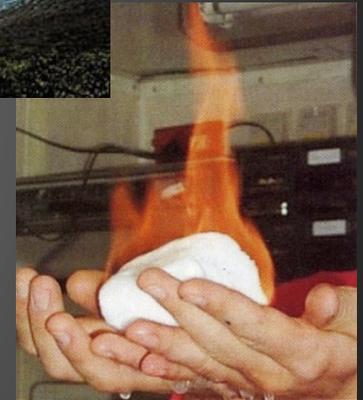
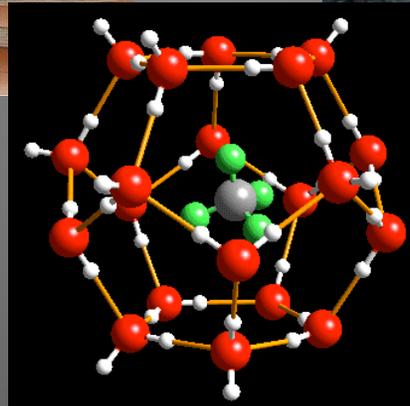
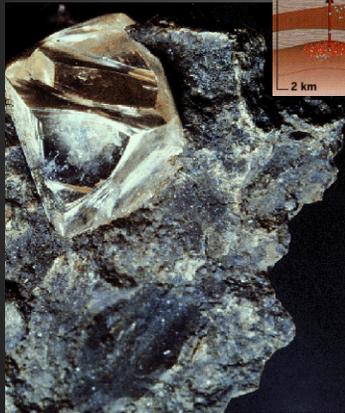
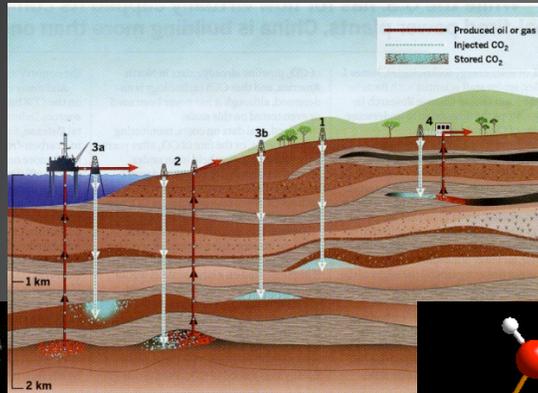


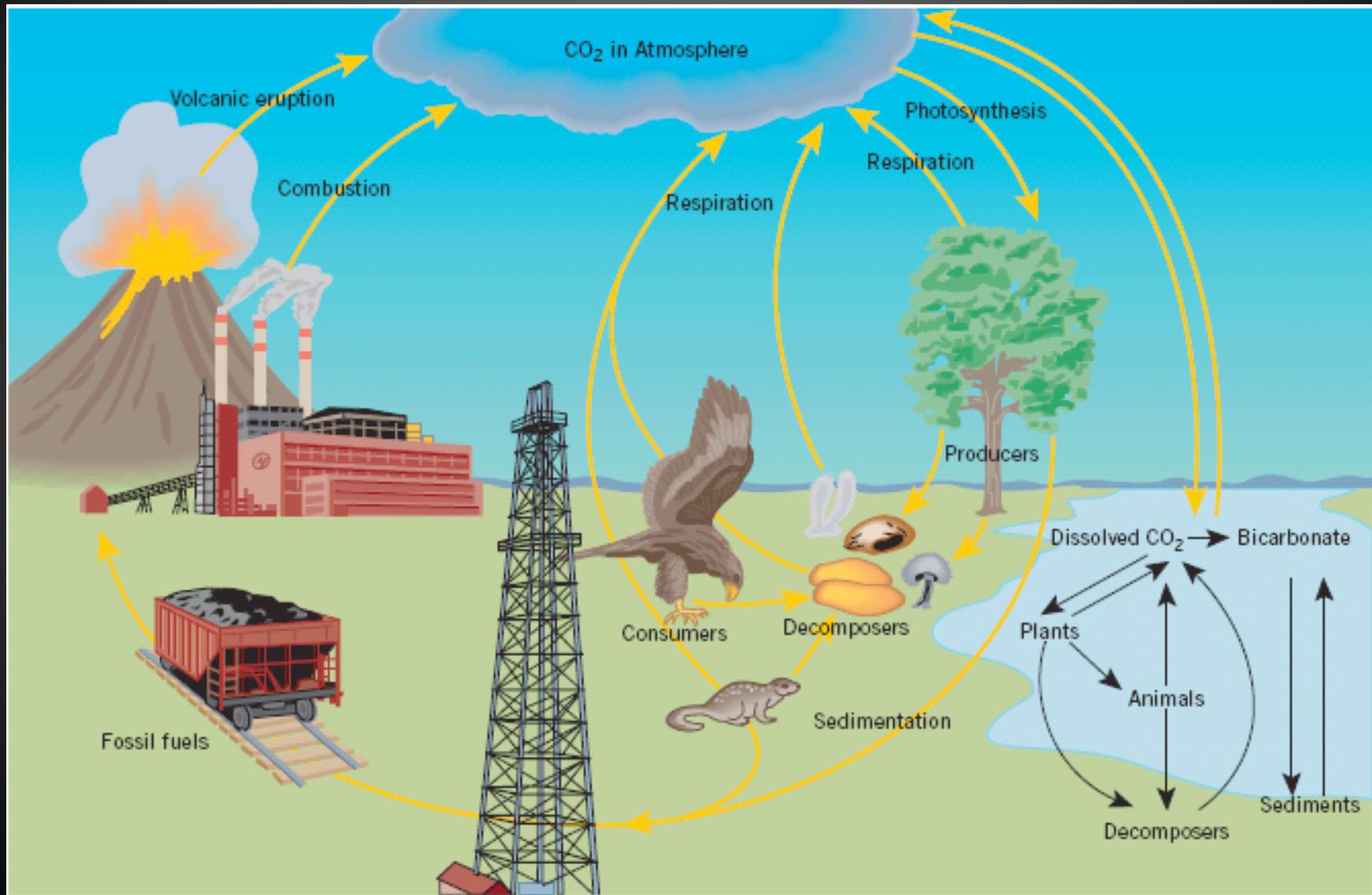
Unanswered Questions in Deep Carbon Research



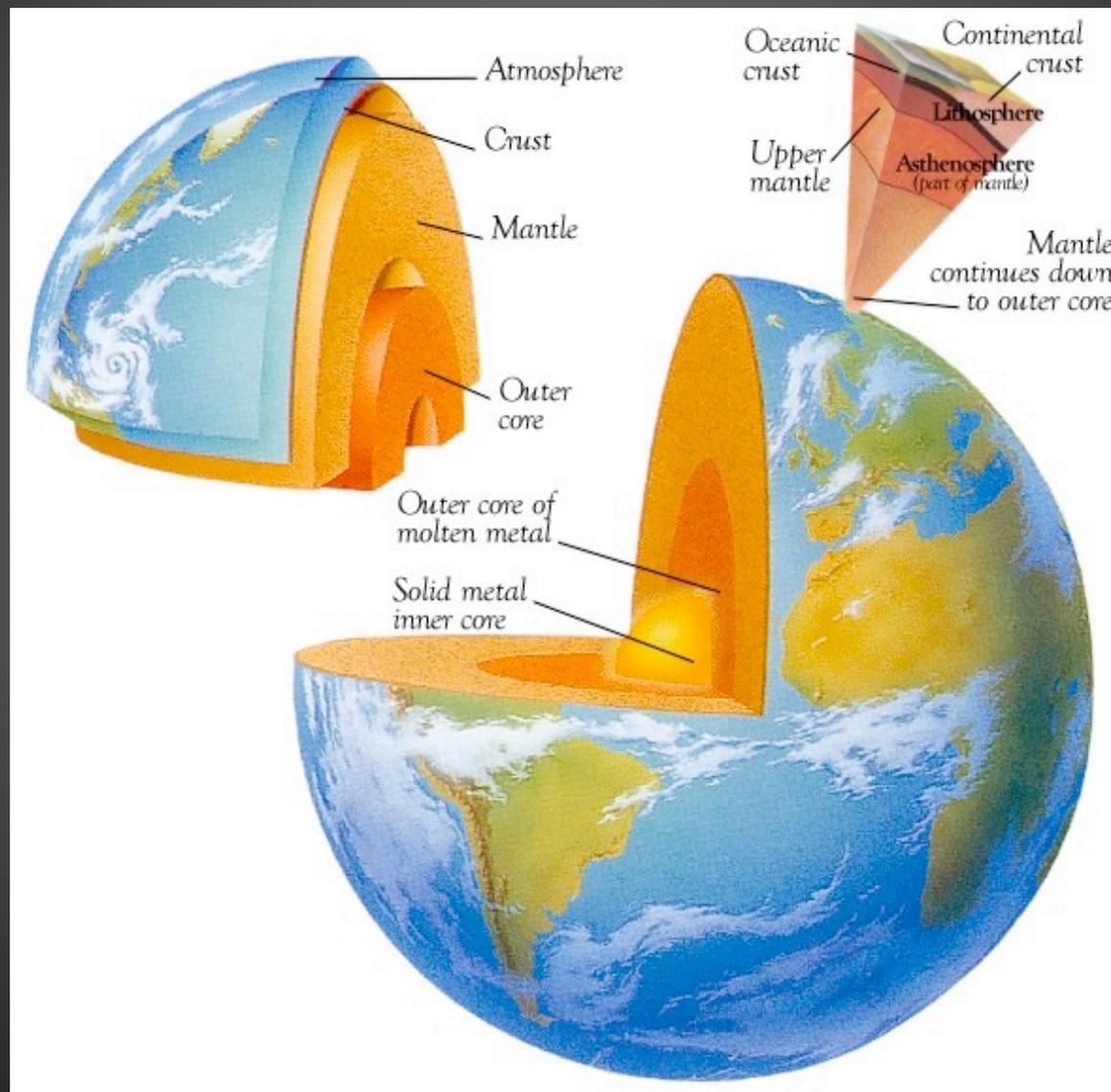
**Deep
Carbon
Observatory**



The Carbon Cycle



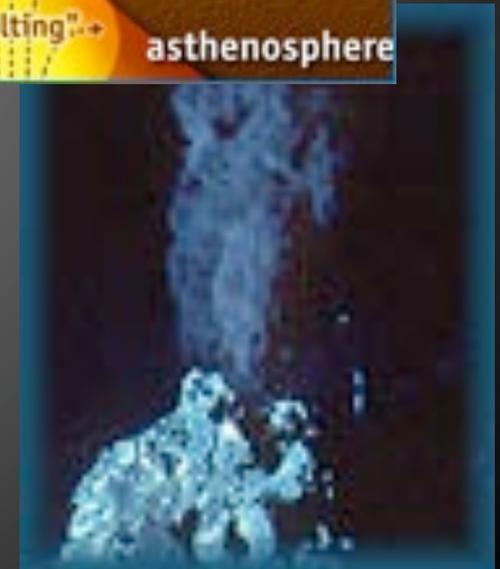
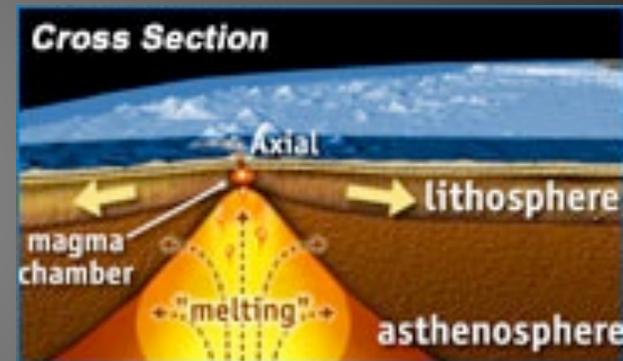
The Deep Carbon Cycle



Deep Carbon: Unanswered Questions

May 2008: We need fundamental advances in understanding Earth's deep carbon:

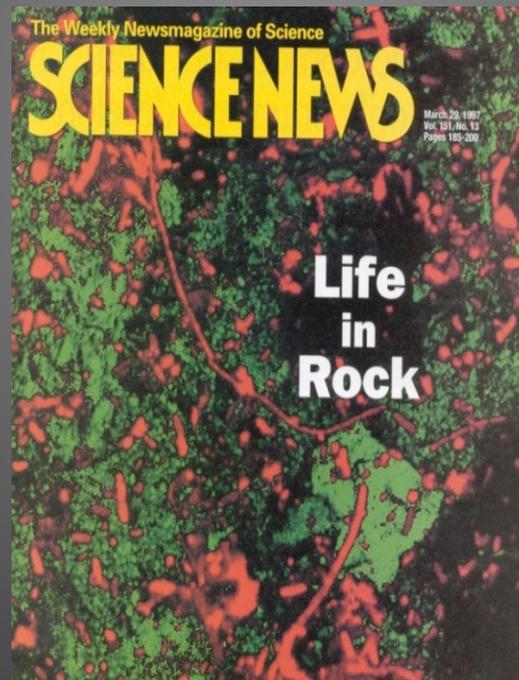
- Where is the deep carbon & how much is there?
- How does carbon move among deep reservoirs and the surface?
- Is there a deep source of organics?
- What is the nature and extent of deep microbial life?



We do not know how much carbon is stored within the Earth.

Estimates of Earth's carbon vary by a factor of >20:

- *Total from known reservoirs: 0.07 wt %* [Kerridge, *Geochim. Cosmochim. Acta* (1985)]
- *Highest literature estimate: 1.5 wt %* [Javoy, *Geophys. Res. Lett.* (1997)]
- *Average carbonaceous chondrites: 3.2 wt. %* [Mason, *USGS Prof Paper* (1979)]



How much & where is Earth's carbon?

Atmospheric
CO₂: 380 ppm

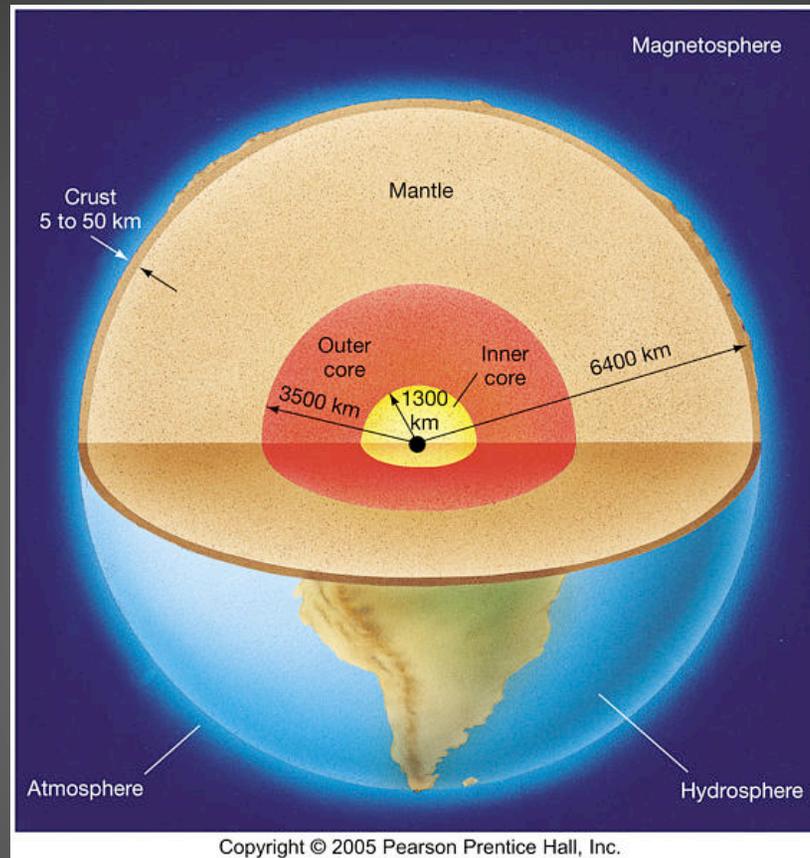
Crust: 200 ppm

Mantle: ? ppm

Seawater C:
30 ppm

Continental crust:
4000 ppm

Core: ? ppm



- *Where is Earth's carbon?*
 - *How much is there?*
- *What are carbon speciation and phases?*

We do not know how much carbon is stored in Earth's deep interior.

| <u>Reservoir</u> | <u>Composition</u> | <u>Structure</u> | <u>Atom % C</u> | <u>Depth</u> | <u>Abundance</u> |
|------------------|---|----------------------|-----------------|--------------|------------------|
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| Metal | Fe,Ni | kamecite/awaurite | minor ??? | ??? | ??? |
| Silicates | Mg-Si-O | various | trace ??? | ??? | ??? |
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| Silicate melts | Mg-Si-O | -- | trace ??? | ??? | ??? |
| CHON fluids | C-H-O-N | -- | variable | ??? | ??? |
| Methane | CH ₄ | -- | 20 | ??? | ??? |
| Clathrates | <i>e.g.</i> , [H ₂ O+CH ₄] | clathrate | variable | ??? | ??? |
| Hydrocarbons | C _n H _{2n+2} | -- | variable | ??? | ??? |
| Organic Species | C-H-O-N | -- | variable | ??? | ??? |
| Deep Life | C-H-O-N-P-S | -- | variable | < 15 km | ??? |

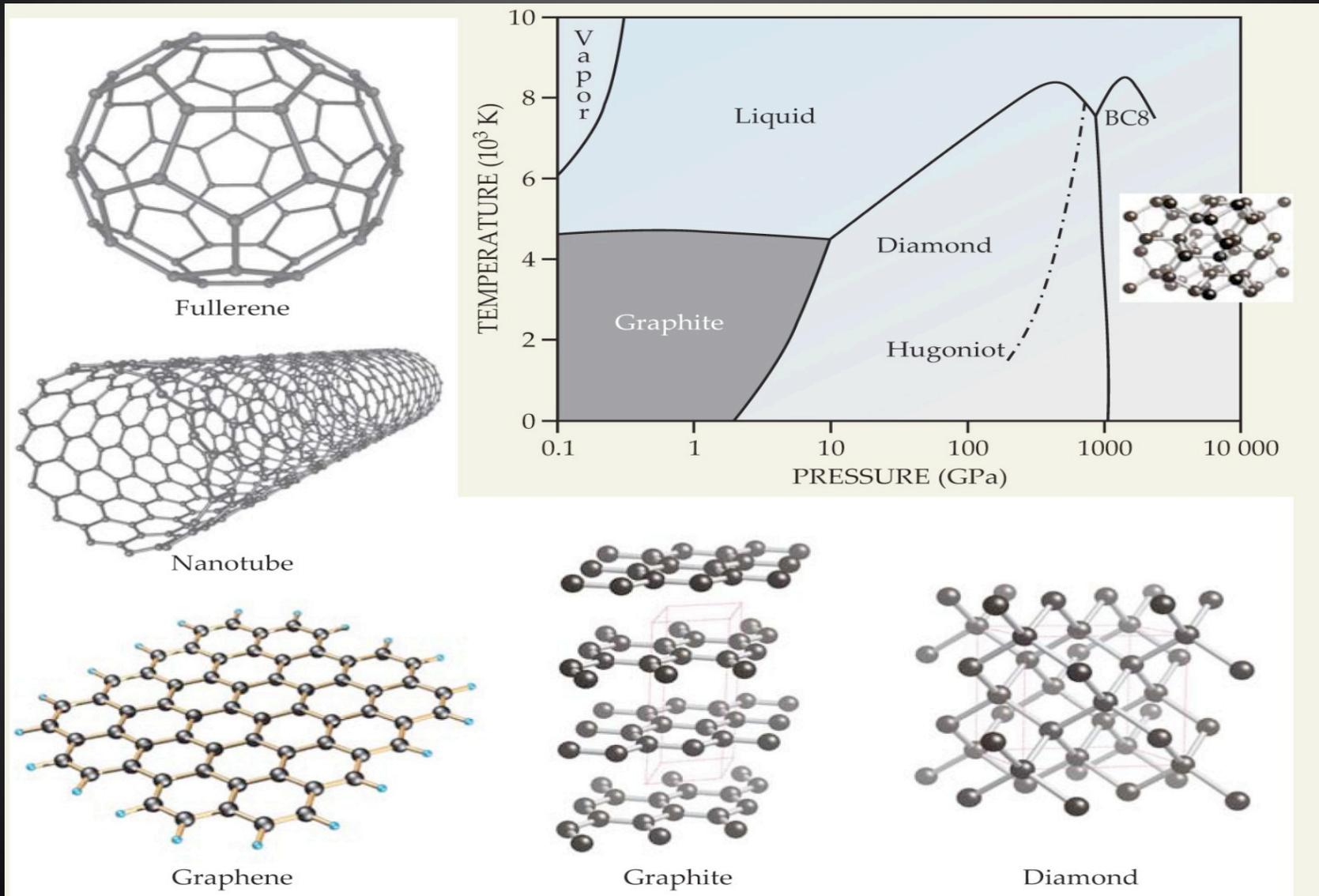
➤ *The nature of these deep repositories is not known.*

We do not know how much carbon is stored in Earth's deep interior.

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Carbon exhibits rich polymorphism, regimes of stability and metastability, and dimensionality.

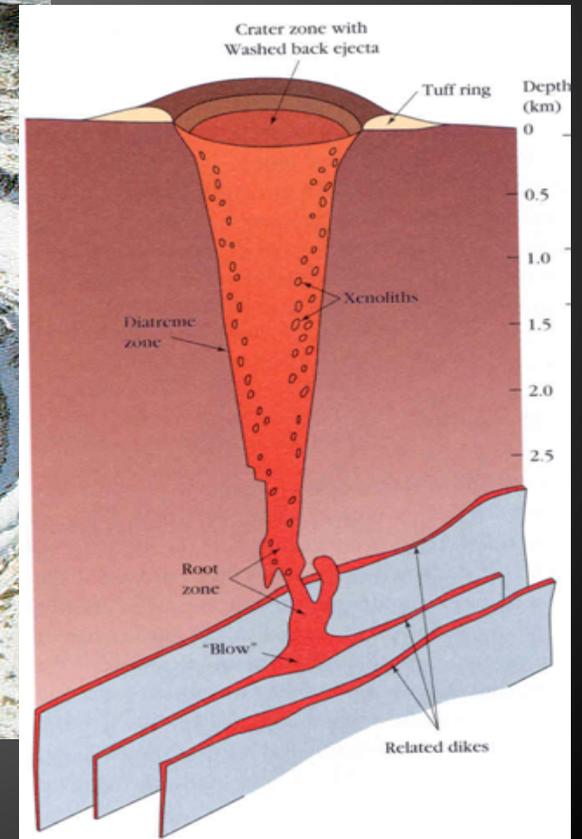
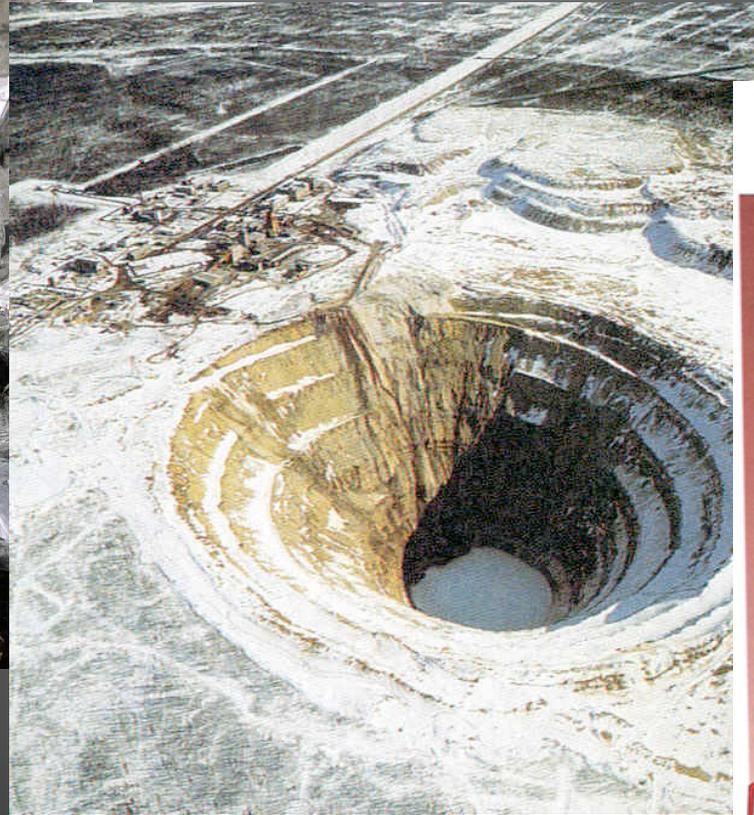


[Hemley, Crabtree & Buchanan, *Physics Today* (2009)]

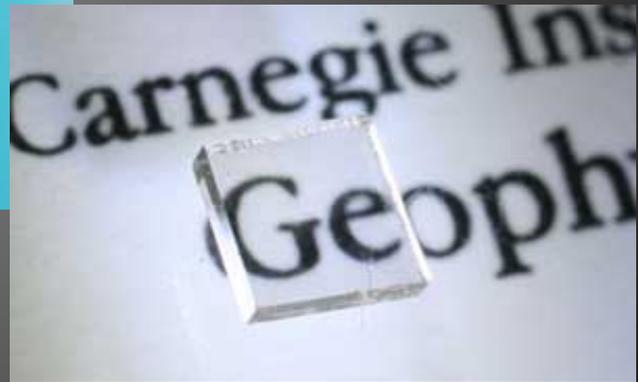
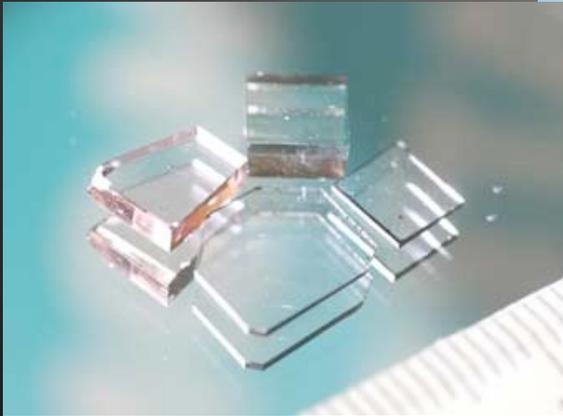
Carbon in the Mantle – Diamonds

How do diamonds form?

By what mechanism do they reach Earth's surface?



Geophysical Lab advances in diamond technology



Design and manufacture of a new generation of supertough synthetic diamonds.

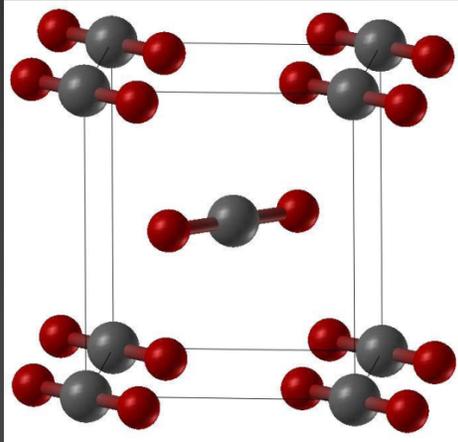
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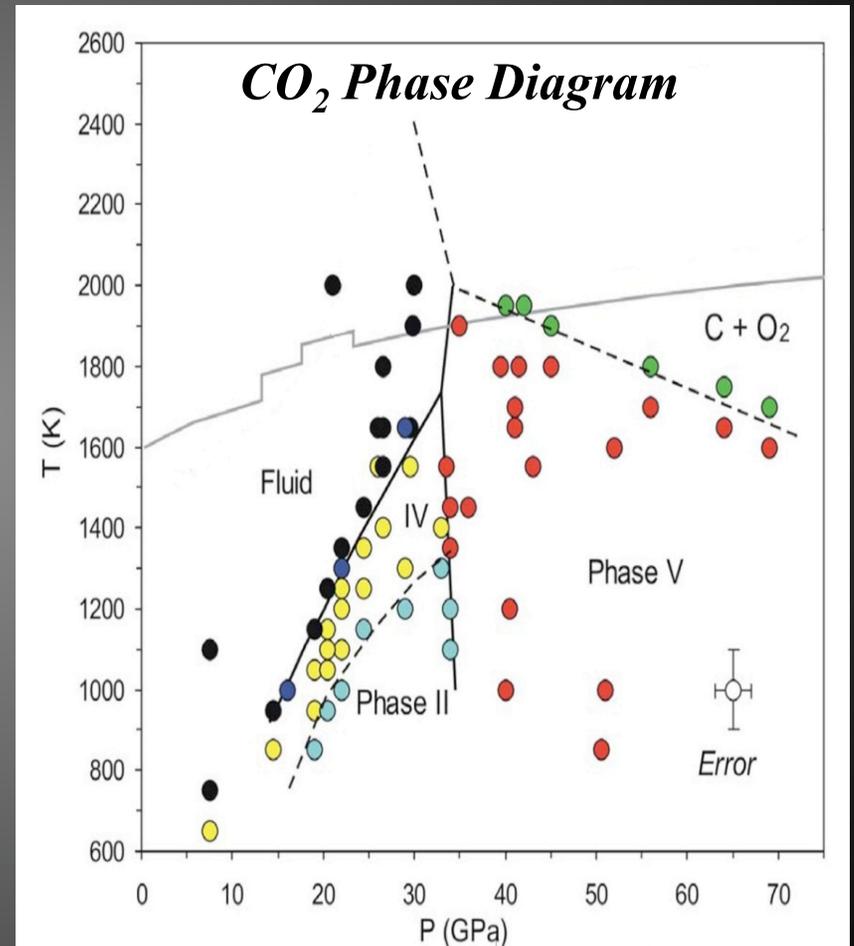
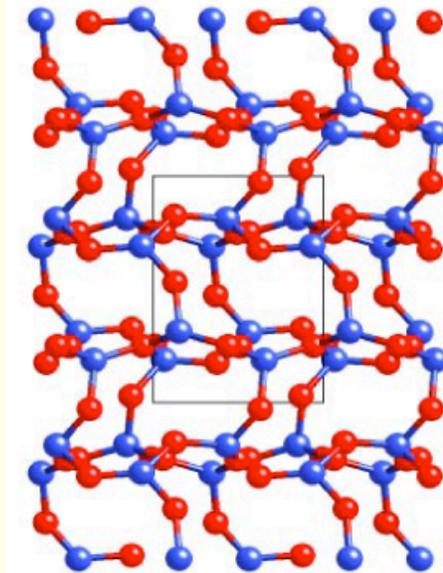
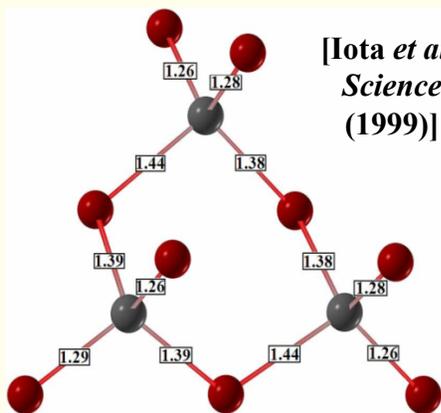
➤ *The nature of these deep repositories is not known.*

High-pressure studies reveal novel deep carbon phases: Polymeric CO₂

Low pressure: Molecular CO₂



*High pressure
Polymeric CO₂
silica-like structures*



[Litasov et al., *submitted*]

We do not know how much carbon is stored in Earth's deep interior.

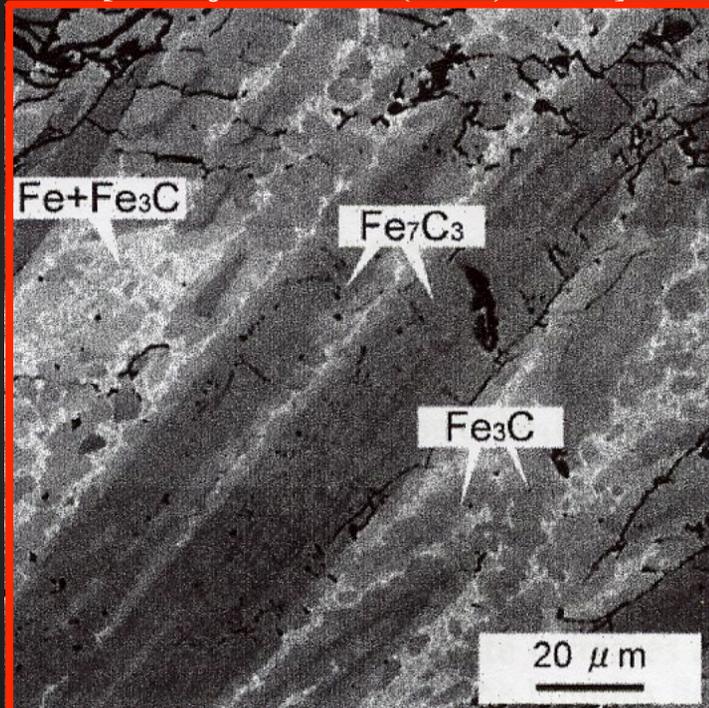
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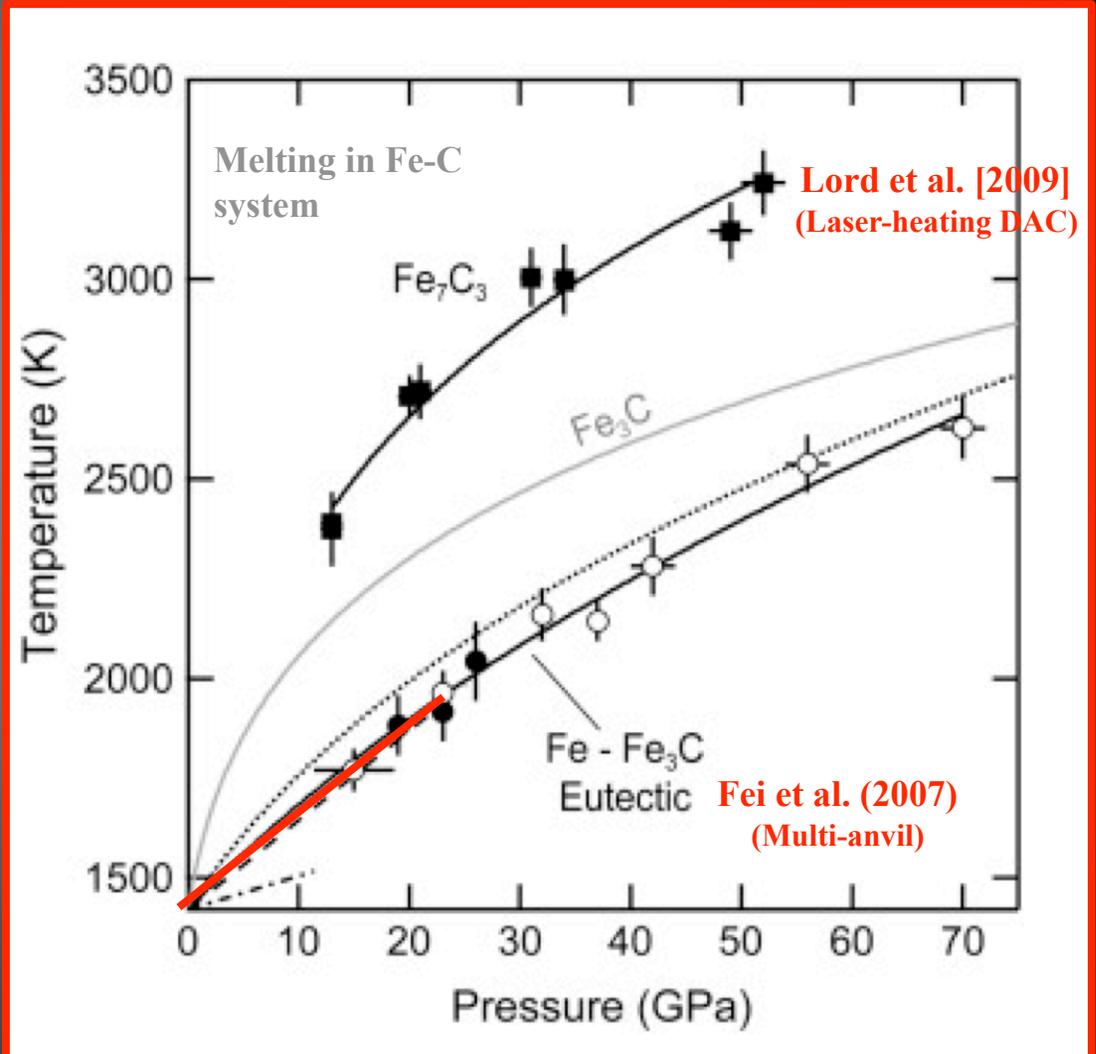
Is there carbon in Earth's core?

- 6-10% density deficit (outer core)
- ~2% density deficit (inner core)
- FeNi alloy + 8-12 wt% S, C, O, Si, H...?

[Nakajima *et al.* (2008) *PEPI*]



The search for new alloys and carbides is fundamental to understanding planetary interiors.



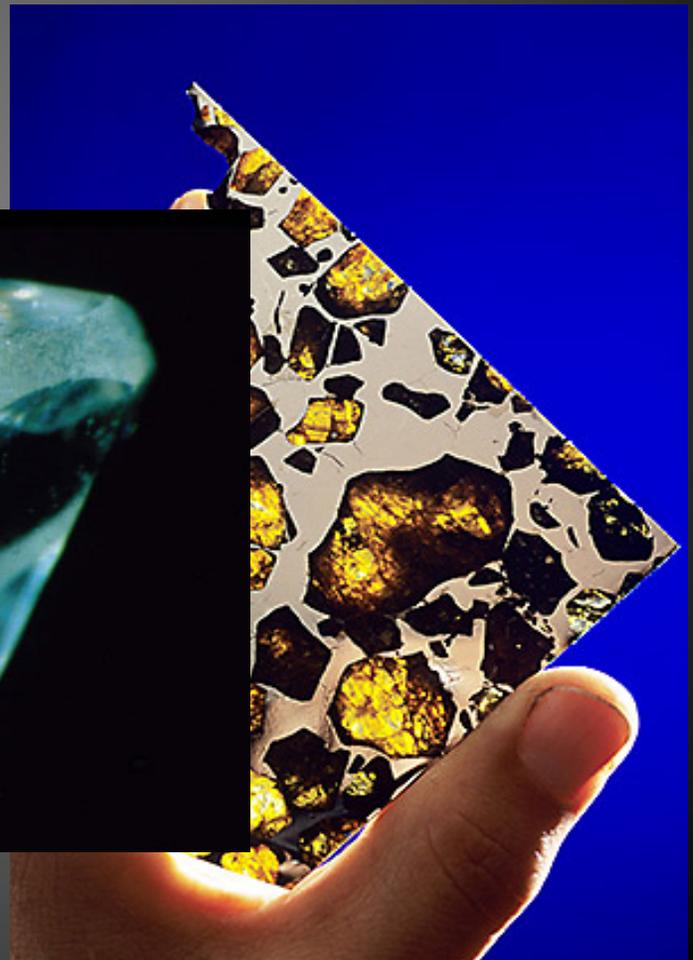
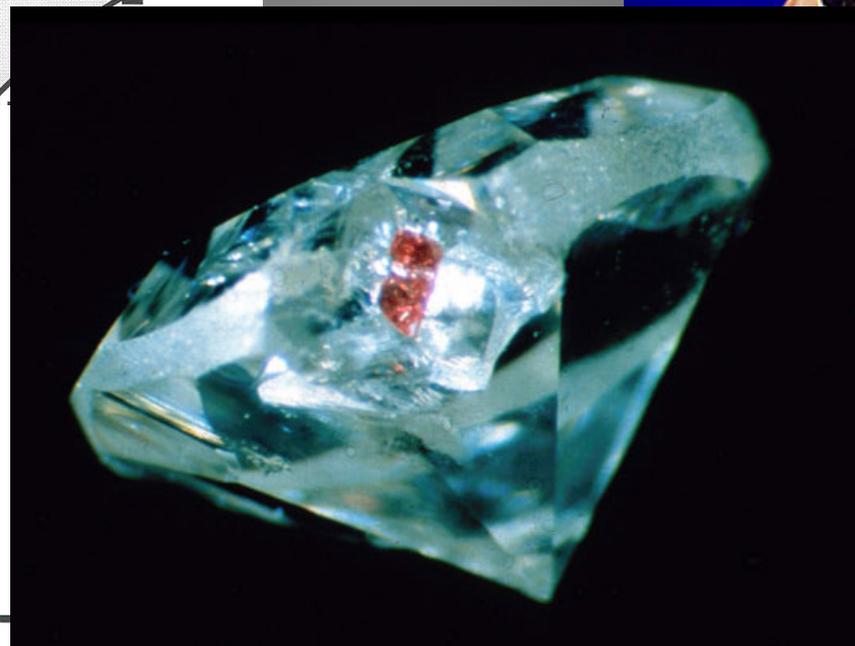
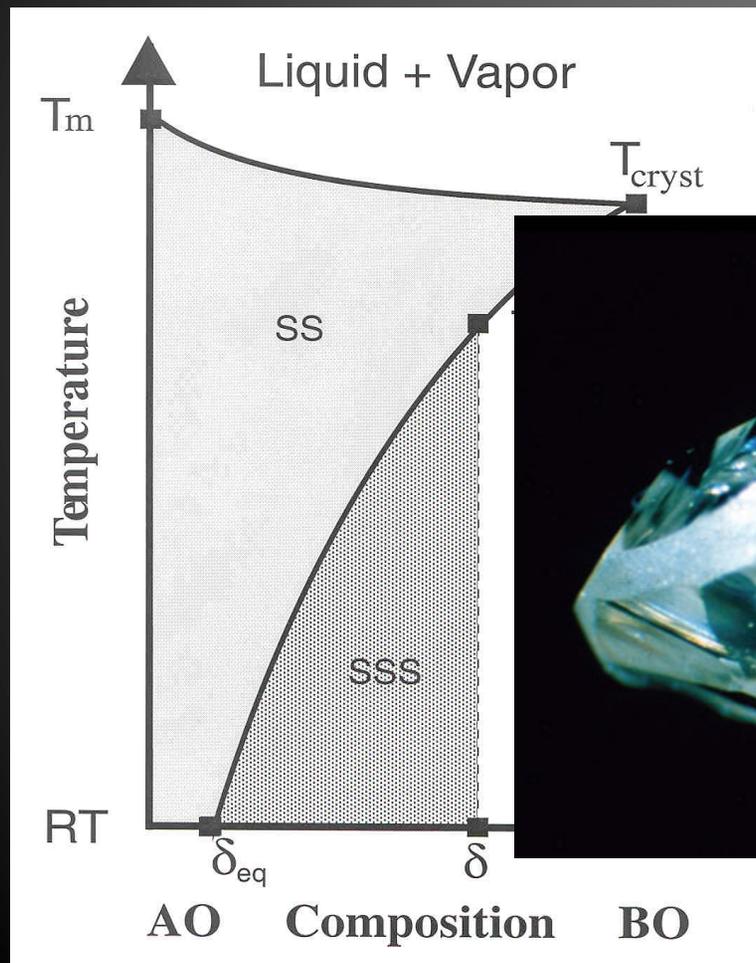
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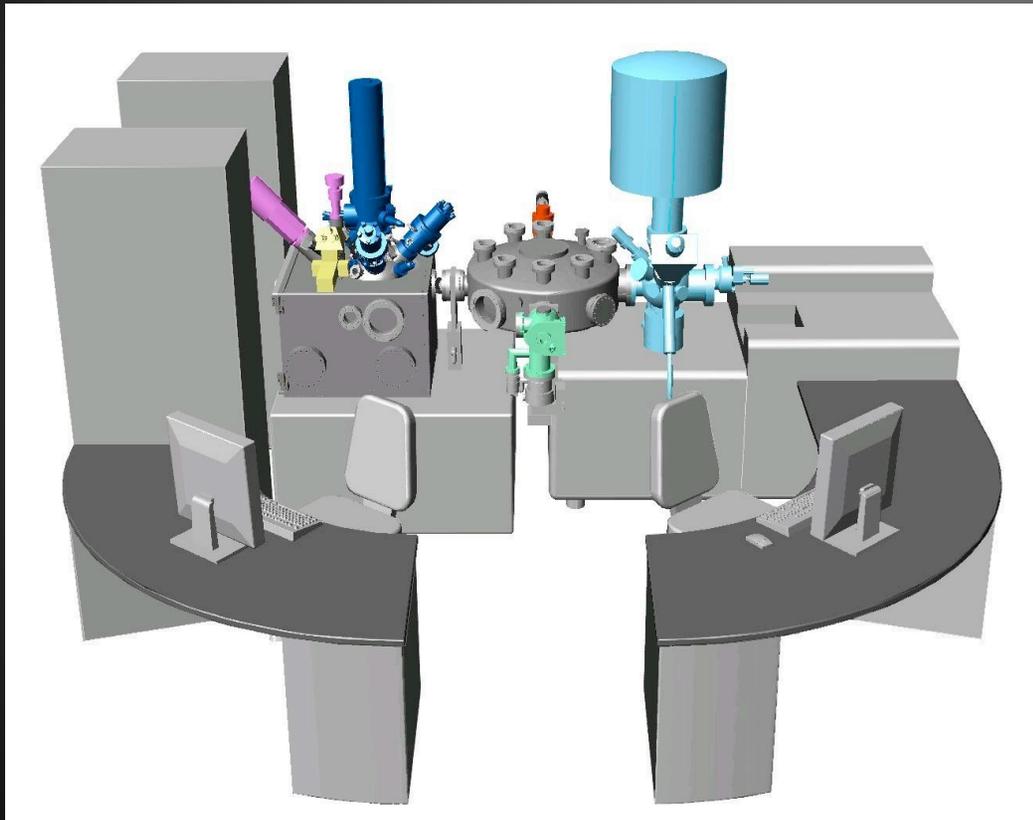
Deep Carbon Reservoirs

How much carbon can be incorporated into mantle oxides and silicates?



Deep Abiotic Organics – Hydrocarbons

Can we detect and characterize trace amounts of organic carbon in mantle samples and experimental runs?



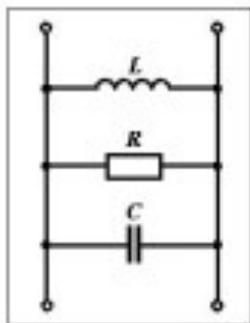
We plan to develop a nano-imaging ToF-SIMS to provide unprecedented resolution and sensitivity of minute C-bearing samples.

Andrew Steele et al.

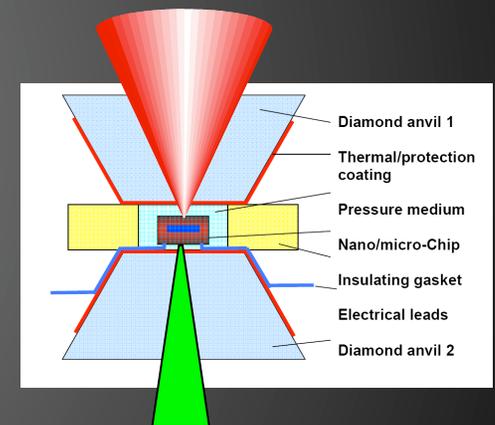
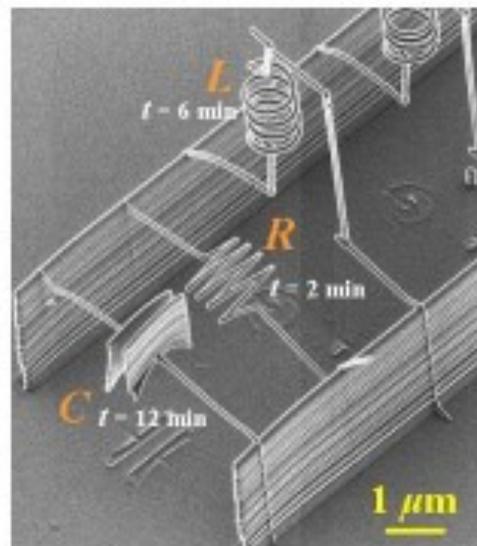
Characterizing Deep Carbon Minerals

What are the properties of deep-Earth
C-bearing minerals?

L, C, R Circuit Structure



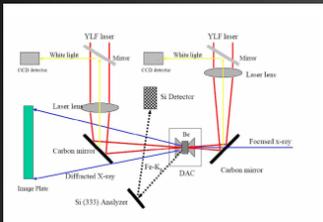
Growth time: 20 min



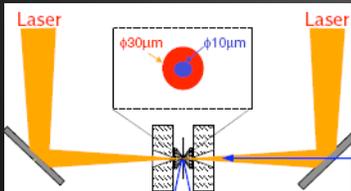
We need studies of thermochemical properties
(micro- and nano-calorimetry) and transport properties

Characterizing Deep Carbon Minerals

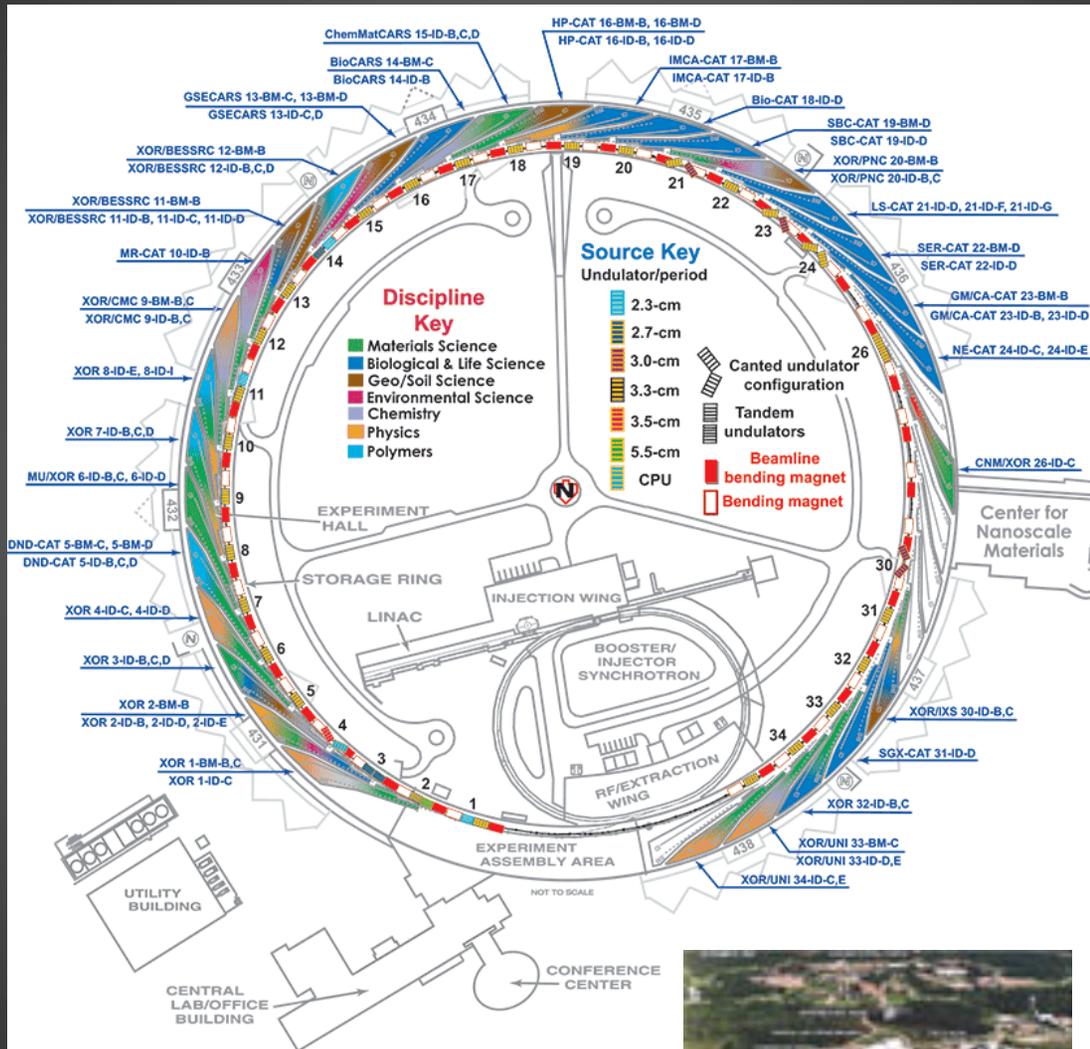
GSECARS
XES, Raman



Sector 3
NFS,
NRIXS



Sector 4
XMCD



HPCAT
XES, Raman,
NFS, NRIXS



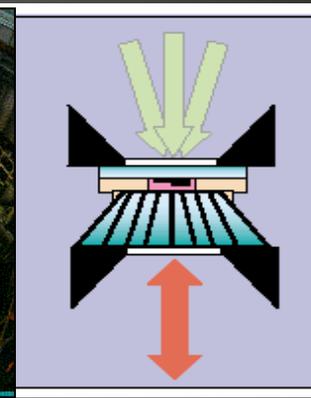
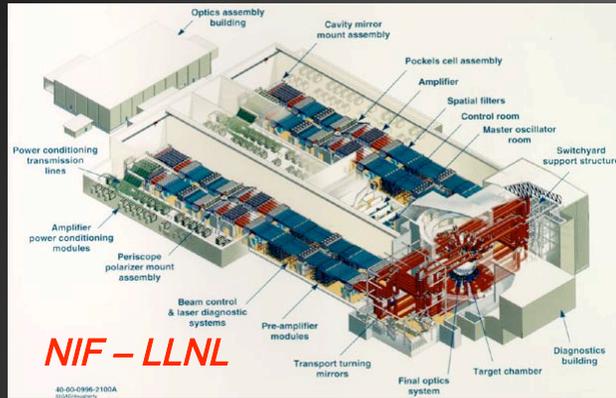
MERIX
RIXS



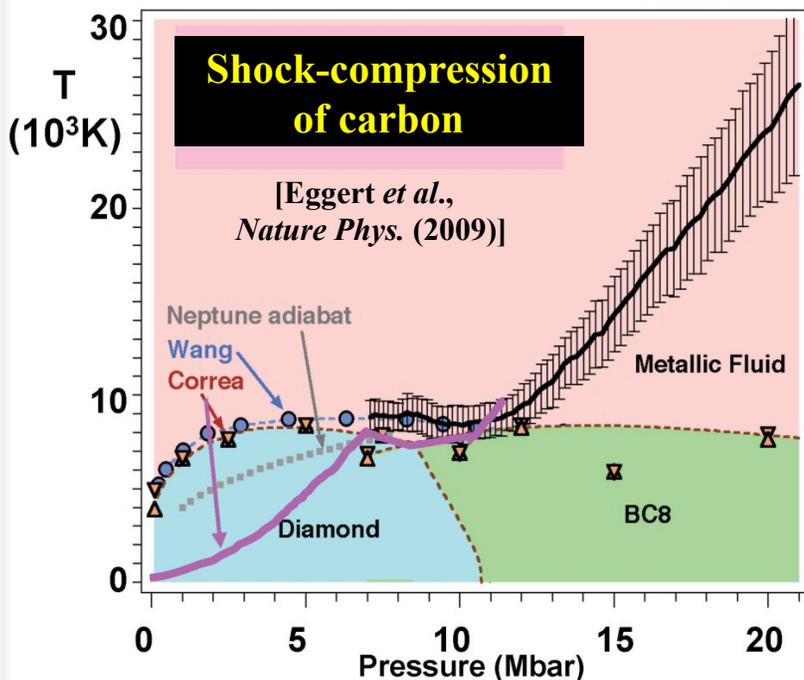
HERIX
Phonons,
quasielastic



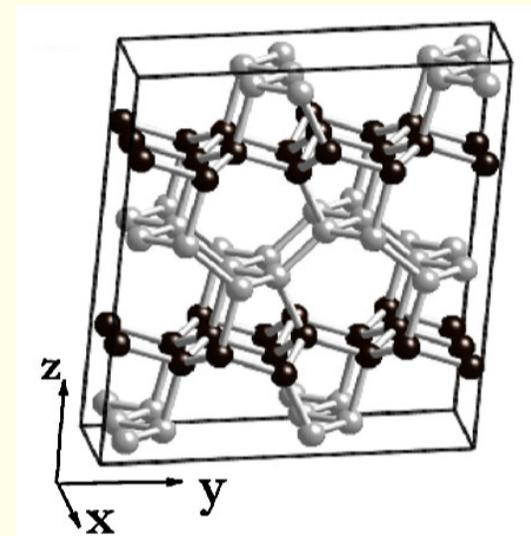
Dynamic compression platforms will probe carbon in new regimes of stability and metastability.



- Combined static/dynamic
- Ramp compression



- Search for new carbon phases
New structure at 16 GPa (theory)



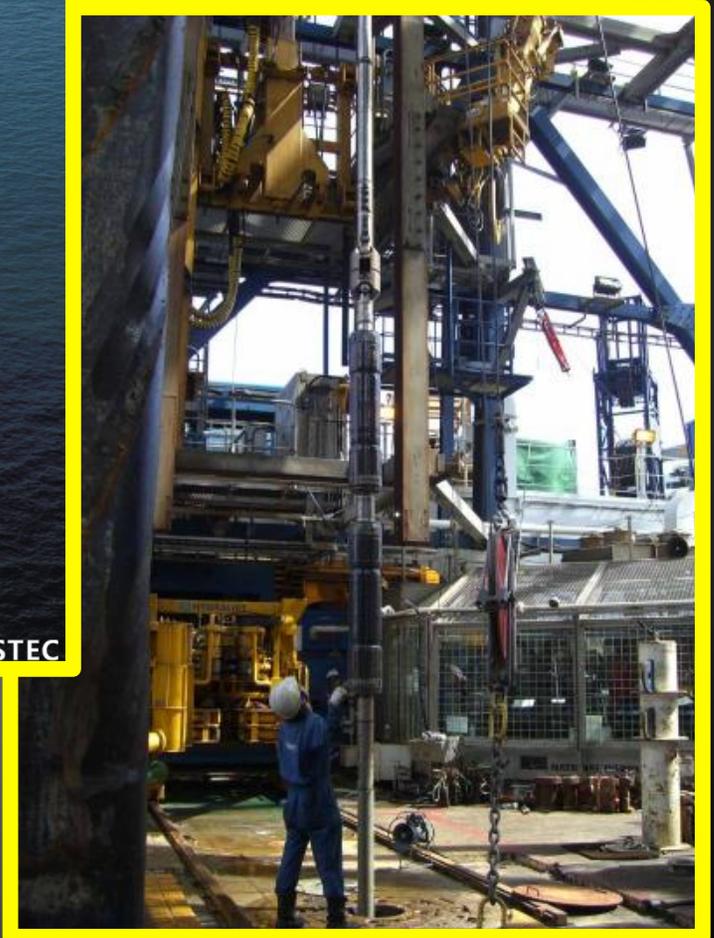
[Li et al., Phys. Rev. Lett. (2009)]

Revisit Project Mohole



©IODP/JAMSTEC

Reaching Earth's mantle and recovering a pristine sample is a major scientific and technological objective of the IODP.

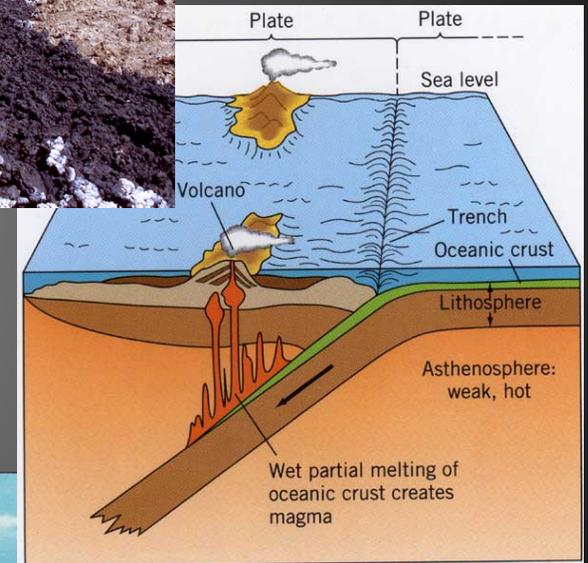


We do not know how much carbon is stored in Earth's deep interior.

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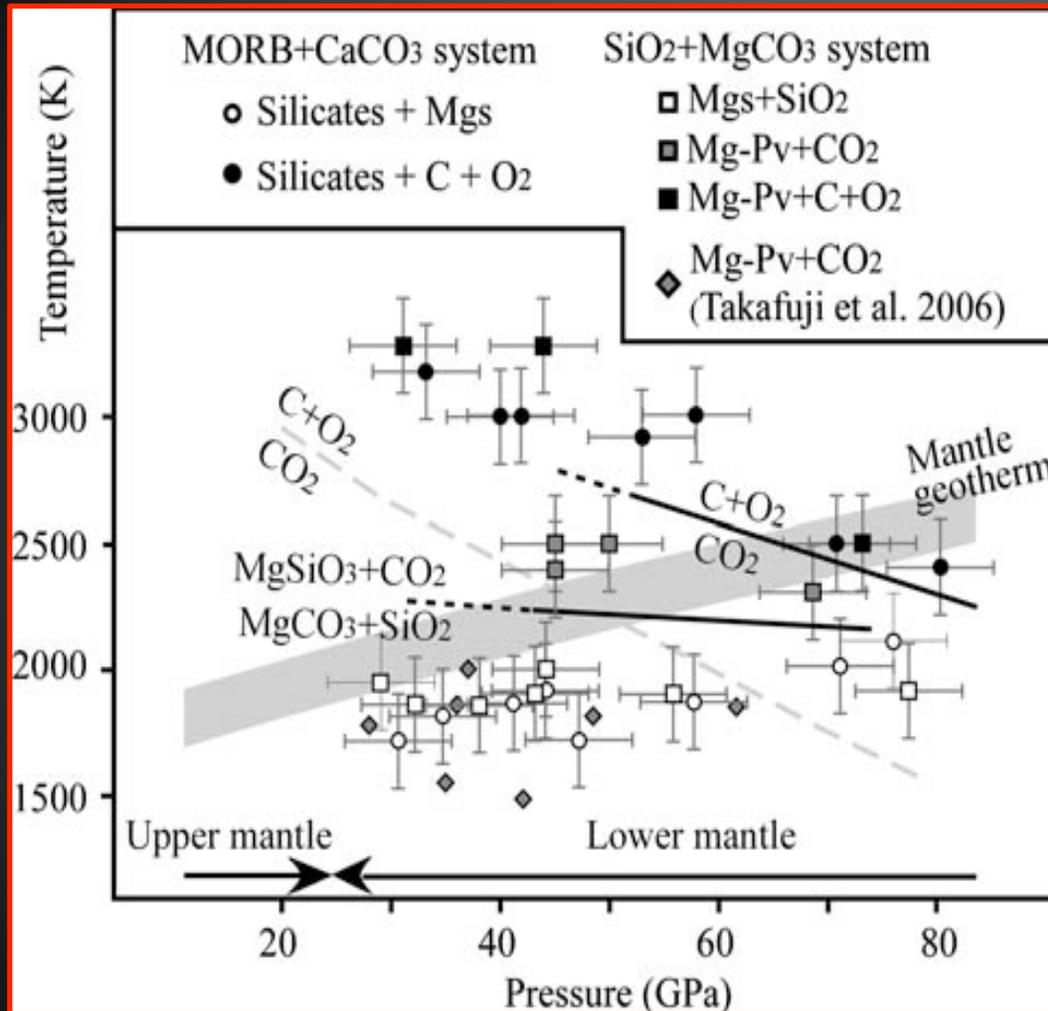
The extent to which carbon moves to and from Earth's surface at subduction zones is not known.



Estimates of the % subducted carbon flux returning to the surface ranged from 2% to 75%

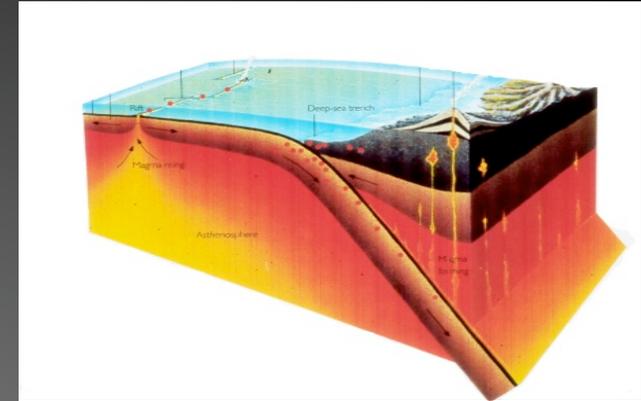
[Sloan Deep Carbon Workshop Report (2008)]

High P - T experiments reveal that carbonates may not decompose in subducting slabs.



CO₂ may persist in the subducted slab.

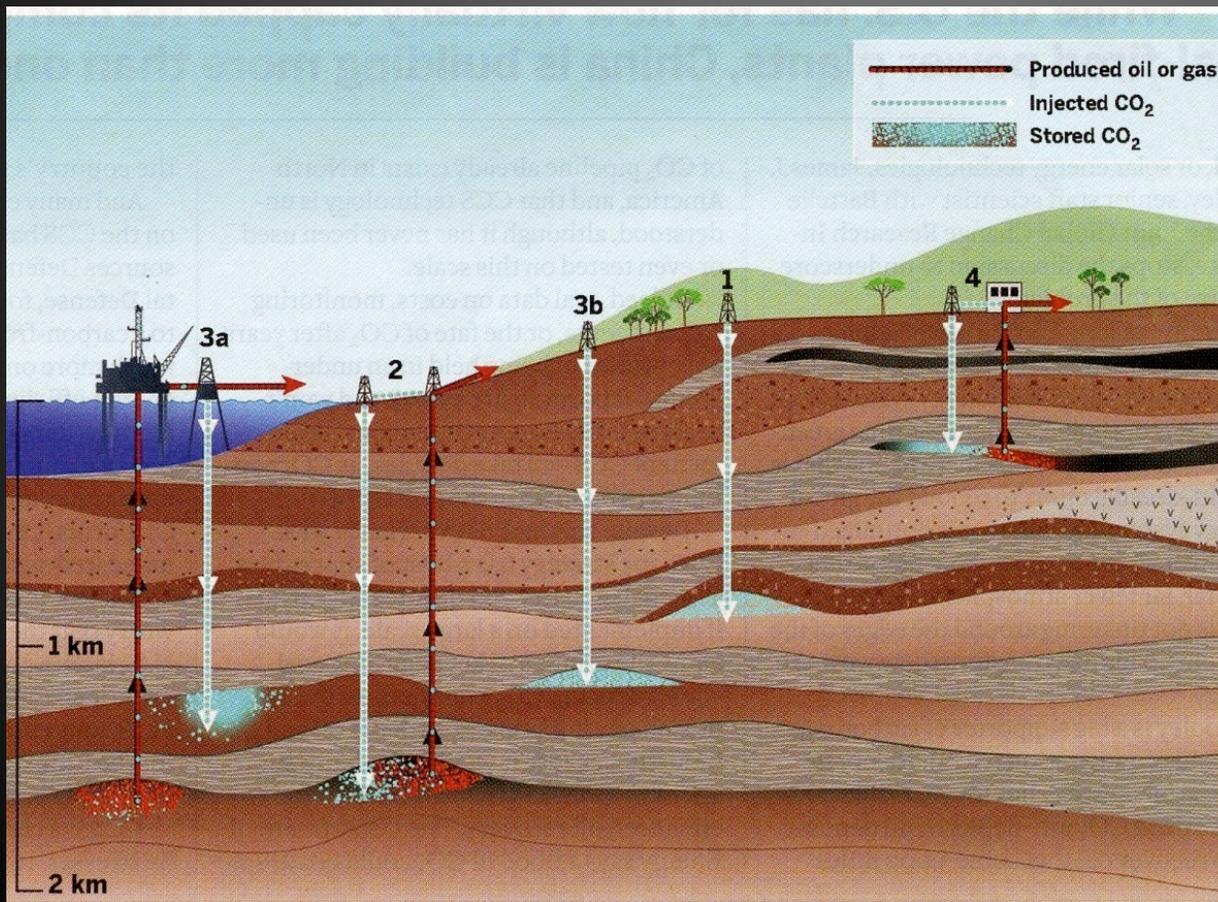
[Seto et al. *Phys Chem. Minerals* (2008)]



This CO₂ may be a source of diamonds

Deep CO₂ Sequestration

What is the mechanism and rate of carbonate formation?

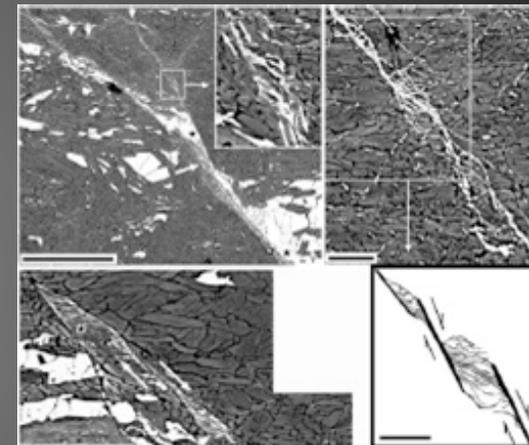
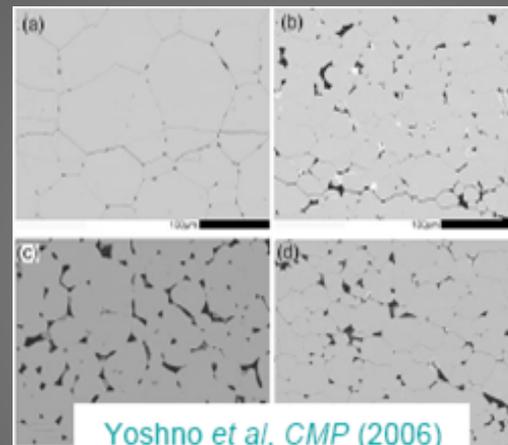
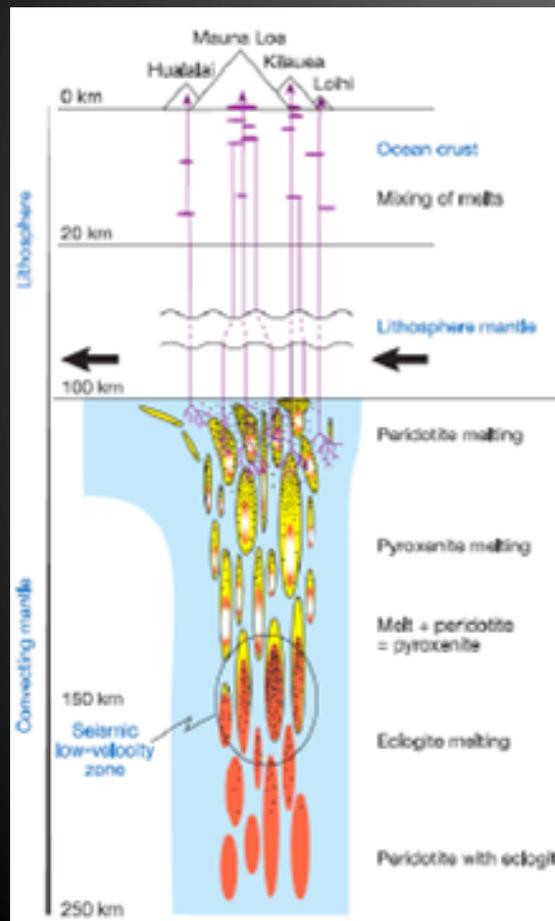


**DRIVING CO₂
UNDERGROUND**

Current capacity =
10⁴ gigatons CO₂

Deep Carbon Fluxes

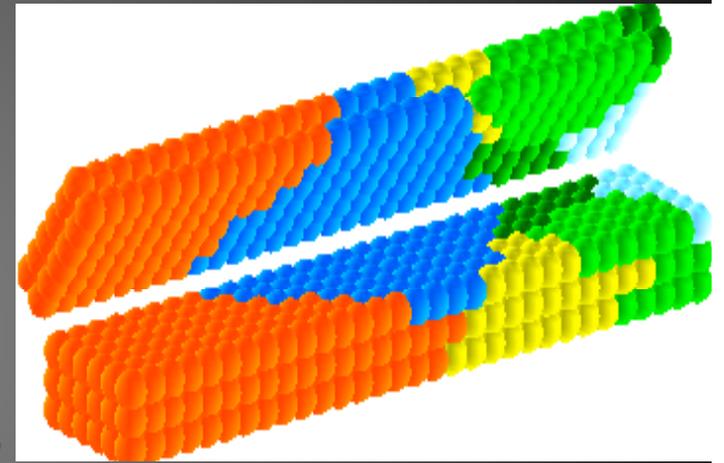
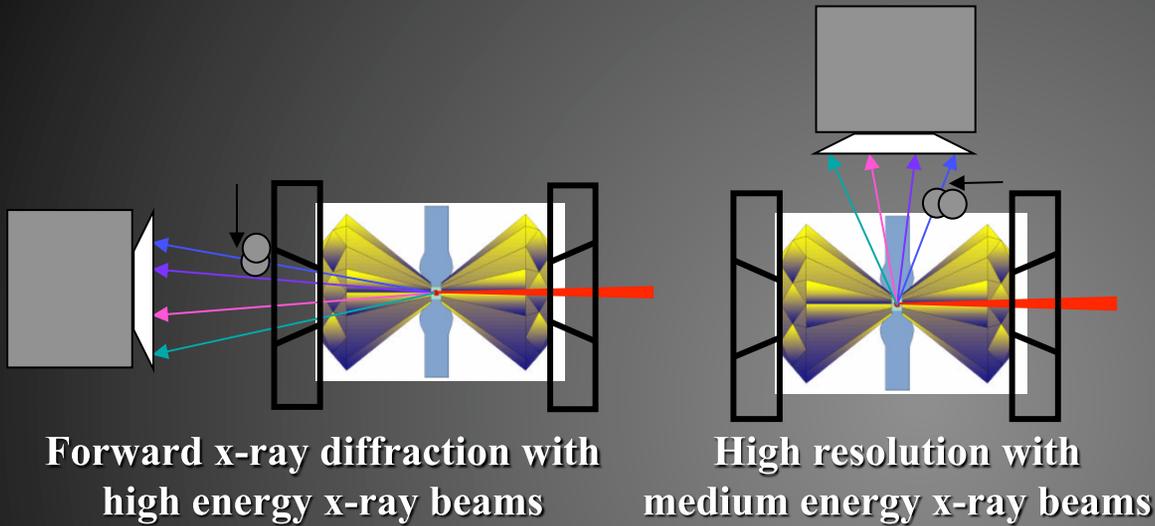
How do methane, CO₂ and other volatiles move through Earth's deep interior?



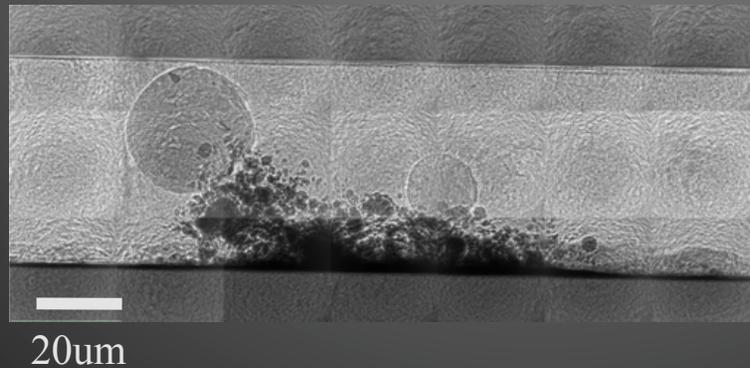
We hope to develop an X-ray nanoscope to explore 3D tomography with 30-nm resolution for exploring fluid-rock interactions in Earth's deep interior.

Nanoscale imaging of heterogeneous materials

3-D grain boundary mapping



Example of 3-D grain boundary mapping at ambient condition

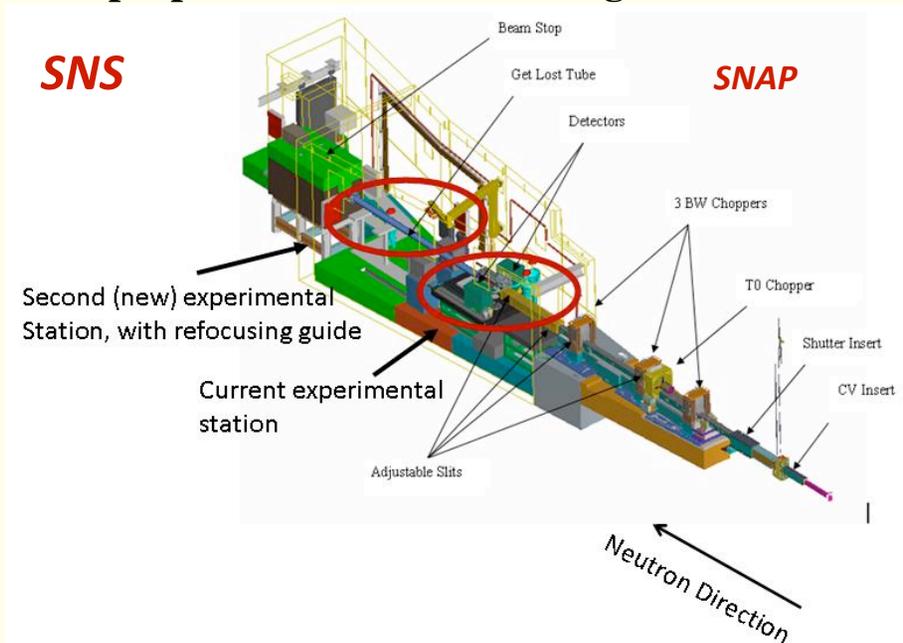


Nano-imaging (TXM)

- 30 nm in 3-D
- Individual grains
- EoS of amorphous, liquid, crystals
- interaction under P

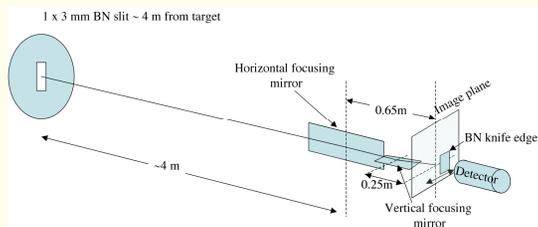
Understanding high P - T fluids and fluid-rock interactions requires advanced neutron scattering techniques.

- Direct measurements of high P - T structure and properties of carbon-bearing fluids

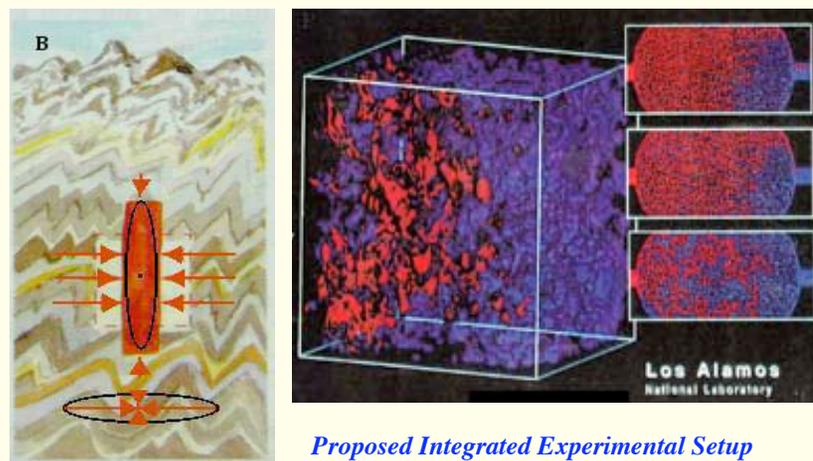


A second experimental station is ideally suited to accommodate a large 1500 tonne multi-anvil press or a dedicated liquids and amorphous extreme environment diffractometer

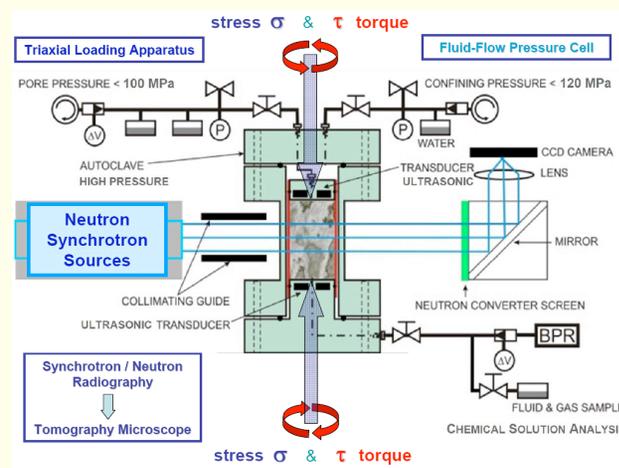
Extend focusing
<math><100 \mu\text{m}</math>



- Imaging C-O-H fluid-rock systems under extreme conditions



Proposed Integrated Experimental Setup for Neutron Tomography and Ancillary Measurements (LANL)



Monitor Every Volcano on Earth



A combination of *in situ*, real time, web accessible measurements and satellite observations.

We do not know how much carbon is stored within the Earth

| <u>Reservoir</u> | <u>Composition</u> | <u>Structure</u> | <u>Atom % C</u> | <u>Depth</u> | <u>Abundance</u> |
|------------------------|---|----------------------|-----------------|-------------------|------------------|
| Diamond | C | diamond | 100 | > 150 km | << 1% |
| Graphite | C | graphite | 100 | < 150 km | << 1% |
| Carbonates | (Ca,Mg,Fe)CO ₃ | unknown | 20 | 0 to ??? | ??? |
| Carbides | SiC, FeC, Fe ₃ C | moissanite, cohenite | 50 ??? | ??? | |
| Metal | Fe,Ni | kamecite/awaurite | minor ??? | ??? | ??? |
| Silicates | Mg-Si-O | various | trace ??? | ??? | ??? |
| Oxides | Mg-Fe-O | various | trace ??? | ??? | ??? |
| Sulfides | Fe-S | various | trace ??? | ??? | ??? |
| Silicate melts | Mg-Si-O | -- | trace ??? | ??? | ??? |
| CHON fluids | C-H-O-N | -- | variable | ??? | ??? |
| Methane | CH₄ | -- | 20 | ??? | ??? |
| Clathrates | <i>e.g.</i> , [H ₂ O+CH ₄] | clathrate | variable | ??? | ??? |
| Hydrocarbons | C_nH_{2n+2} | -- | variable | ??? | ??? |
| Organic Species | C-H-O-N | -- | variable | ??? | ??? |
| Deep Life | C-H-O-N-P-S | -- | variable | < 15 km | ??? |

➤ *The nature of these deep repositories is also not known.*

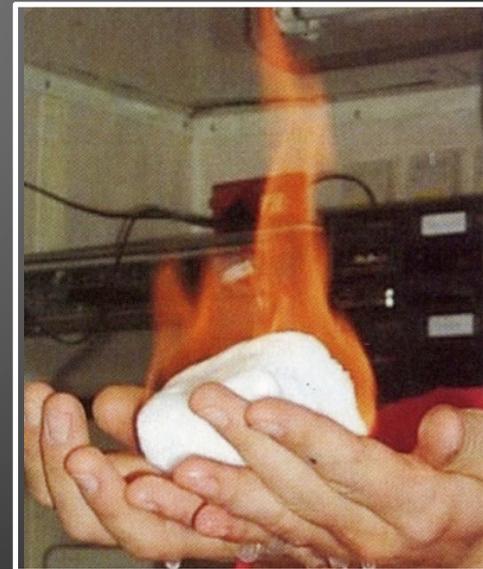
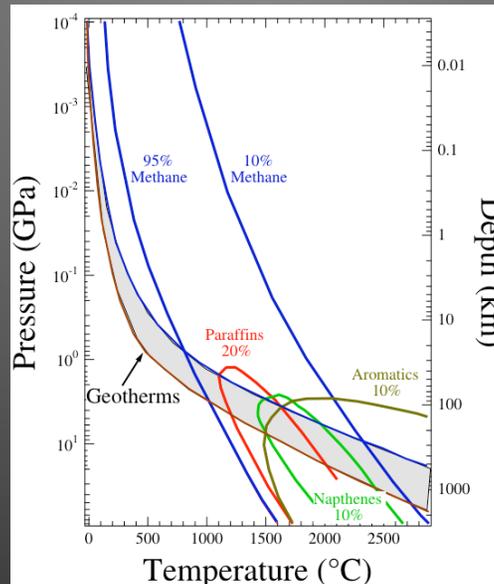
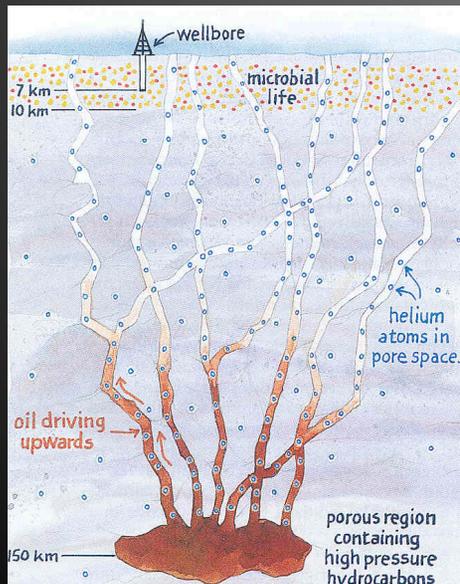
The extent of deep abiotic organic synthesis is an open question

Conventional wisdom points to a predominantly biological source for the origins of deep hydrocarbons.

Nevertheless, many fundamental experiments to assess the role of deep abiotic organic synthesis have yet to be undertaken.

Is there a mantle source of methane and higher hydrocarbons?

Did deep organic synthesis play a role in life's origins?



Deep Abiotic Organics – Methane

BIOGENIC

Microbial

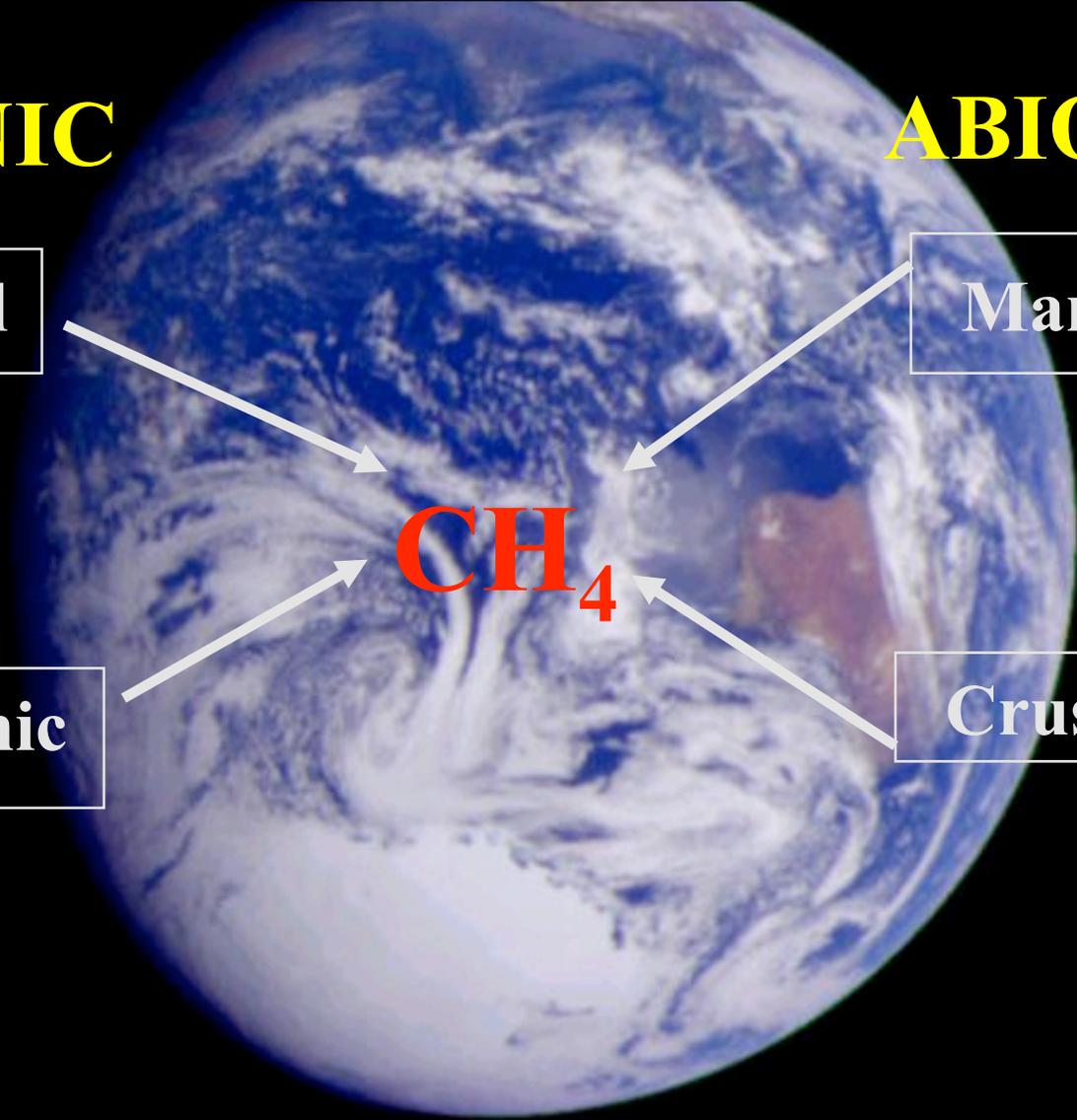
ABIIOGENIC

Mantle derived

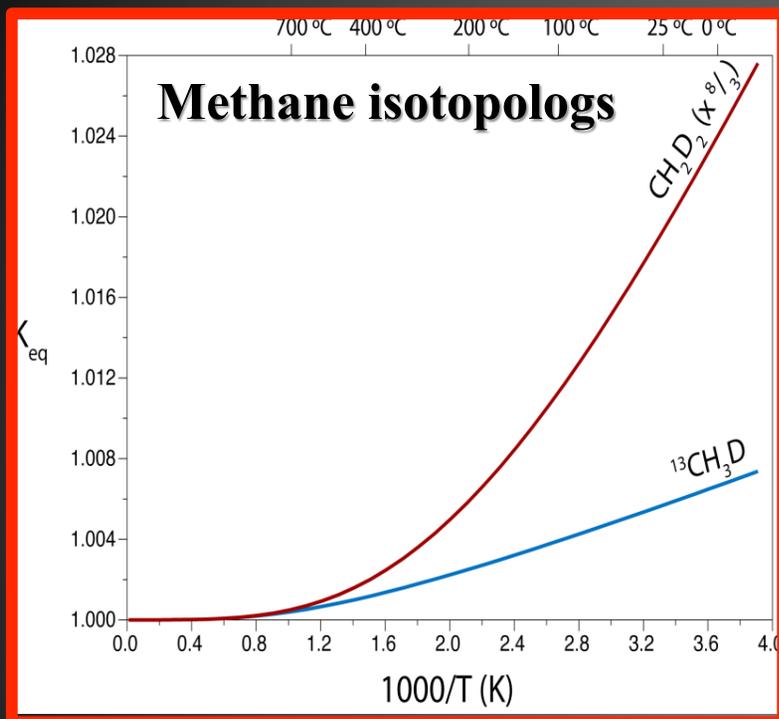
Thermogenic

Crustal derived

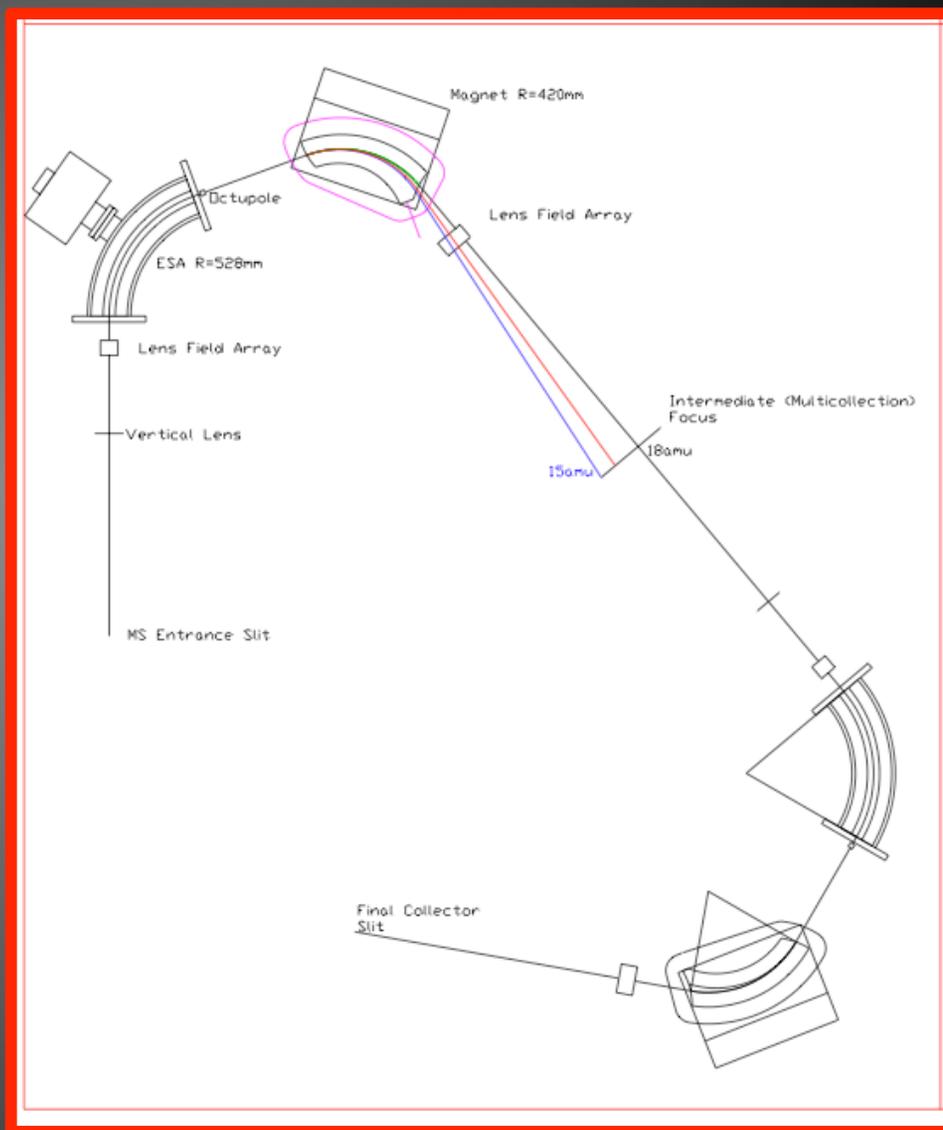
CH₄

A satellite-style image of Earth from space, showing the Western Hemisphere. The image is centered on the Atlantic Ocean, with North and South America visible on the right. The text 'CH4' is overlaid in the center of the image. Four white arrows point towards the center from the four quadrants, each originating from a text box. The top-left box is labeled 'Microbial' under the heading 'BIOGENIC'. The top-right box is labeled 'Mantle derived' under the heading 'ABIIOGENIC'. The bottom-left box is labeled 'Thermogenic'. The bottom-right box is labeled 'Crustal derived'.

Deep Abiotic Organics – Methane

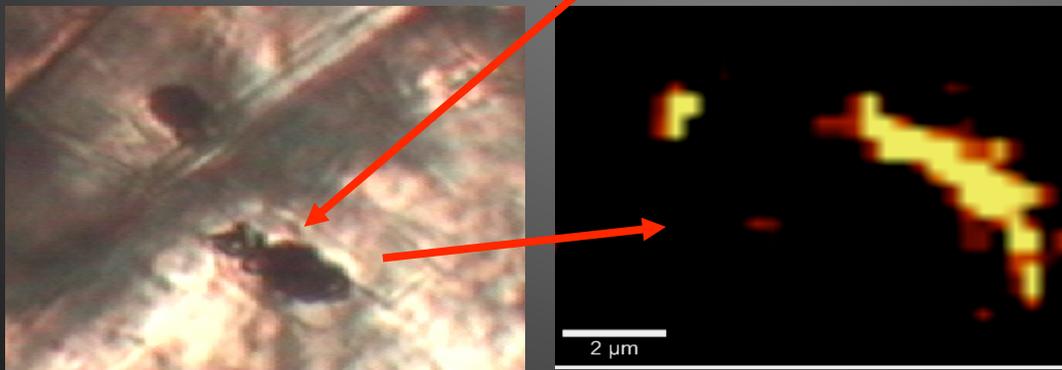
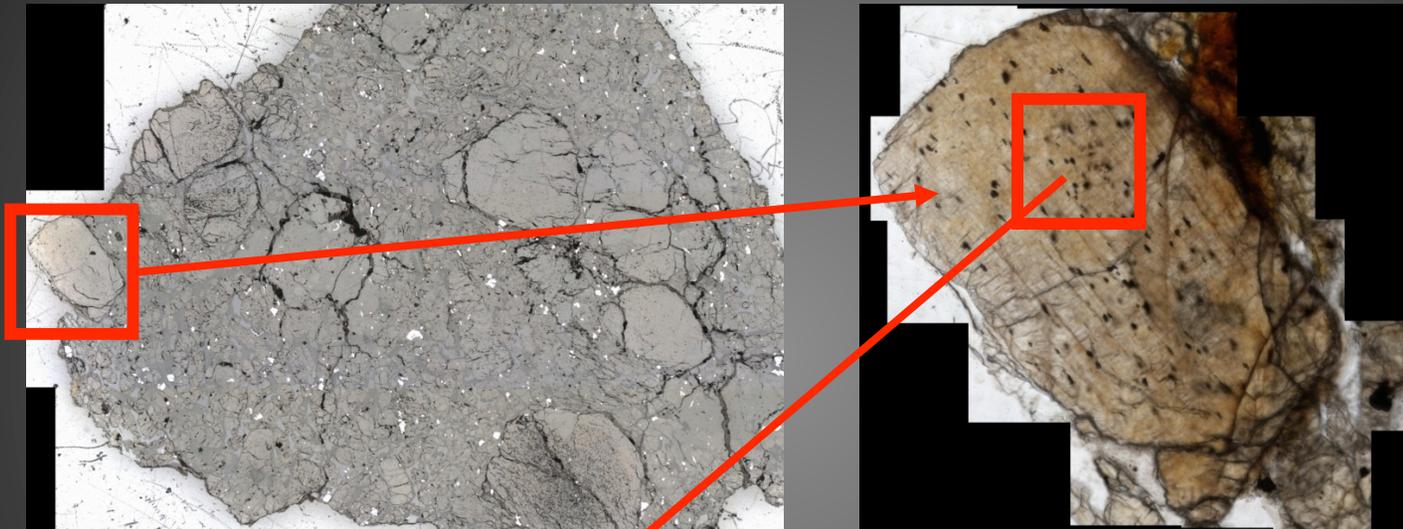


Sloan and Shell are helping to fund a high-resolution tandem mass spectrometer to measure CH_4 isotopolog ratios. This instrument is designed to distinguish biotic and abiotic methane. (Young & Rumble)



Deep Abiotic Organics – Hydrocarbons

Can we detect and characterize trace amounts of organic carbon in mantle samples and experimental runs?



Organic Carbon 4-microns deep within an Mars meteorite inclusion reveals 4.45 billion years of organic synthesis on Mars. [Steele et al.]

Confocal micro-Raman

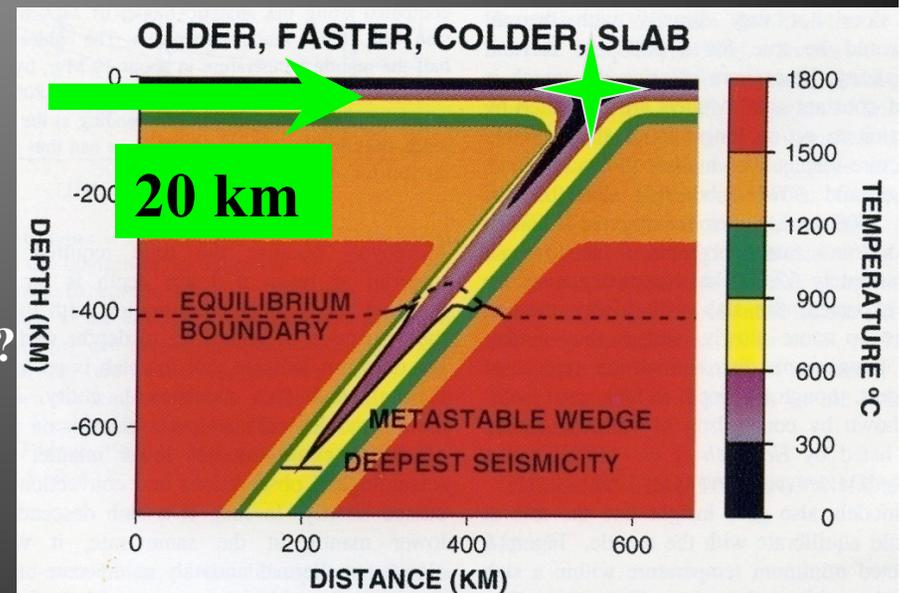
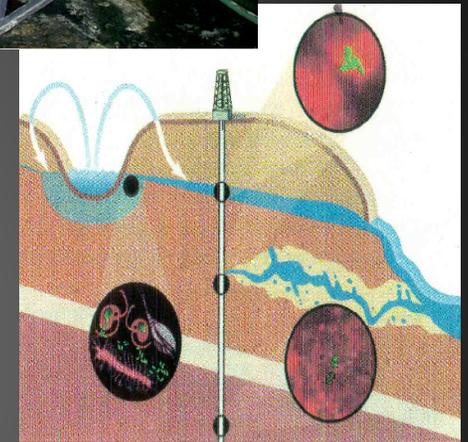
We do not know how much carbon is stored in Earth's deep interior.

| <u>Reservoir</u> | <u>Composition</u> | <u>Structure</u> | <u>Atom % C</u> | <u>Depth</u> | <u>Abundance</u> |
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| Deep Life | C-H-O-N-P-S | -- | variable | < 15 km | ??? |

➤ *The nature of these deep repositories is not known.*

The nature and extent of the deep microbial biosphere is unknown.

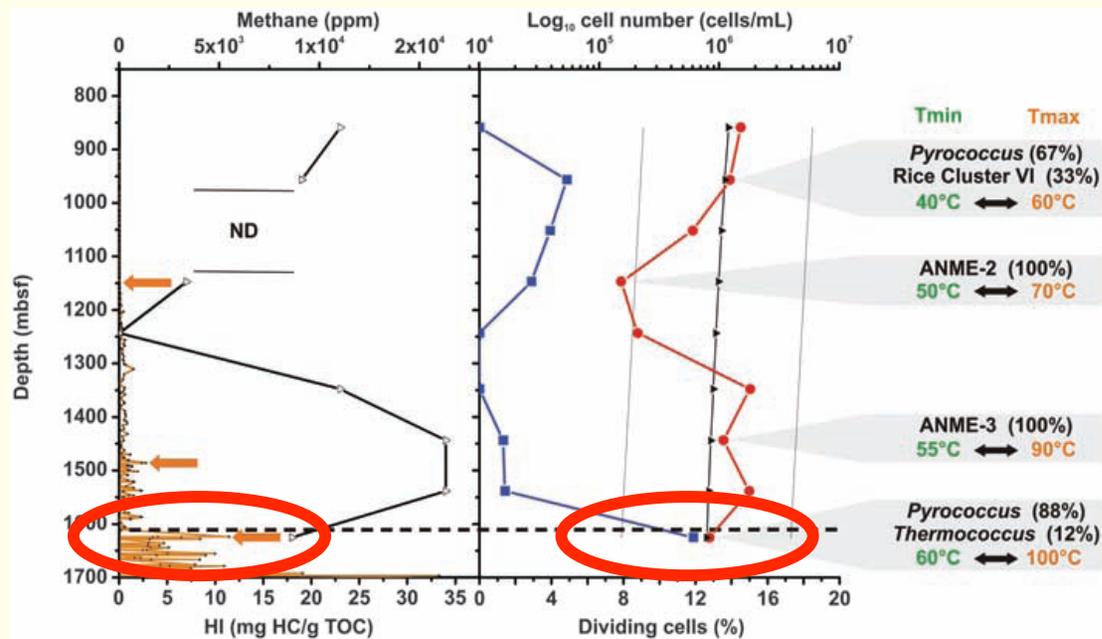
- What are the P - T limits of deep life?
 - *Most estimates suggest $T < 130^{\circ}\text{C}$* [Kashefi & Lovley *Science*, (2003)]
 - *Recent reports hint at biological activity at $T > 200^{\circ}\text{C}$* [Kelley et al. *AGU Fall Meeting*, (2004); Dong et al. (2010) China DCO meeting]
- What is the extent (biomass) of deep life?
 - *Some recent estimates exceed 50%* [Pfiffner et al. *Geomicrobiol J* (2006)]
- How do deep microbes survive?
- Can we take advantage of deep life's unique biochemistry for technological applications: i.e., sequestration, remediation, or prospecting?



Ocean drilling is revealing an extremophile microbial biosphere in ancient sediments at depths greater than 1 km.

Extending the deep sub-seafloor biosphere

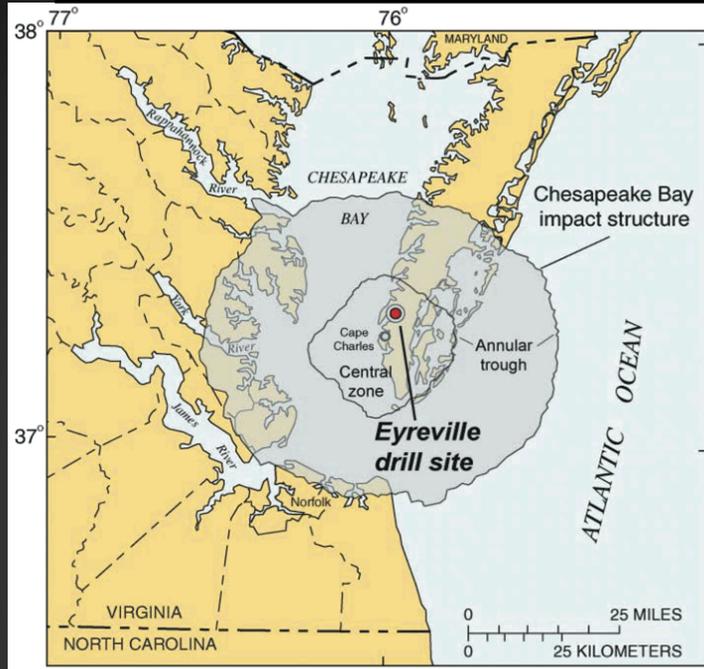
[Roussel *et al.*, *Science* (2008)]



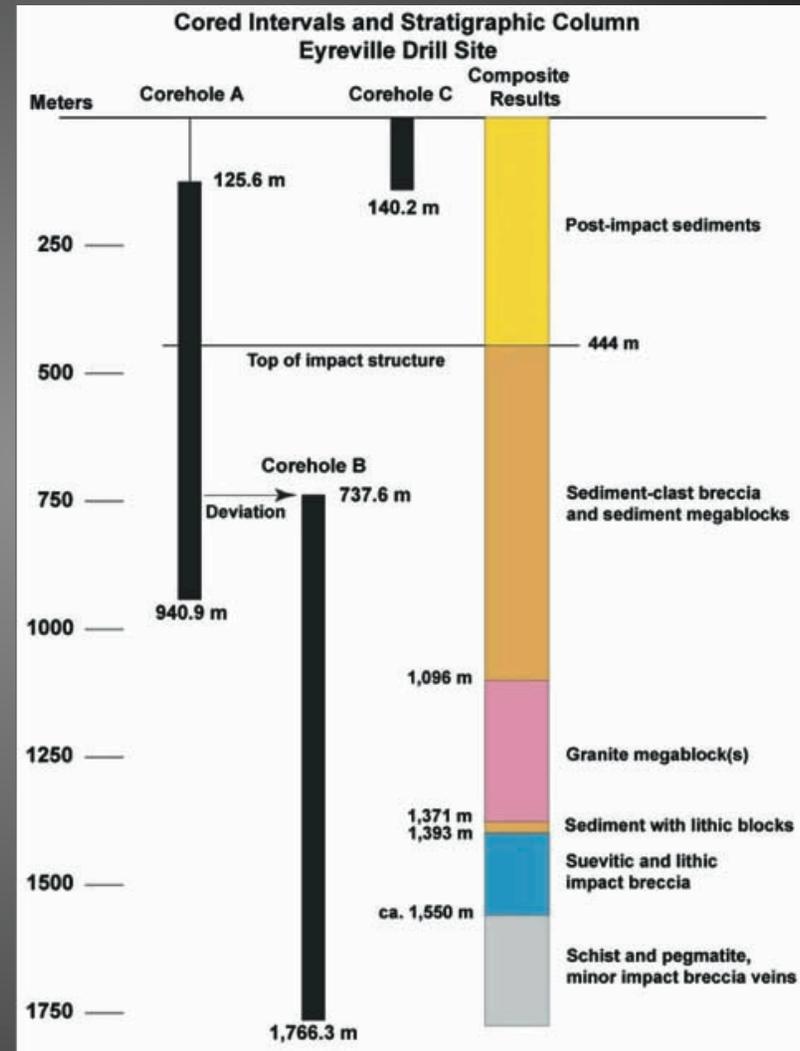
Low diversity of Archaea, dominated by
Thermococcus and *Pyrococcus*
Anaerobic CH₄ oxidizers
111 My sediments



Deep Microbial Life – Drilling

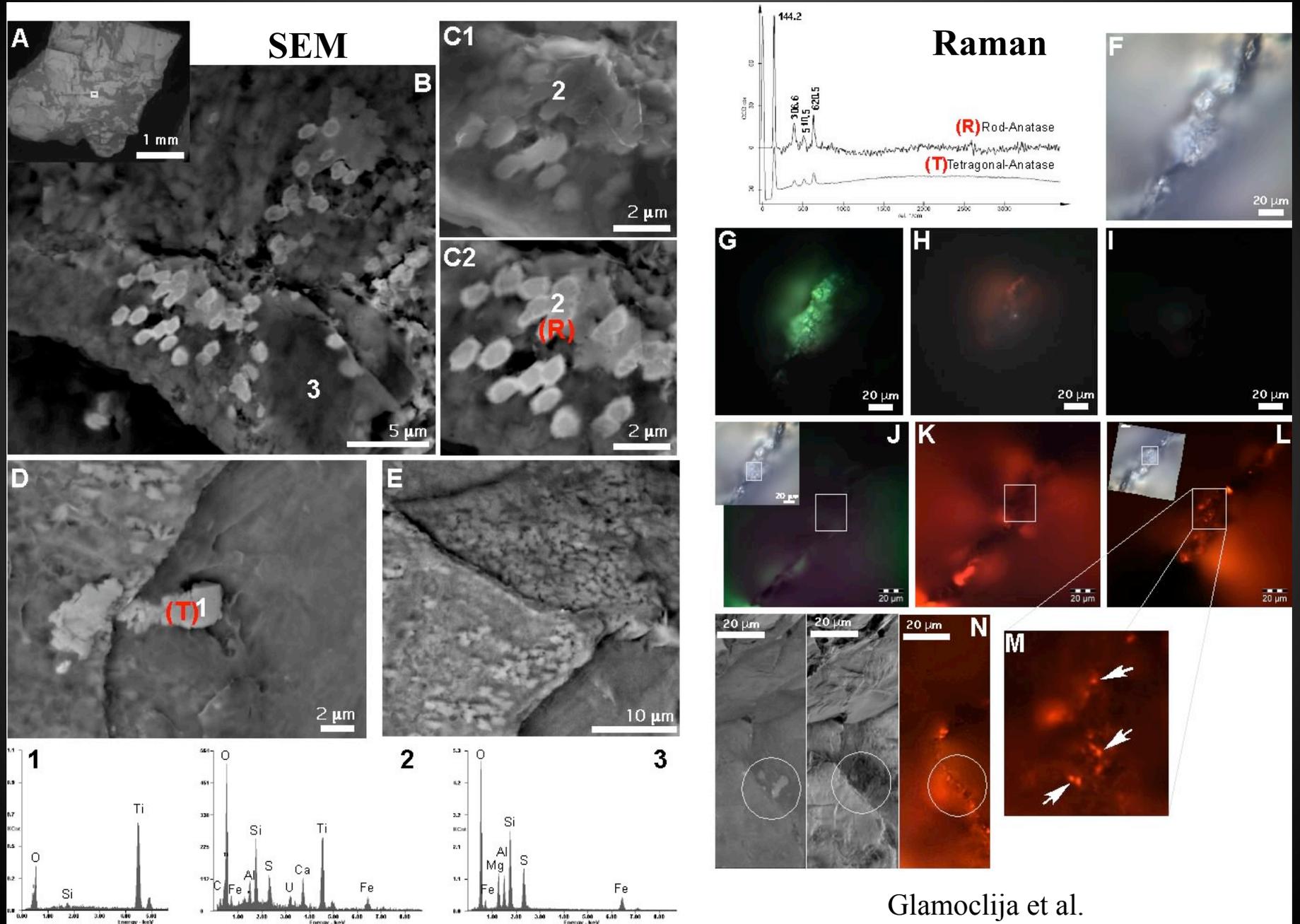


Eyreville drill site.



Gohn et al. 2006

Microbes from a pyrite vein within the biotite granite mega block from 1,353m depth.



Glamoclija et al.

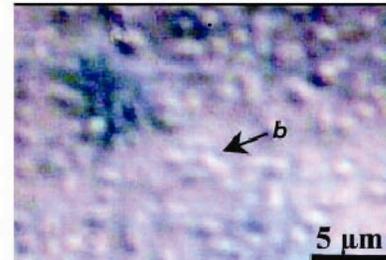
In situ experiments reveal that life can persist to pressures > 14,000 atmospheres

22 FEBRUARY 2002 VOL 295 SCIENCE

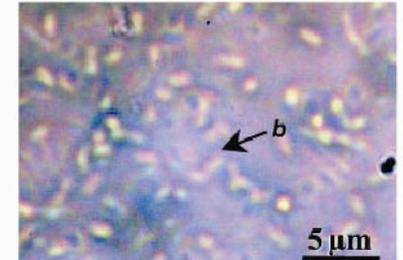
Microbial Activity at Gigapascal Pressures

Anurag Sharma,* James H. Scott,* George D. Cody,
Marilyn L. Fogel, Robert M. Hazen, Russell J. Hemley,
Wesley T. Huntress

Shewanella MR1



Escherichia coli



Before compression
0.1 MPa

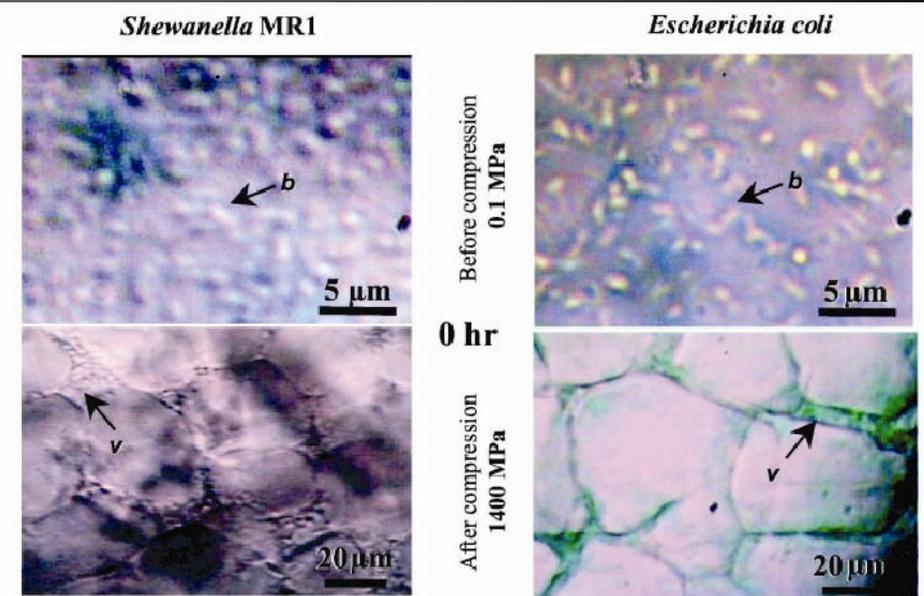
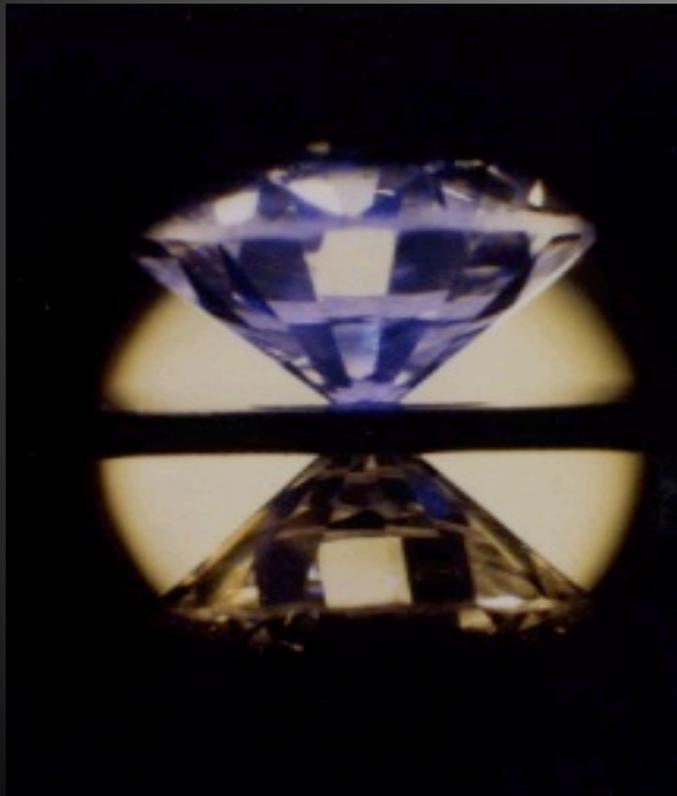


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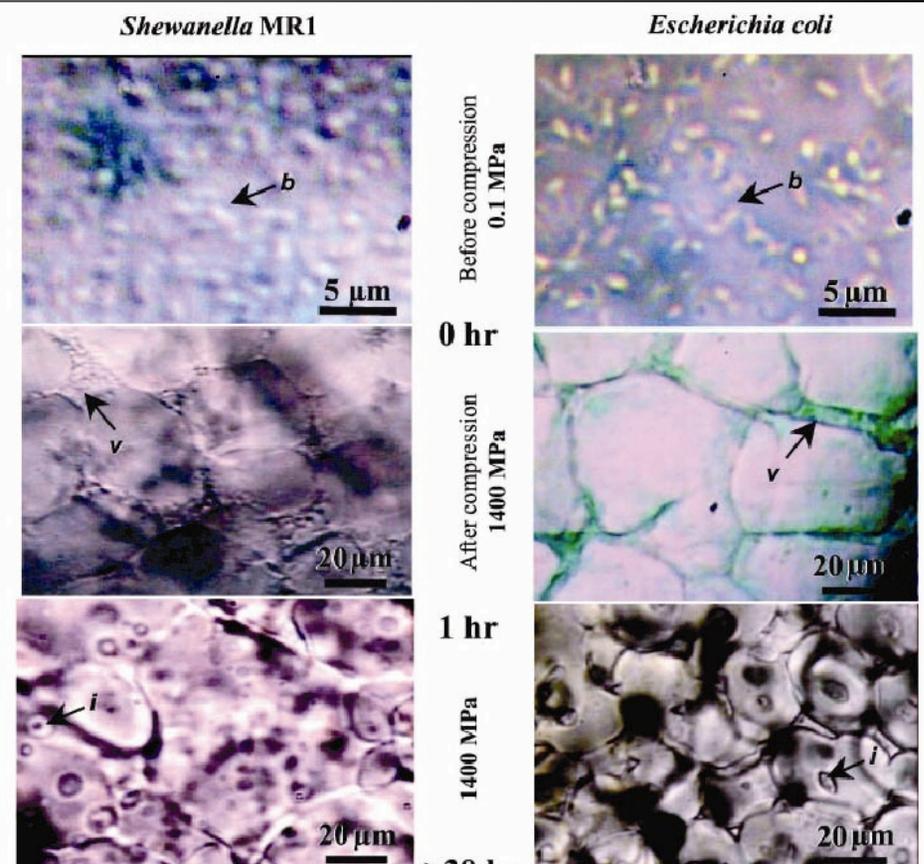


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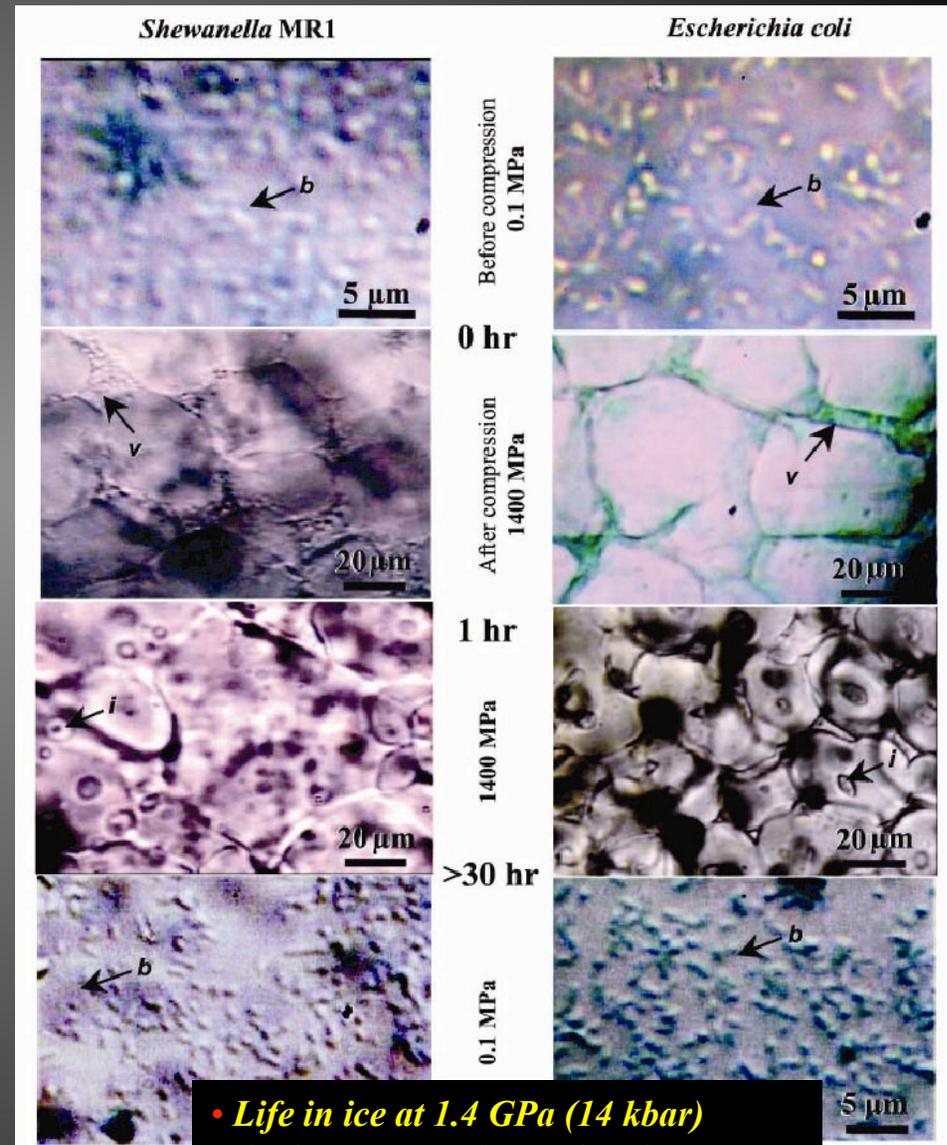


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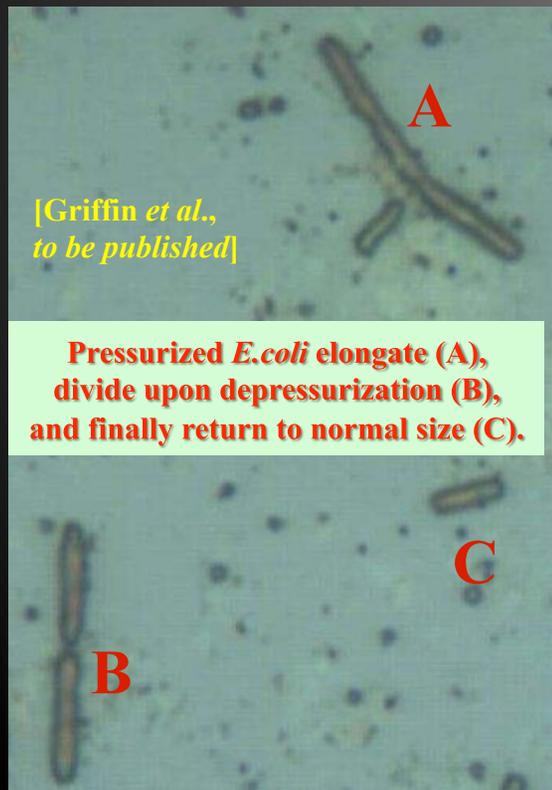
- Life in ice at 1.4 GPa (14 kbar)
- Archaea, Bacteria, and Eukarya

In situ experiments reveal that life can persist to pressures > 14,000 atmospheres

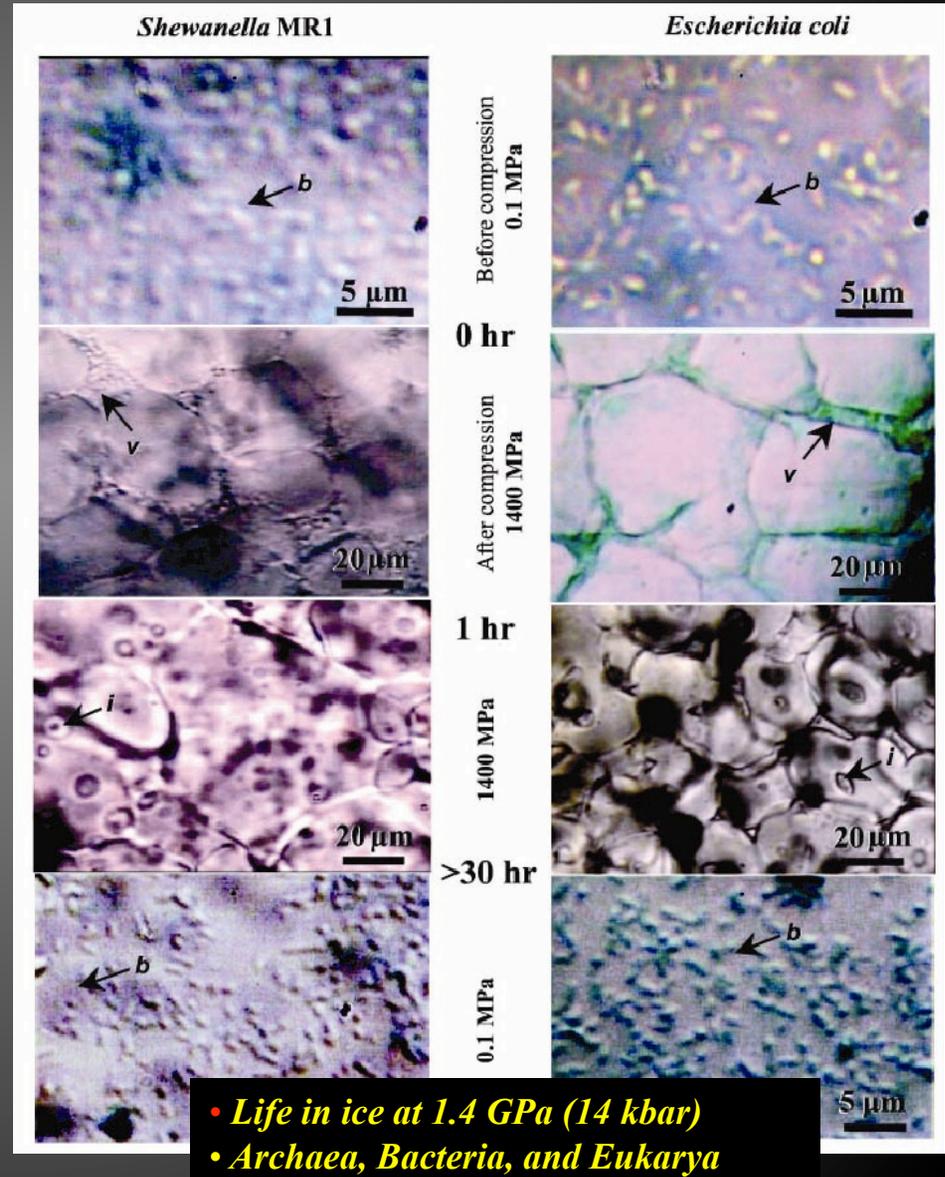
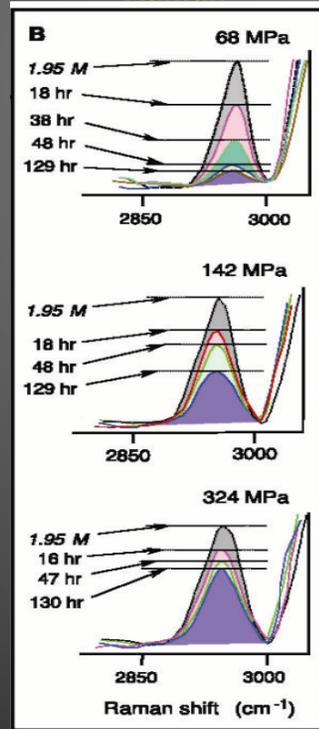
22 FEBRUARY 2002 VOL 295 SCIENCE

Microbial Activity at Gigapascal Pressures

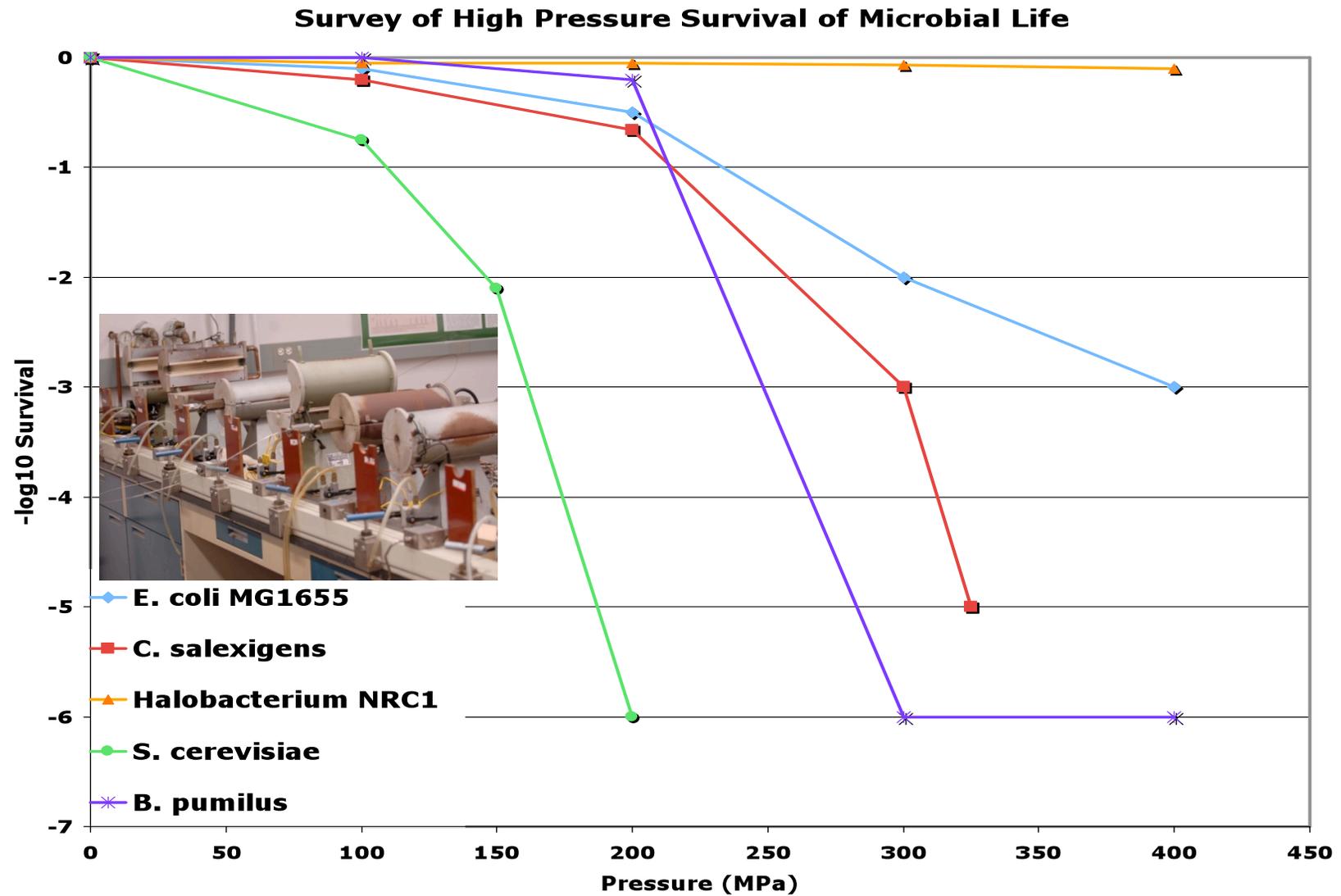
Anurag Sharma,* James H. Scott,* George D. Cody,
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Wesley T. Huntress



Nutrient Uptake Raman



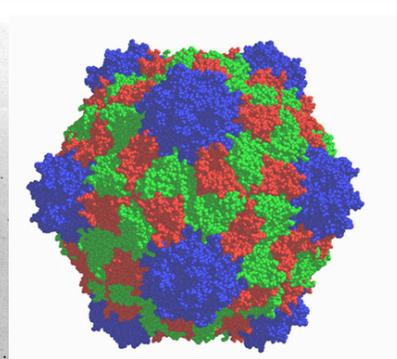
Surveys demonstrate high-pressure viability.



[Kish *et al.*, to be published]

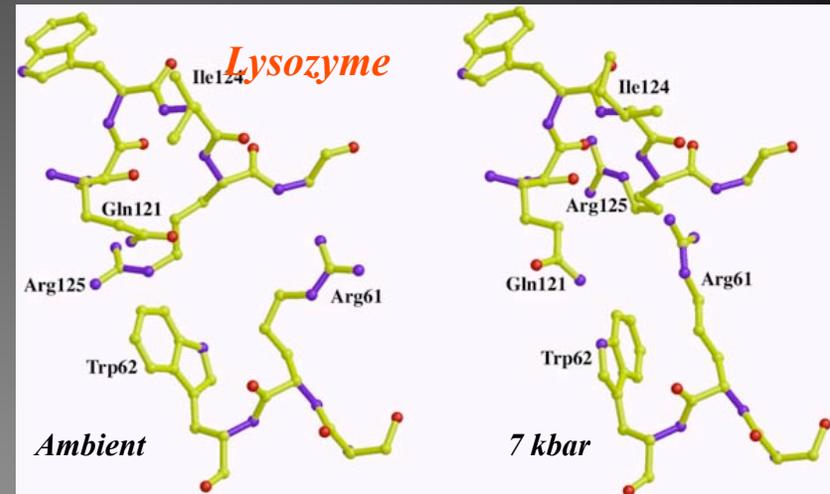
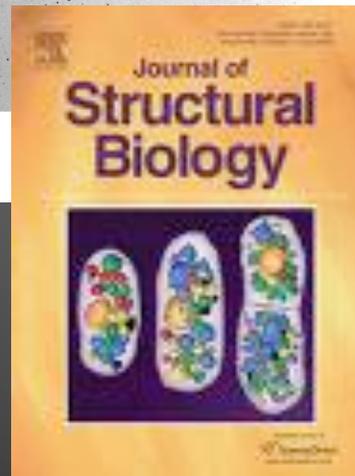
These findings require new probes of structure-property relations in biomolecules

Single Crystal
Diffraction of Cow
Pea Mosaic Virus



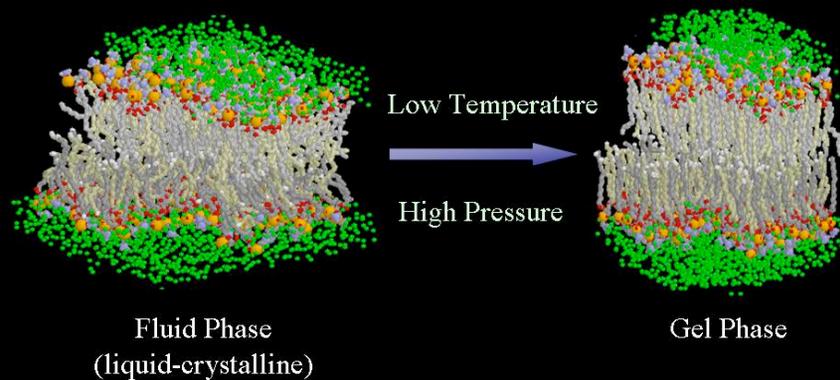
3.5 kbar

[Lin *et al.*, *Acta Cryst. D* (2005)]



[Fourme *et al.* (2002)]

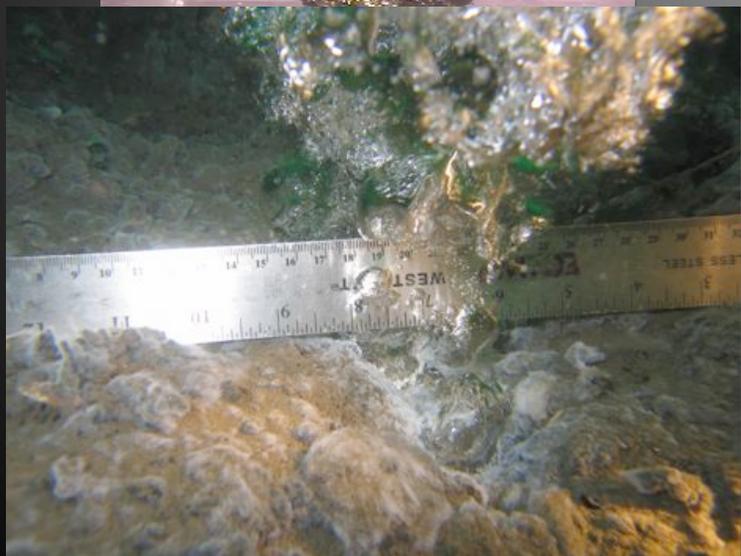
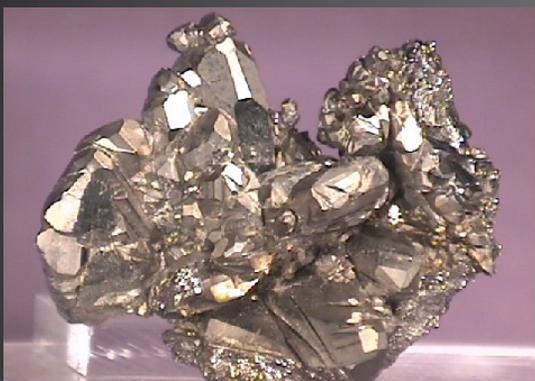
Pressure / Temperature Effects on Membranes



[after Bartlett, Sloan Workshop (2008)]

Deep Organic Synthesis and Life

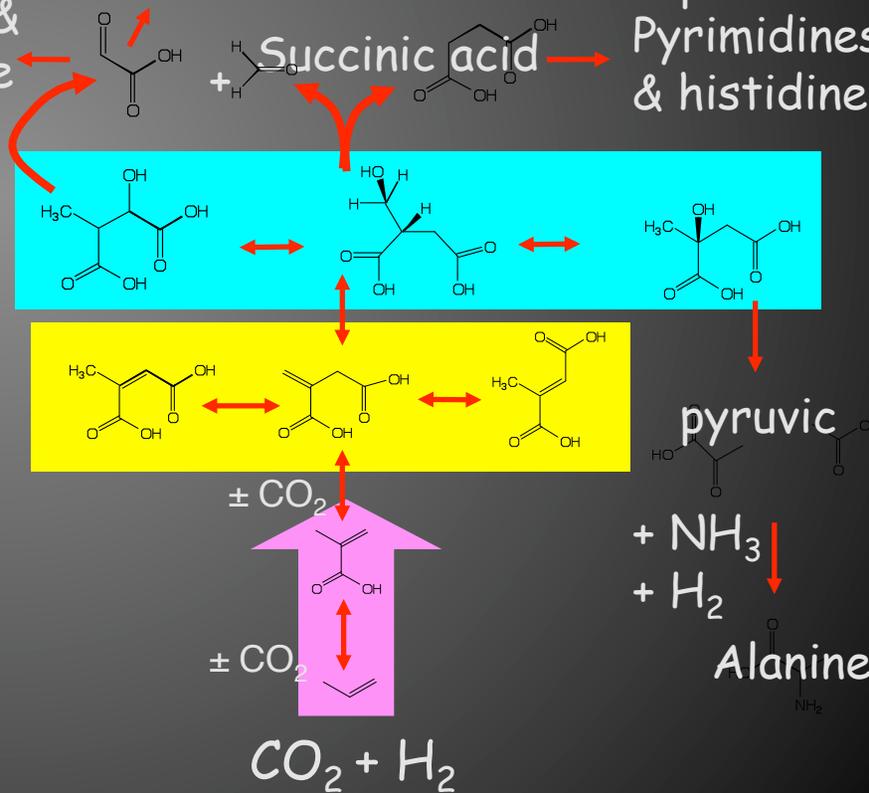
Did deep organic synthesis contribute to the origins of life?



Towards Serine & cysteine

To glycine

Towards aspartate Pyrimidines & histidine



(Cody et al. 2001, 2004)

There are fundamental gaps in our understanding of deep carbon.

- 1. We do not know how much carbon is stored within the Earth, nor do we know the nature of those deep repositories.*
- 2. We do not know how carbon moves from one deep repository to another, nor do we know the extent to which carbon moves to and from Earth's surface.*
- 3. We do not know the physical and thermochemical properties of deep carbon-bearing fluids, nor do we know how these fluids migrate within the deep interior and to the surface.*
- 4. We have only vague hints of a potentially vast deep microbial biosphere; we do not know the nature or extent of this deep ecosystem, nor do we know the potentially unique biochemical characteristics of deep life.*
- 5. We do not know the nature of the deep carbon cycle, nor how it might impact societal issues concerning energy, environment and climate.*



Thank You!

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