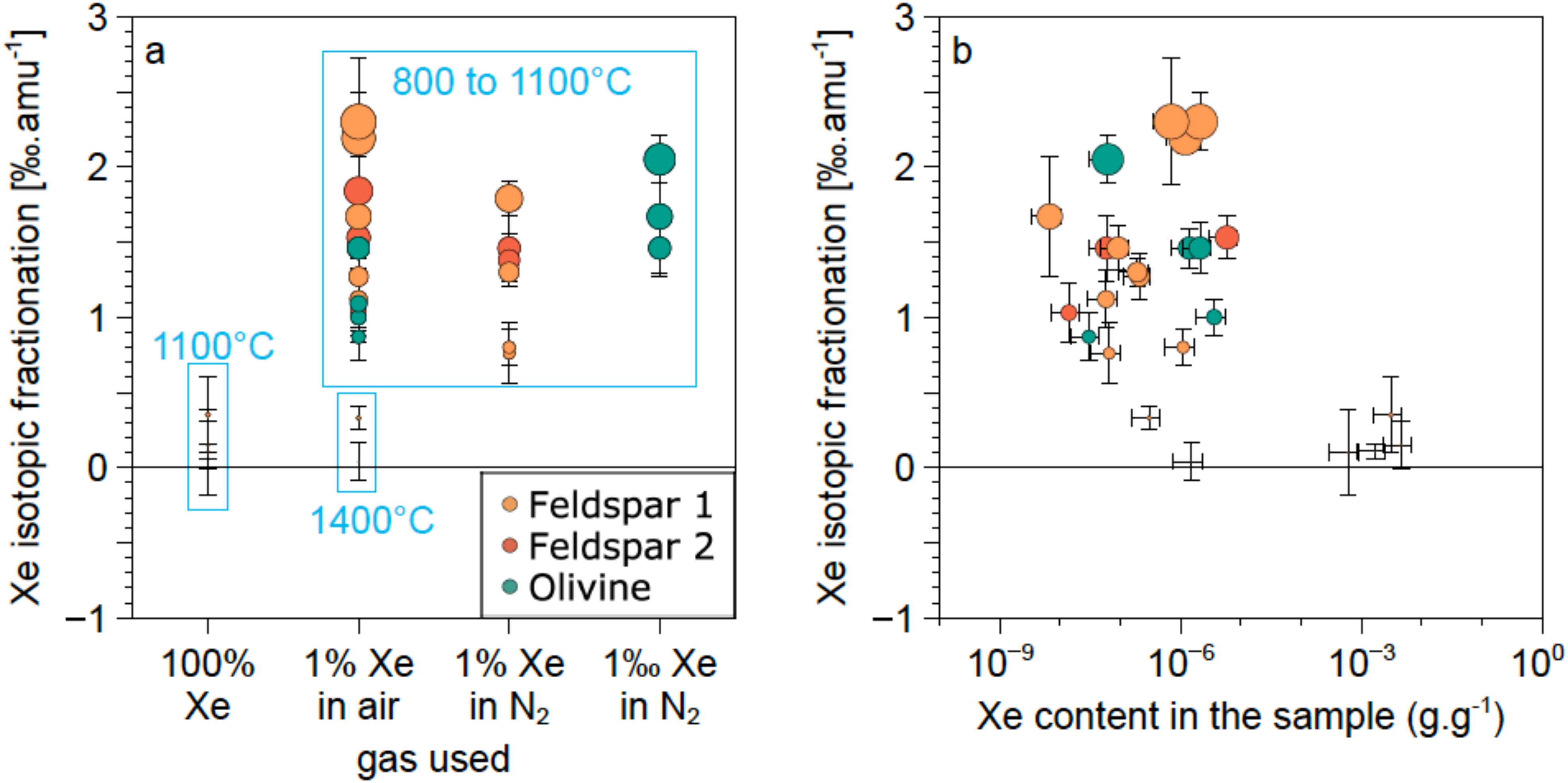


Rzeplinski et al., Nature 2022

+0.8 to +2.3 ‰/a.m.u. fractionation for olivine and feldspar doped with diluted Xe (1 % or 1‰)

Accounting for remaining unreacted gas fraction, max. estimated fractionation is 4 ‰/a.m.u.

Xe isotopic fractionation

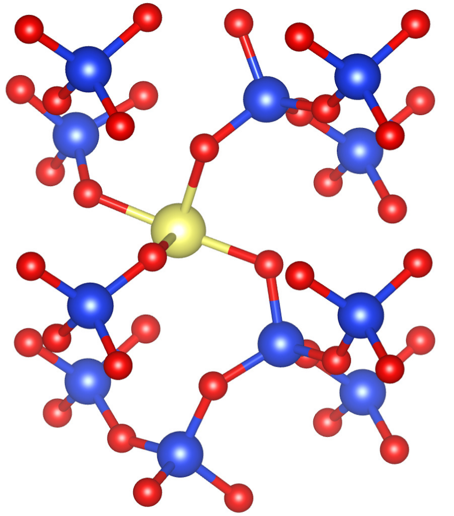


Systematic enrichment in heavy isotopes for diluted gaz (1 % or 1 Xe) in either olivine or feldspars

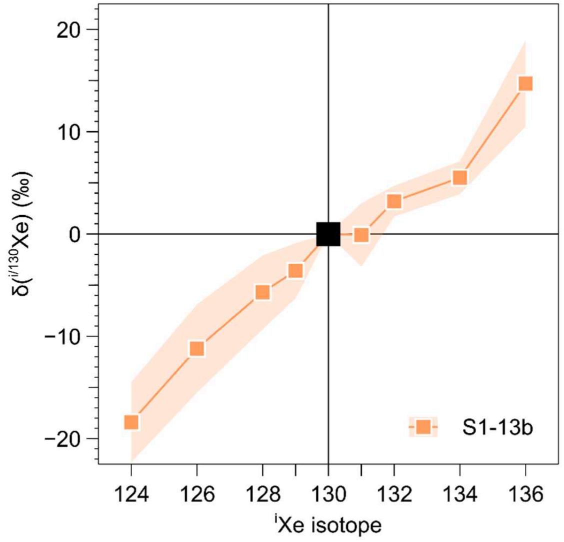
No fractionation observed for pure Xe gas and for molten feldspar

Missing Xe: pieces of the puzzle

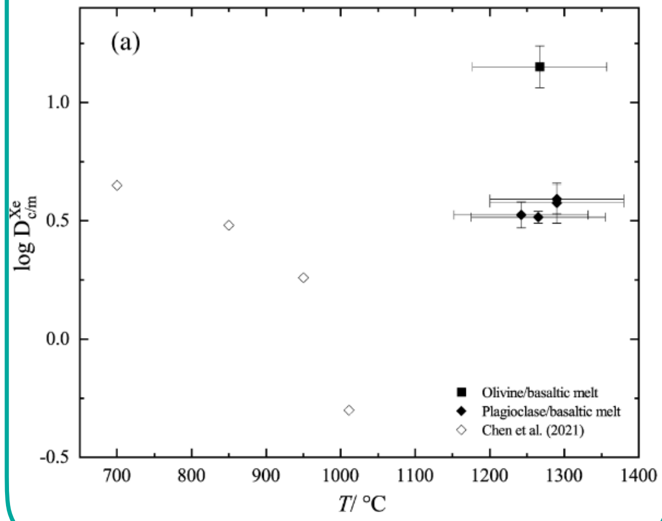
Xe substitutes to Si in tetrahedral silicates



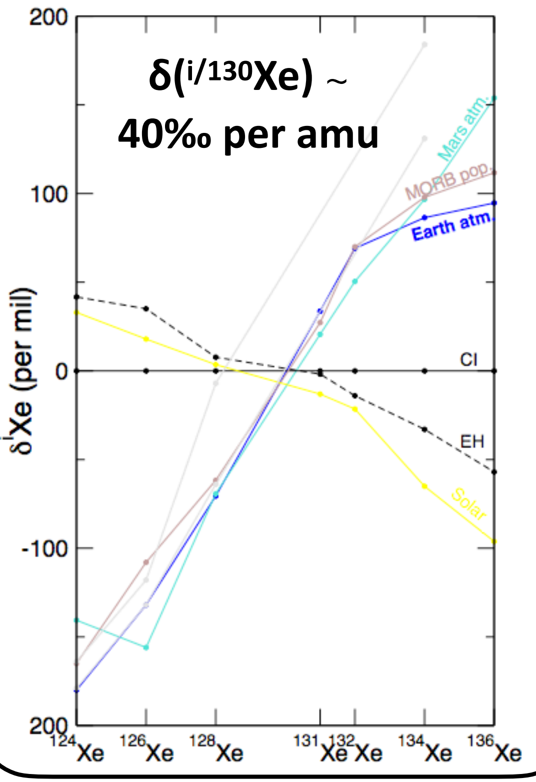
δ(i/130Xe) ~ 2‰ per amu



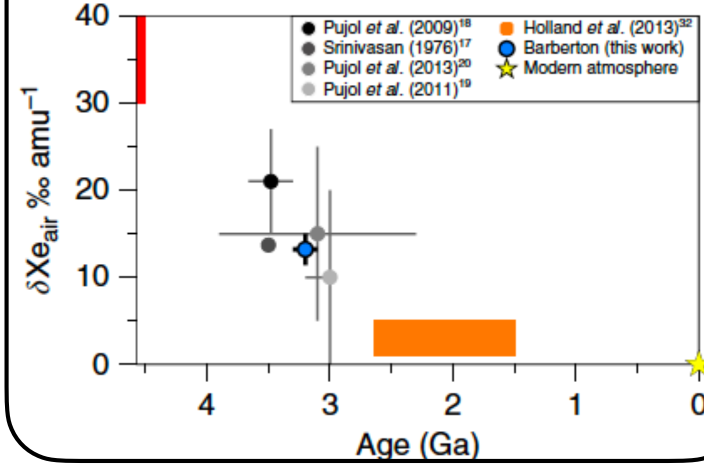
$D_{crystals/melt}$ > 1



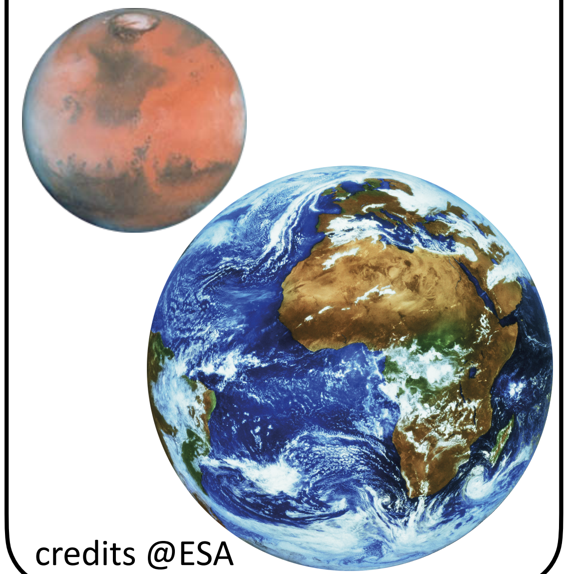
δ(i/130Xe) ~ 40‰ per amu



Earth: light isotopes depletion recorded through the Archean



Earth and Mars: same Xe depletion within the first 100 My



Multiple magma ocean stages: case of Xe

a. Xe retention in silicates triggers trapping of heavy Xe in minerals crystallising at depth
b. Light Xe released in the atmosphere, lost upon impacts
Iteration of a and b upon successive collisions between planetary embryos
Xe loss and isotopic fractionation settled at the Mars-size embryo stage
c. In the case of the Earth, degassing of the trapped heavy Xe throughout the Archean

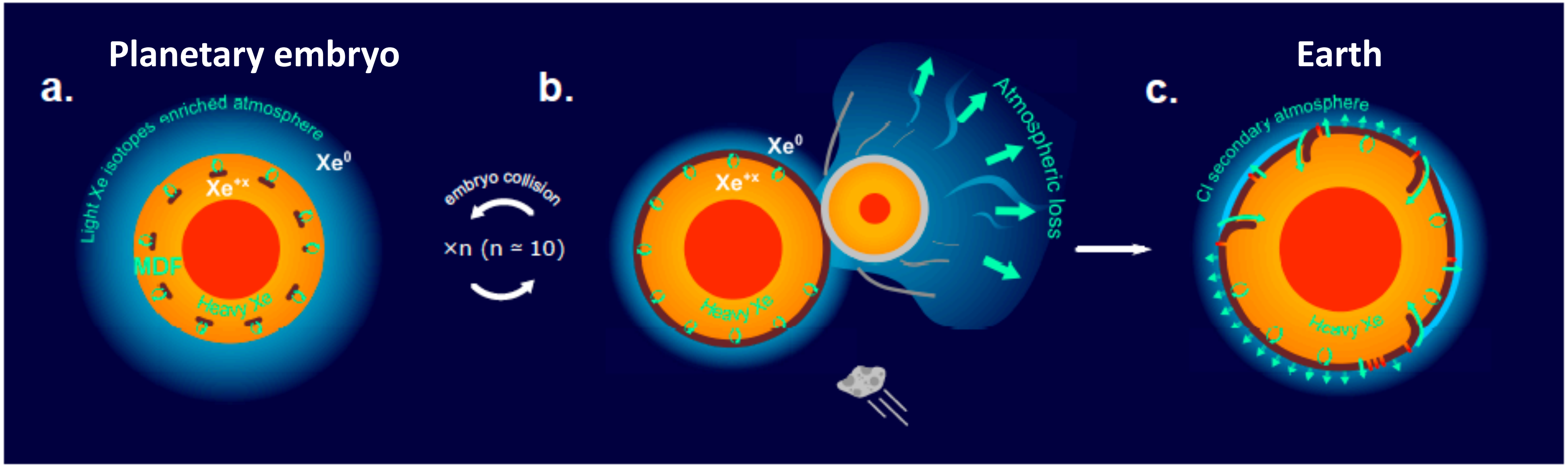
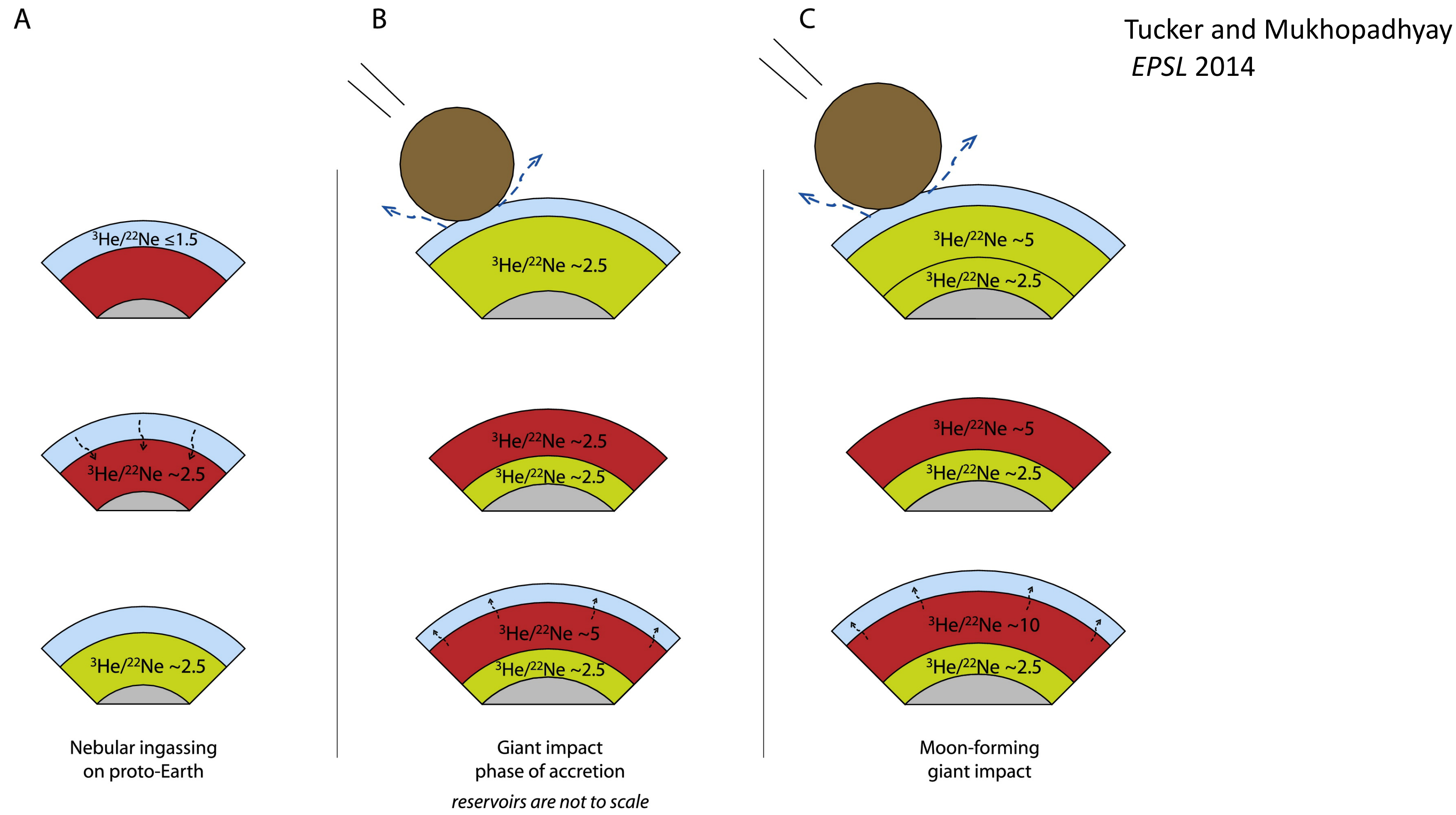


image: I. Rzeplinski

Multiple magma ocean stages: case of Ne



At least 2 magma ocean stages required to raise the $^{3}He/^{22}Ne$ ratio from solar to observed values in the mantle

But 2 is only a minimum value, more needed if partial atmosphere loss, incomplete equilibrium, and if more recent solubility values are used

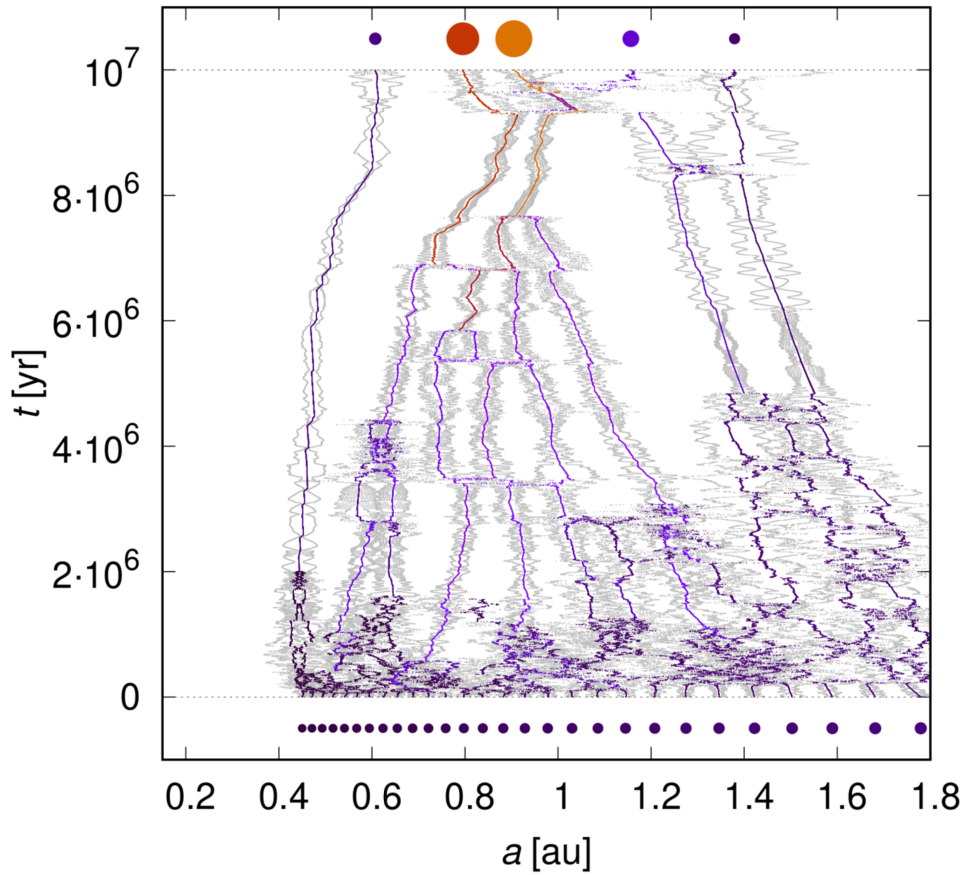
Multiple magma ocean stages: case of Xe

N-body simulations of planetary formation:

✓ Gas driven migration of protoplanets

✓ Terrestrial planets formed within 10 Myrs

Xenon isotopic signature acquired at Mars-size protoplanet stage, *i.e.* collisions of about 10 Moons



Brož et al., *Nat. Astron.* 2021.

Back to Geophysical Laboratory history

SCIENCE'S COMPASS • EDITORIAL

Experimental Technology

Philip H. Abelson

Most of the important advances in scientific knowledge have followed improvements in experimental techniques. Tools created by physical scientists and engineers are leading to new discoveries in science and technology. These tools include lasers, nuclear magnetic resonance, synchrotron radiation, mass spectrometry, extremely high pressures, and devices for observing atoms at surfaces. Here I discuss some of the results of using these tools.

When substances are subjected to pressures of millions of atmospheres, their volumes diminish by as much as a factor of 10. Their normal crystal and electronic structures are drastically changed. Nonmetals usually become conductors. Among these nonmetals is sulfur, which becomes a superconductor at low temperatures and remains a superconductor at temperatures at which other elements lose that capability.

At high pressures, chemical reactions are seen that do not occur under ambient conditions. Neon combines with helium to form $NeHe_2$. Argon reacts with hydrogen to form ArH_4 and with oxygen to form ArO_6. When the pressure is lowered, most of the compounds formed under high pressure decompose. In the future, however, substances may be discovered that are metastable and have valuable properties, such as diamond.

The development of new or improved experimental techniques is flourishing.

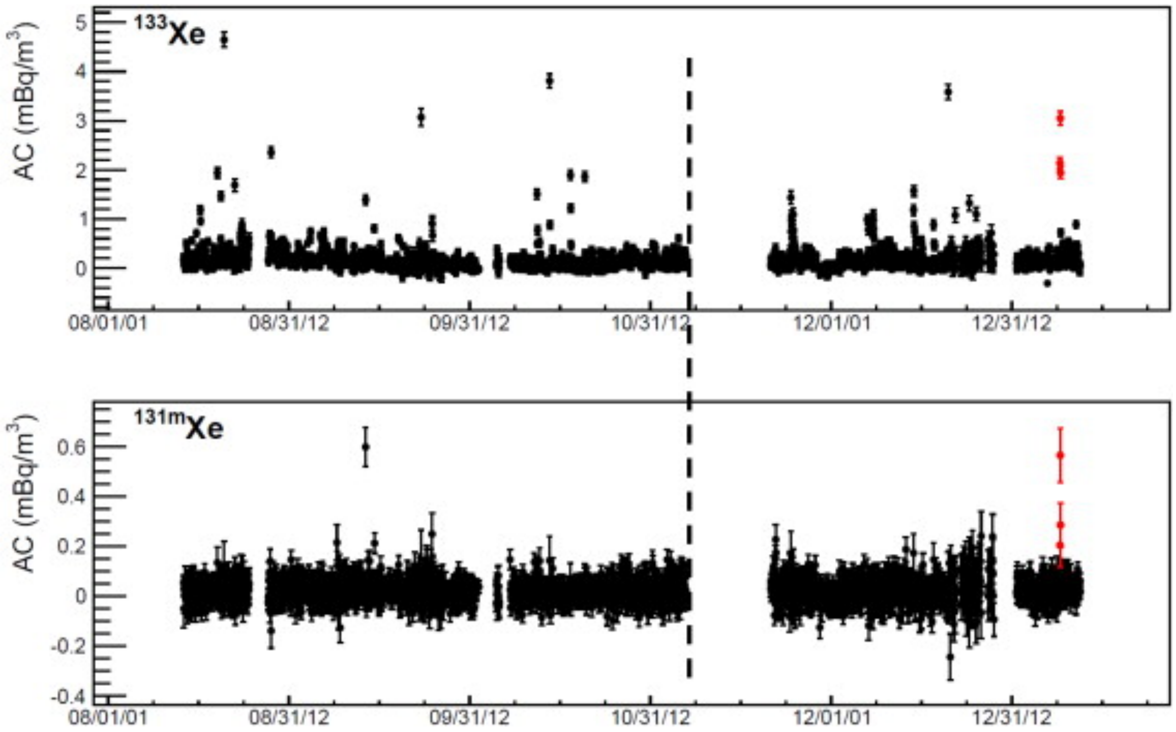
It has long been known that atoms at surfaces behave differently from those deep in a crystal. To study such phenomena, more than 25 experimental techniques have been developed and used in a host of applications. These include scattering; absorption or emission of photons, electrons, atoms, and ions; and scanning tunneling microscopy and atomic force microscopy. These techniques have allowed observation of unique chemical, optical, electrical, magnetic, and mechanical properties.

Abelson *Science* 1999

'At high pressures, chemical reactions are seen that do not occur under ambient conditions. Neon combines with helium to form $NeHe_2$. Argon reacts with hydrogen to form ArH_4 and with oxygen to form ArO_6.'

Xenon isotopes: tracers of nuclear processes

International network of stations for radio-nuclides monitoring in compliance with the Comprehensive Nuclear-Test-Ban Treaty (1996) to ban nuclear explosions, for both civilian and military purposes, in all environments



Tagasaki station, Japan

Ringbom et al., *J. Env. Rad.* 2014.

Identification of North Corea underground nuclear test in 2013

Underground nuclear tests generate extreme P and T, on very large volumes of rocks

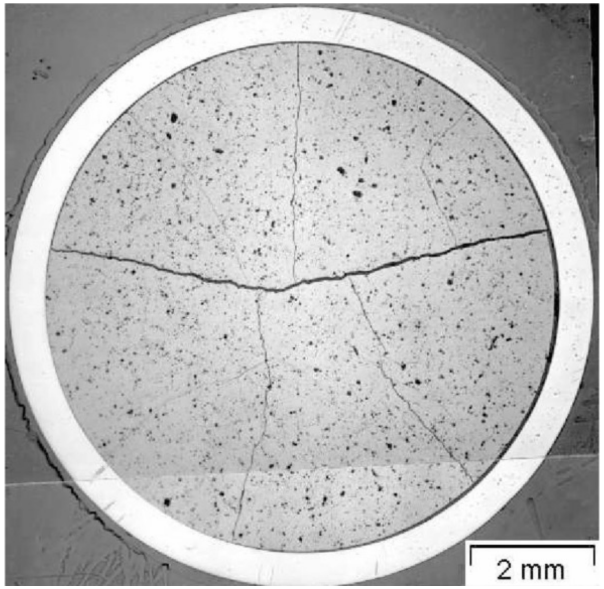
Impact of Xe reactivity on the interpretation of these measurements?

Xenon in nuclear reactors

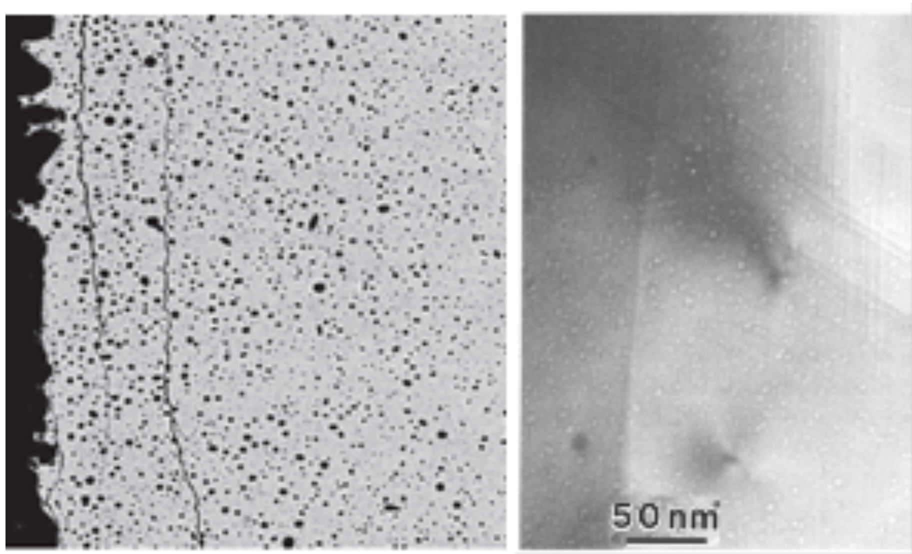
Used UO_2 fuel:

xenon (and krypton) release from decay of ^{235}U et ^{239}Pu
accumulation in micro to nano-bubbles

Local high P-T conditions in bubbles:
from a few GPa to 15 GPa, T=1300 K.



Cross-section of fuel pin. Guillet et al.2008



⇒ Poor mechanical and thermal properties that limit nuclear fuel yield

Could we either add Xe-resorbing materials or at least Xe-selective materials (recycling)?

Acknowledgments

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[1]Soleil, [2]DESY, [3]APS

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