Multiple-length-scale Study of Sandstone for Carbon Sequestration

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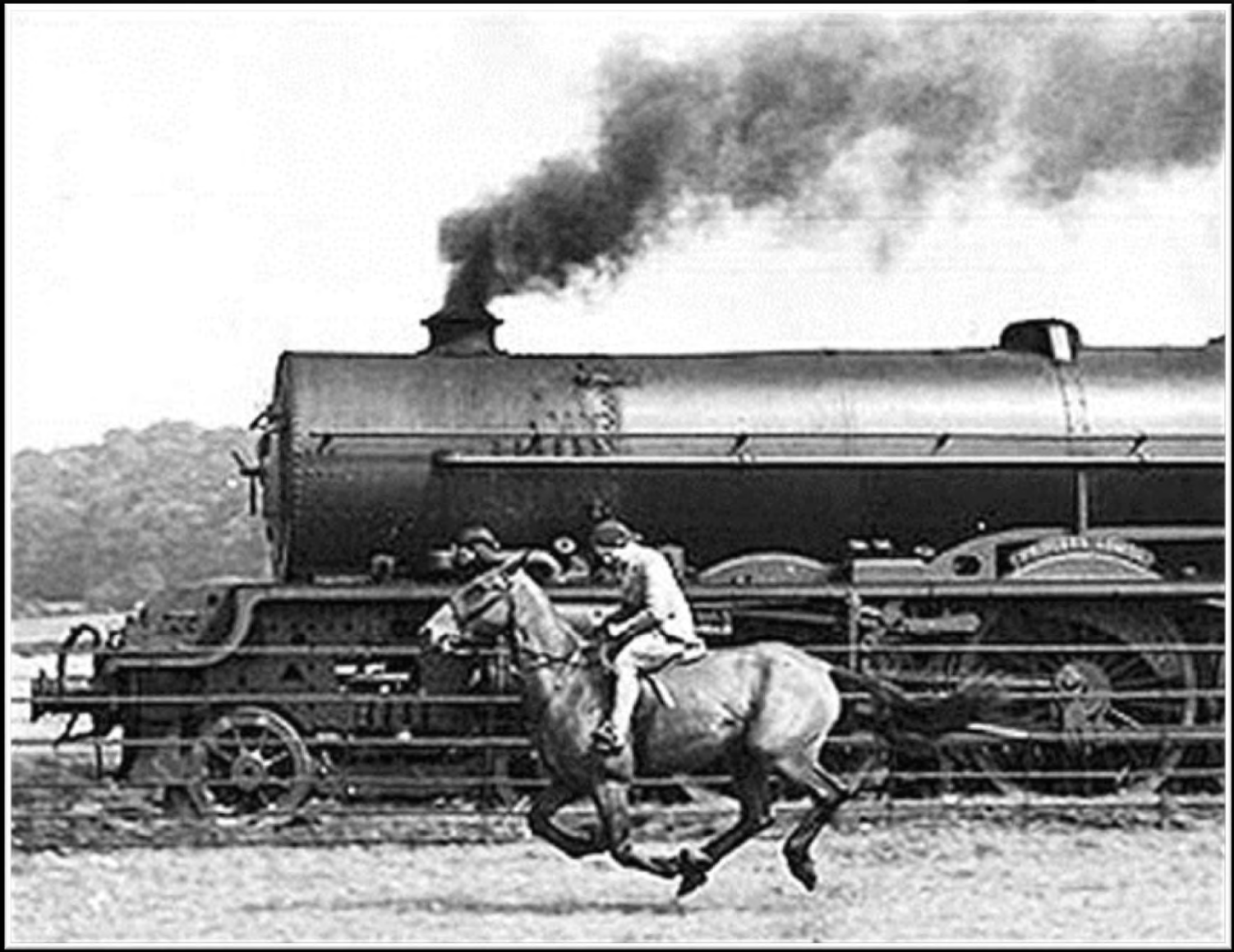
U.S. DEPARTMENT OF ENERGY
Office of Science

SLAC NATIONAL ACCELERATOR LABORATORY

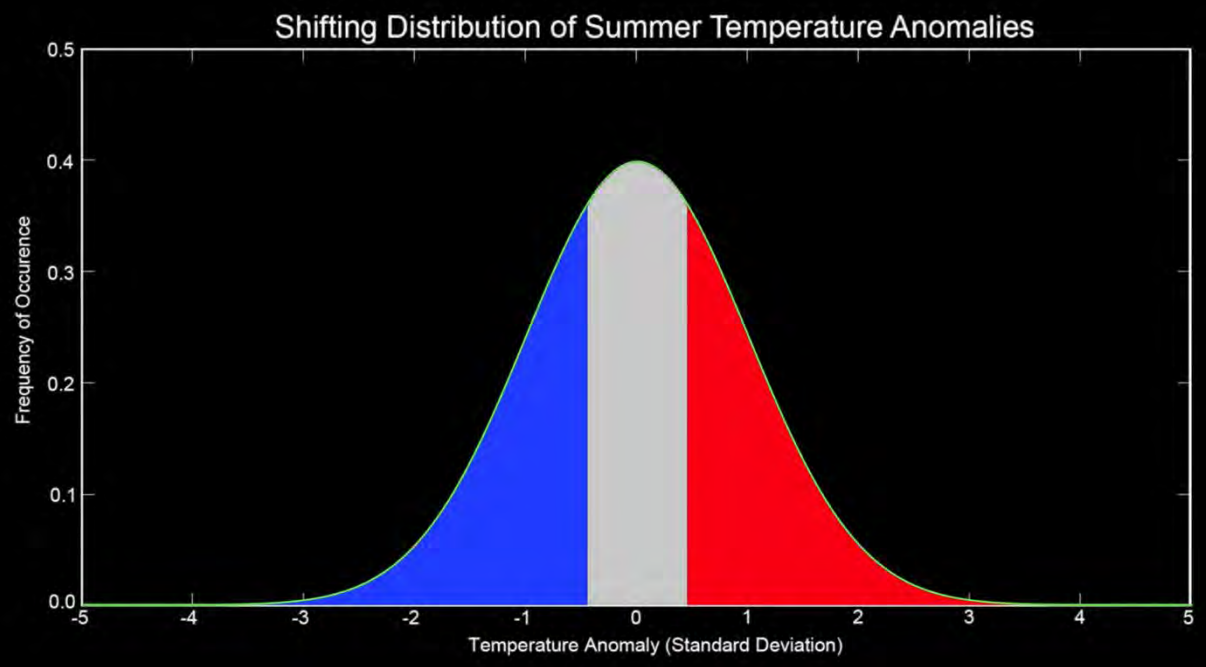
From “horse power” to “horsepower”



The industrial revolution has changed the world dramatically.

The horsepower comes with cost to us

There are side effects to the use of fossil fuels such as global worming



rk Times

National Edition

Northern California: Morning coastal clouds. Sunny. Hot inland valleys. Highs 60s to upper 90s. Clear tonight except some coastal clouds. Weather map, Page A18.

1, 2013 Printed in California $2.50

Heat-Trapping Gas Passes Milestone, Raising Fears

CO_2 at Level Not Seen in Millions of Years, Portending Major Climate Changes

By JUSTIN GILLIS

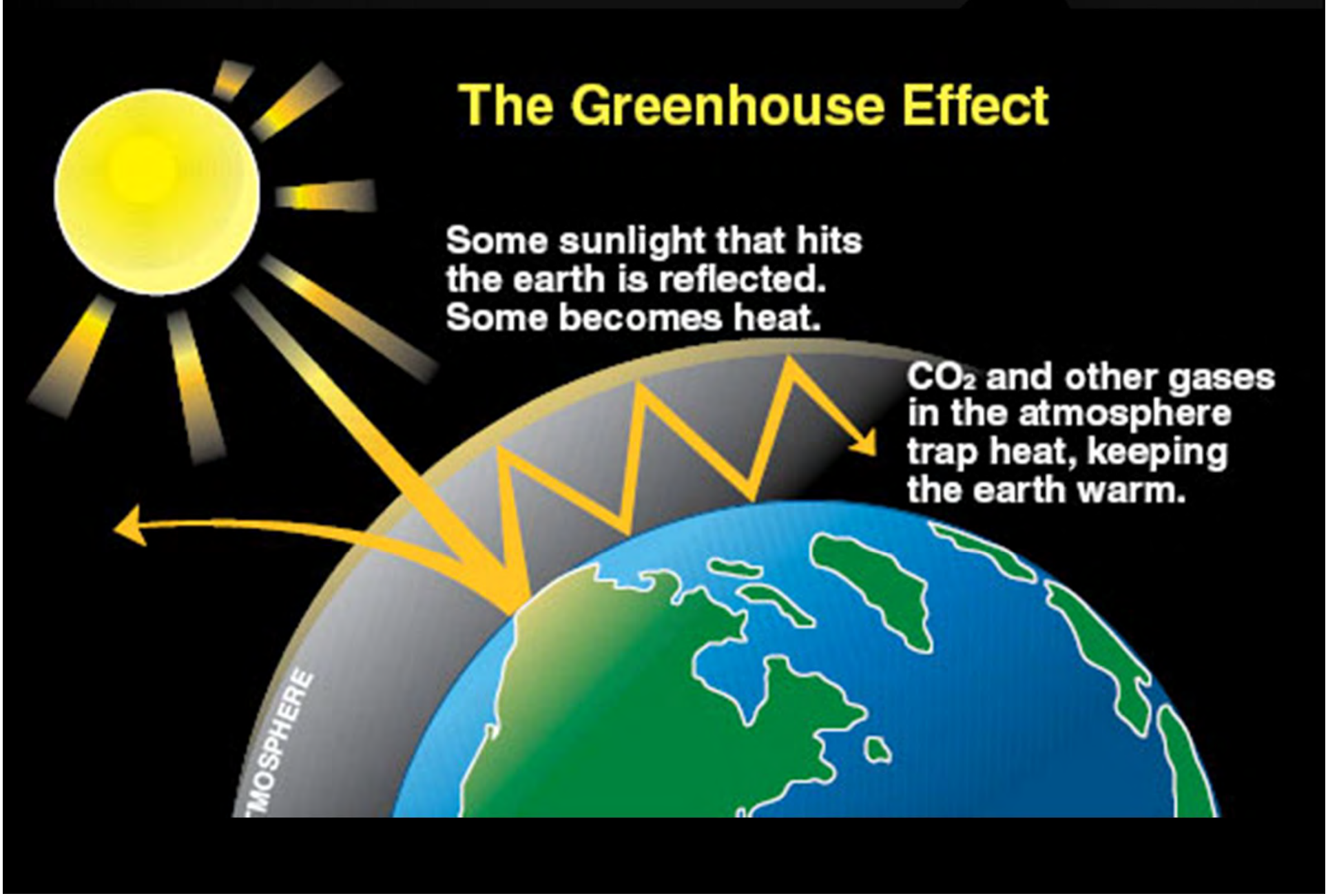
The level of the most important heat-trapping gas in the atmosphere, carbon dioxide, has passed a long-feared milestone, the high level.

The new measurement came from analyzers atop Mauna Loa, the volcano on the big island of

As the graph moves forward in time, the bell curve shifts to the right, representing an increase in the frequency of the various hot anomalies. It also gets wider and shorter, representing a wider range of temperature extremes.

Movie courtesy of NASA/Goddard Space Flight Center GISS

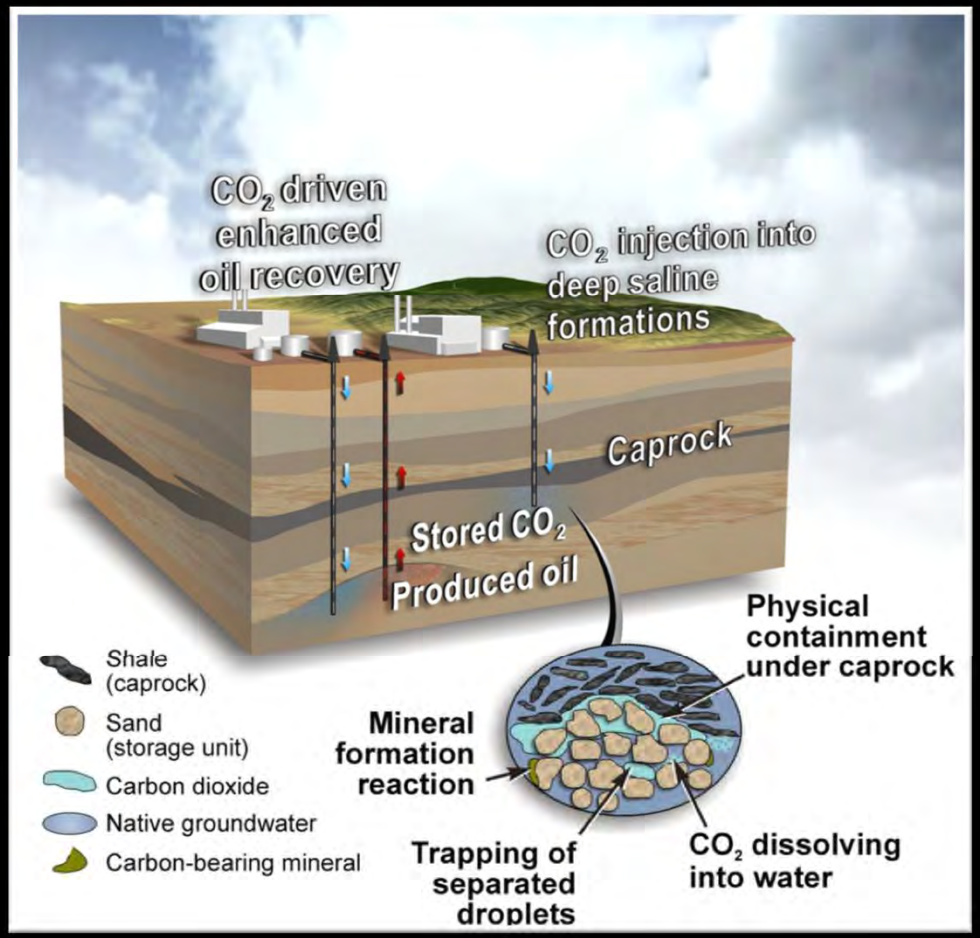
The Greenhouse Effect

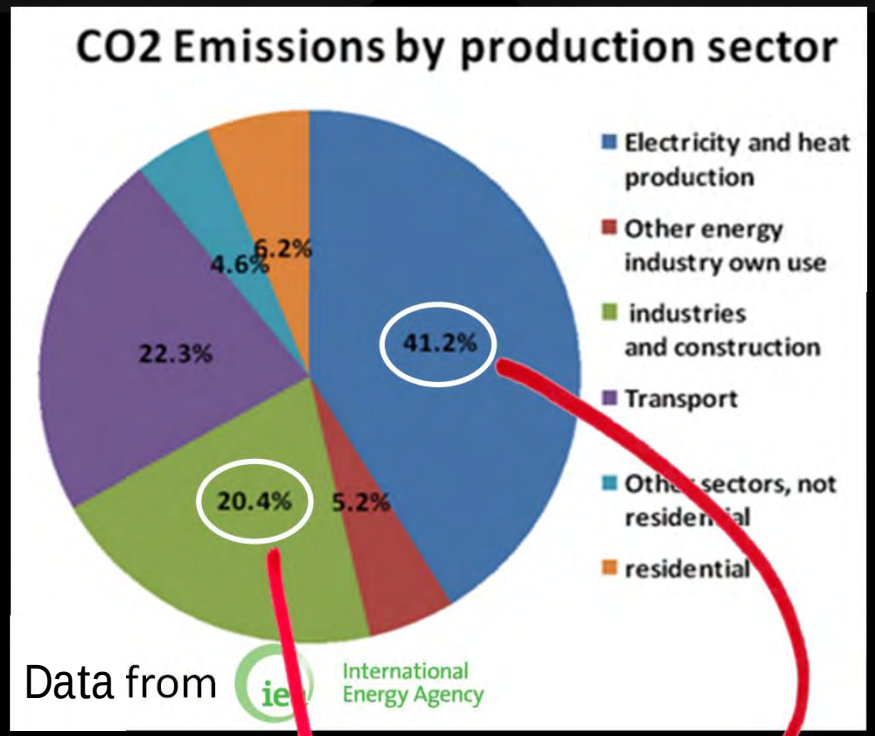


- We have generated 1.1 trillion tons of CO_2 since the industrial revolution (1750s).
- If we burn all the known gas/oil reserves, we will double this number
- This will happen in the next 75-100 years, depending on our lifestyles

What to do?

Geological sequestration of carbon dioxide is an important component of global greenhouse gas emission reduction strategy

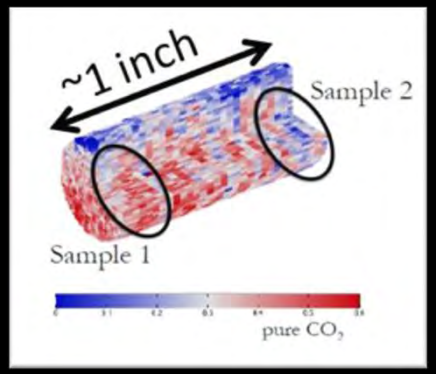


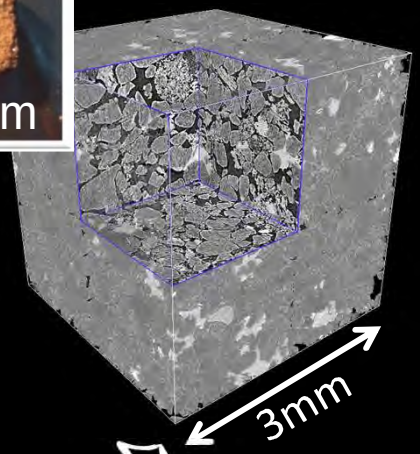


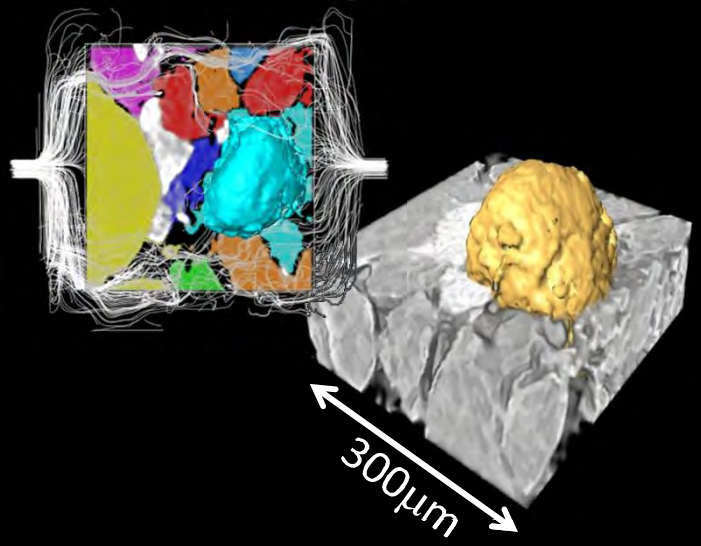
Considerable amount of CO_2 generated by large stationary source making it feasible to capture and then for further treatment

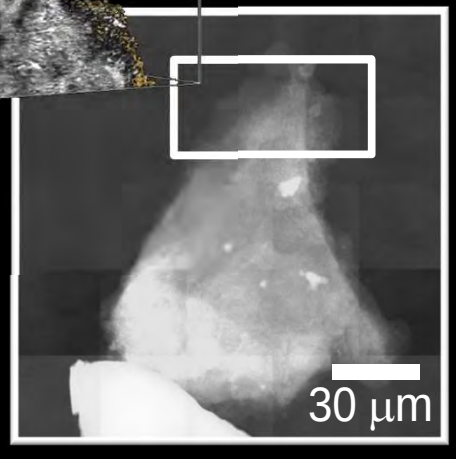
Obviously it is critical to understand and ultimately identify suitable reservoir zones for CO2 injection and storage

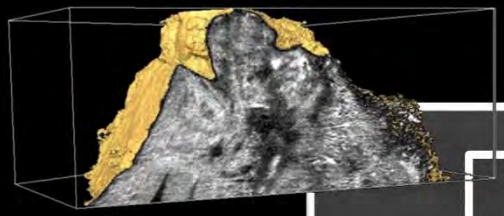
This is a question needs to be addressed at multiple length-scales.











Even smaller

Good resolution and large field view

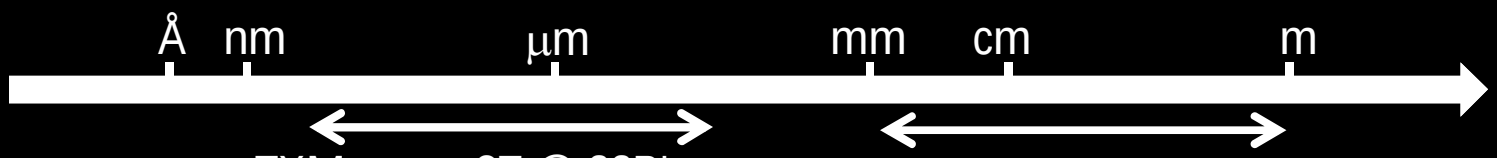
In an ideal world, one would study the sample(s) with very fine spatial resolution over very large area (at least over the minimum representative volume).
Unfortunately, it is not possible/practical.
Many studies desire more than good resolution.

Although (b) provides much better resolution, people choose to use (a) for reading for a good reason.

Spatial resolution ⇄ field of view

We need a suite of complementary techniques to do the job.

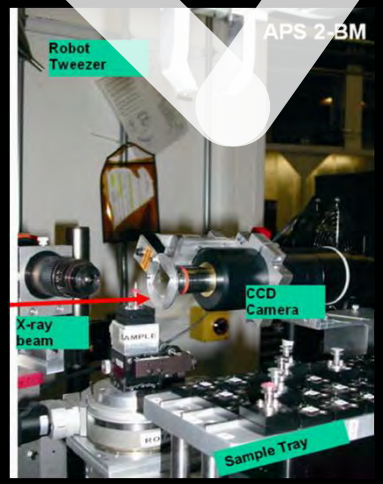
How do we cover the multiple length scales?



TXM nano-CT @ SSRL

Medical CT @ Stanford

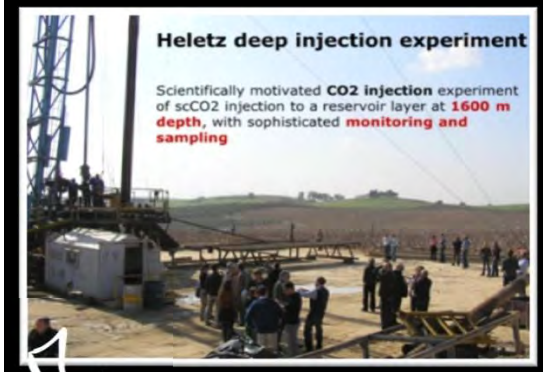
SEM/TEM @ Stanford

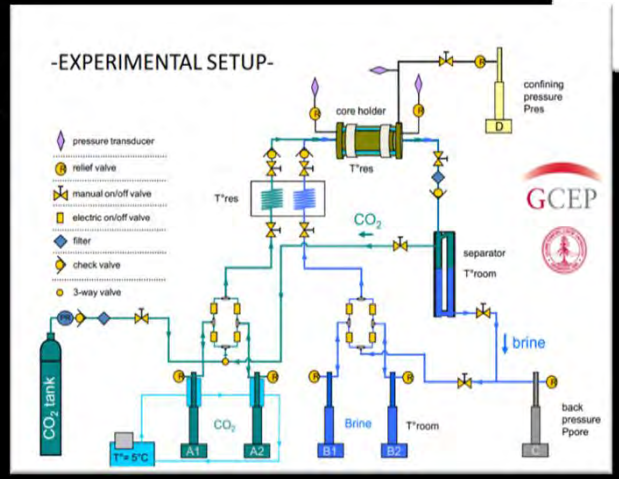


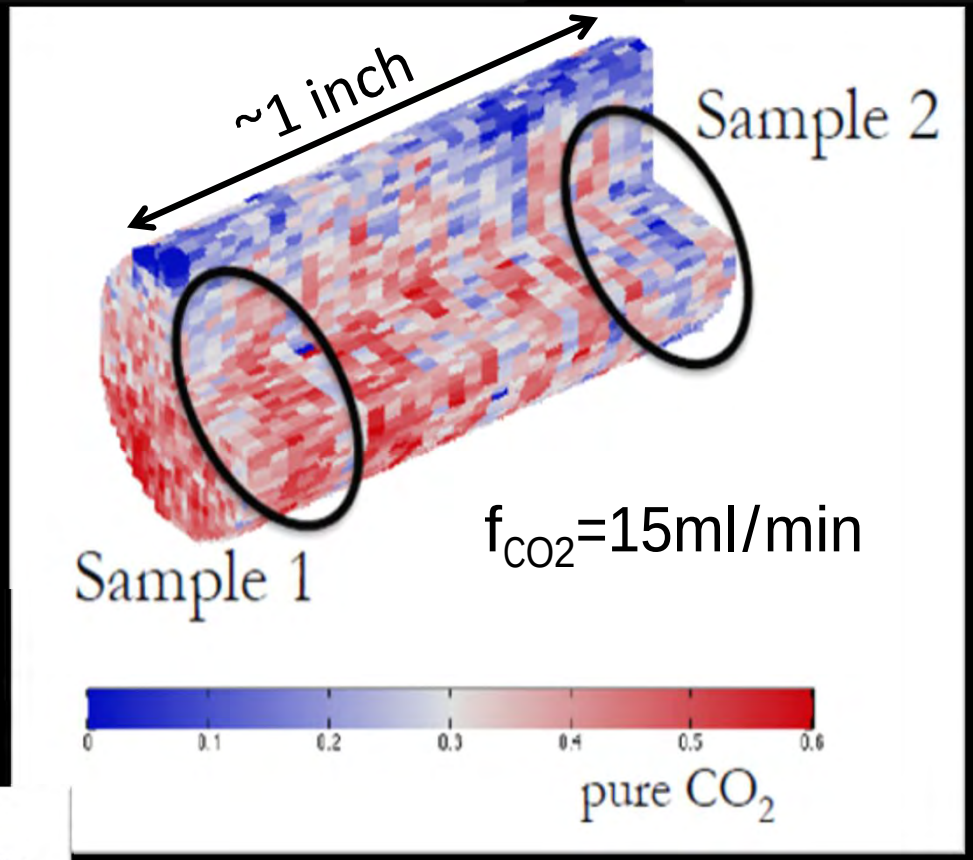
Synchrotron μ-CT @ APS

- X-ray microscopy techniques cover a good range of the length scales.
- Electron microscopy provides ultra high resolution in case needed.

The question we try to answer in this study





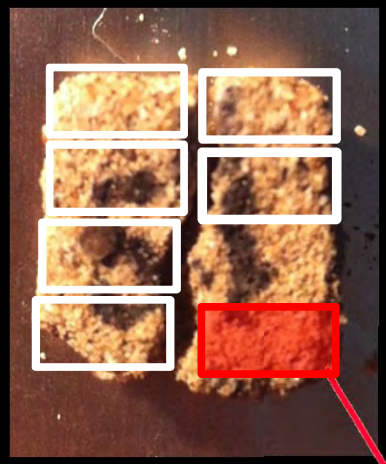


The density measured using medical CT indicates different CO_2 concentration through out the core.

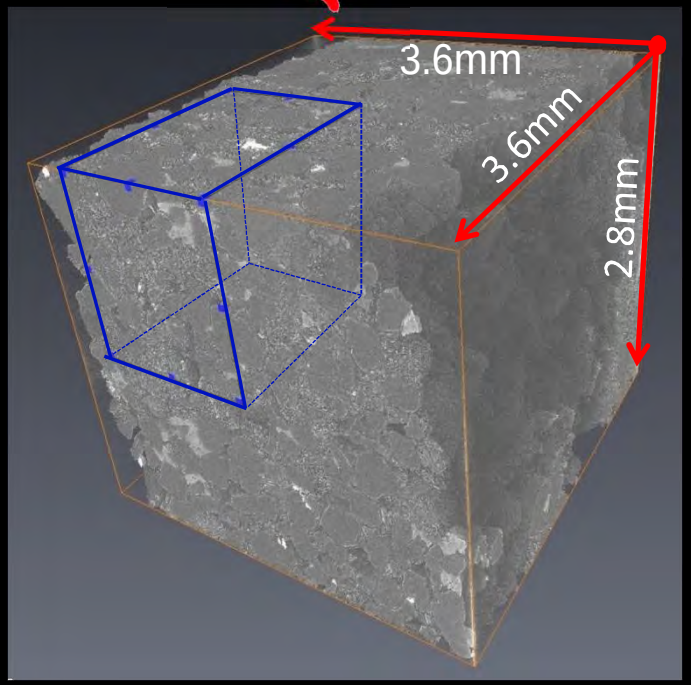
Why the sample 1 and sample 2 shows difference in CO_2 saturation experiment?

How do we manage the “oversized” sample: to break it down

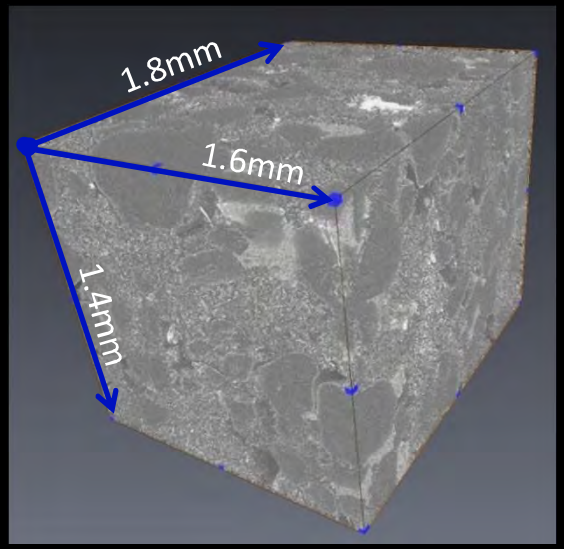
Physically broken down into smaller pieces for μ-CT experiment (limited field of view)



- Several positions on the sample were scanned.
- Each scanned area results in a 3D volume, which is still too big for the computer to handle.

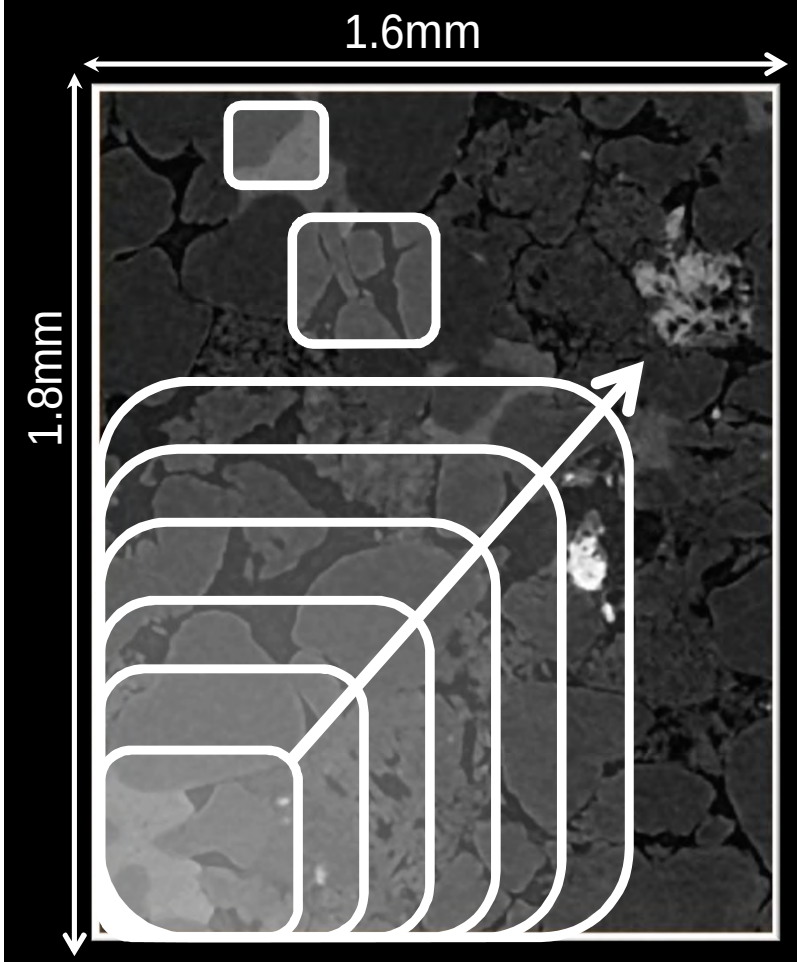


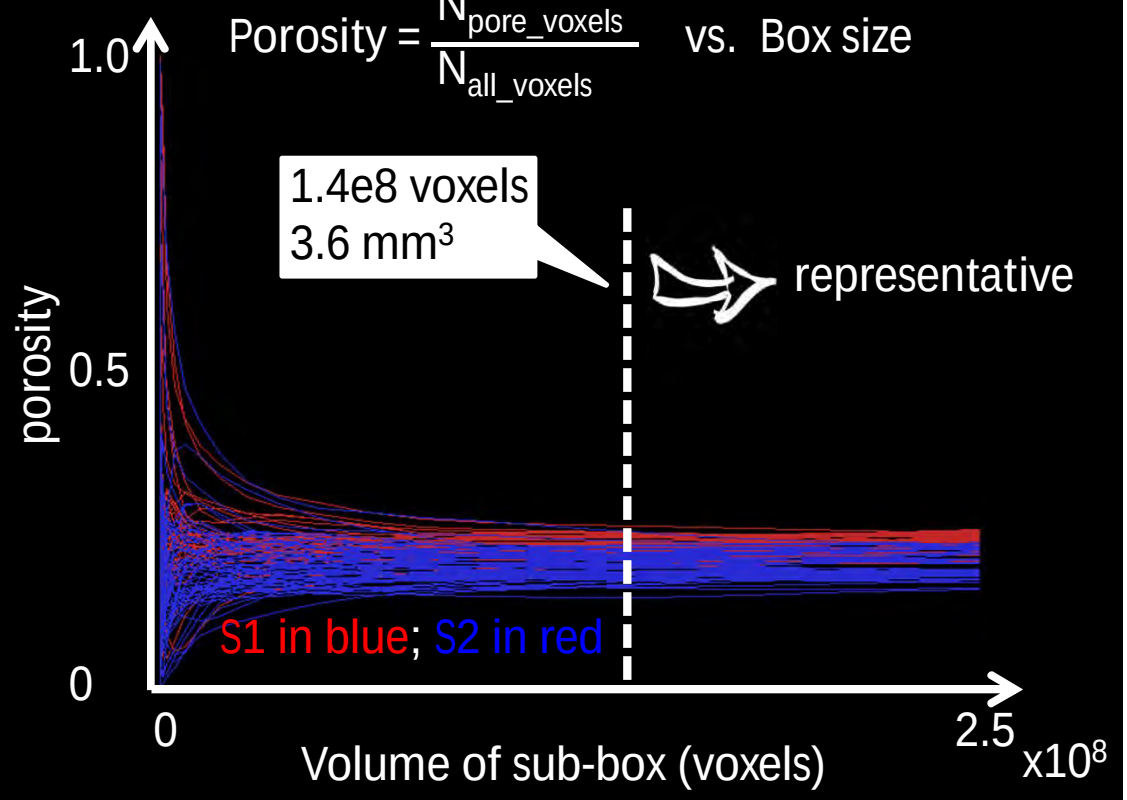
Numerically broken down into smaller pieces for analysis (we have limited computational power)



However, we need to be careful when doing this.
The boxes must be big enough to be meaningful.

The minimum representative volume



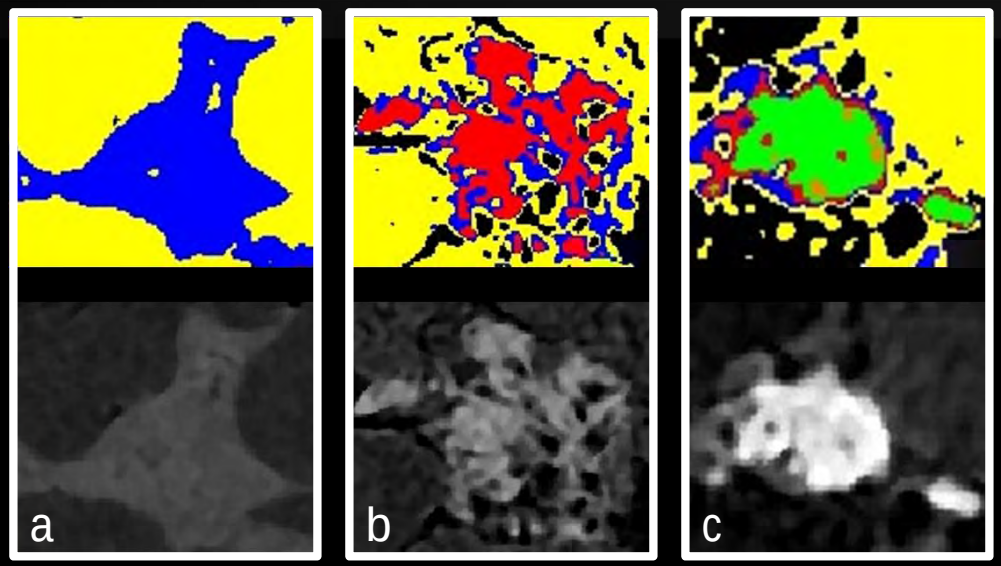


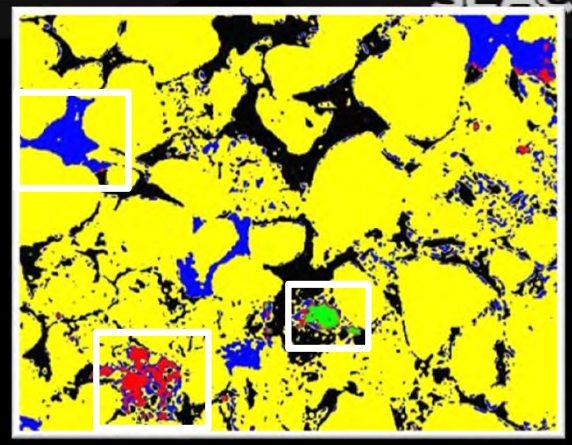
We use porosity to evaluate the "size effect". We expect that it will be convergent as the volumes of the cube grows.

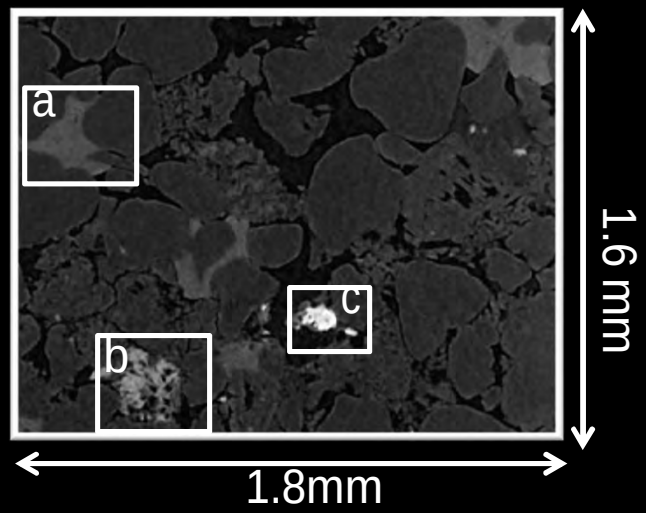
The minimum representative volume is determined as V_{min} =(1.4×10^8 Voxels , 3.6mm^3)

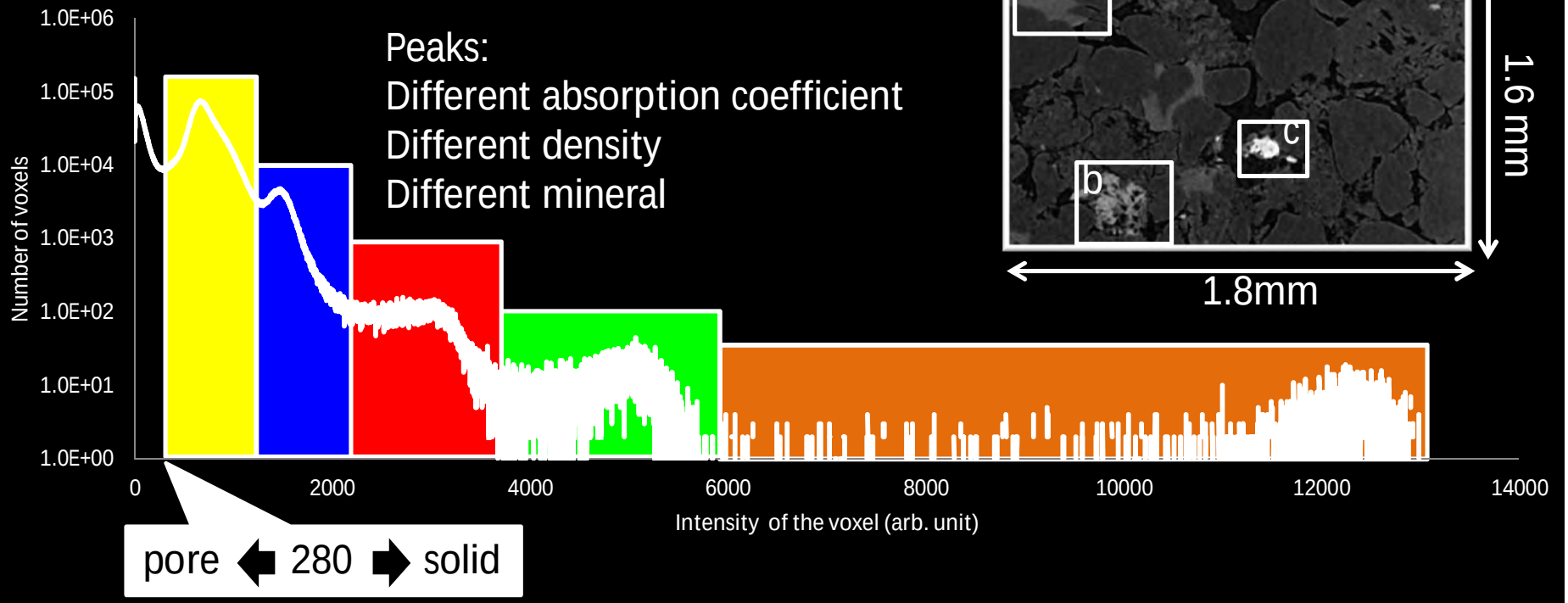
We get 36 sub-boxes for each sample, provided good and meaningful statistics.

Histogram helps for identifying different minerals

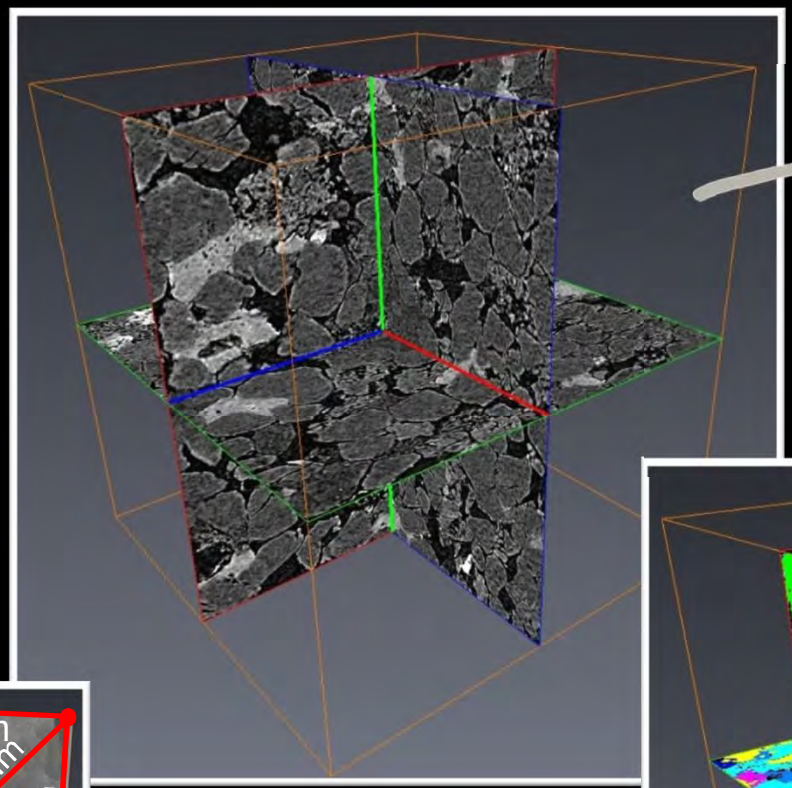




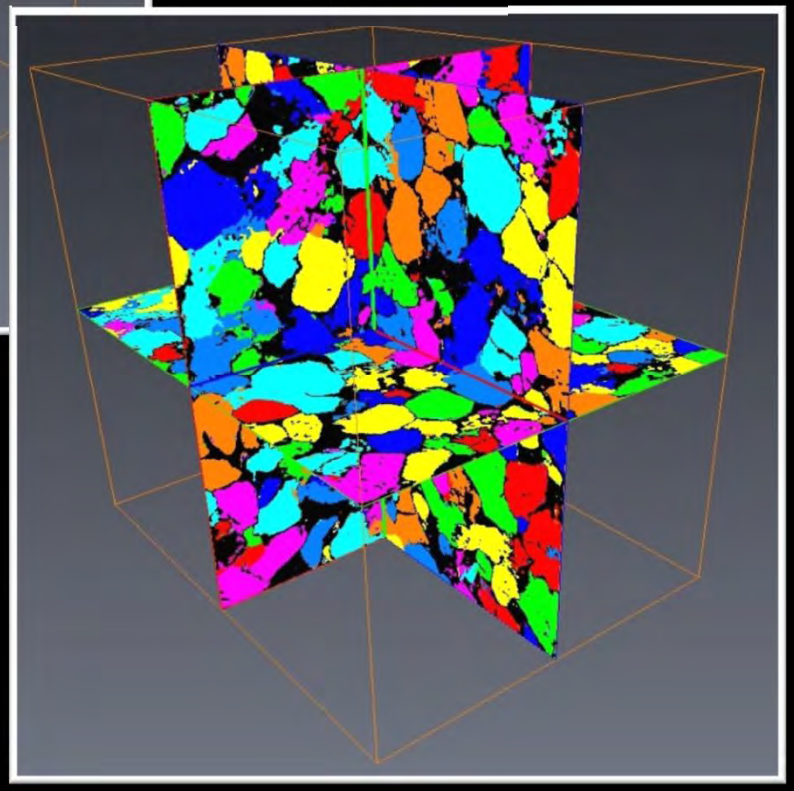




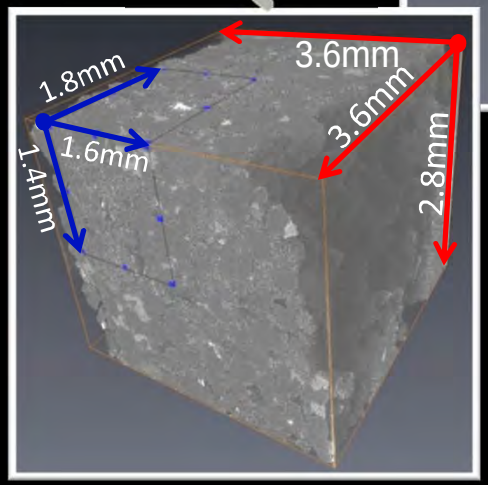
Segmentation beyond histogram-based thresholding



Separation and labeling give each individual grain an ID, enabling a lot of sophisticated statistical analysis



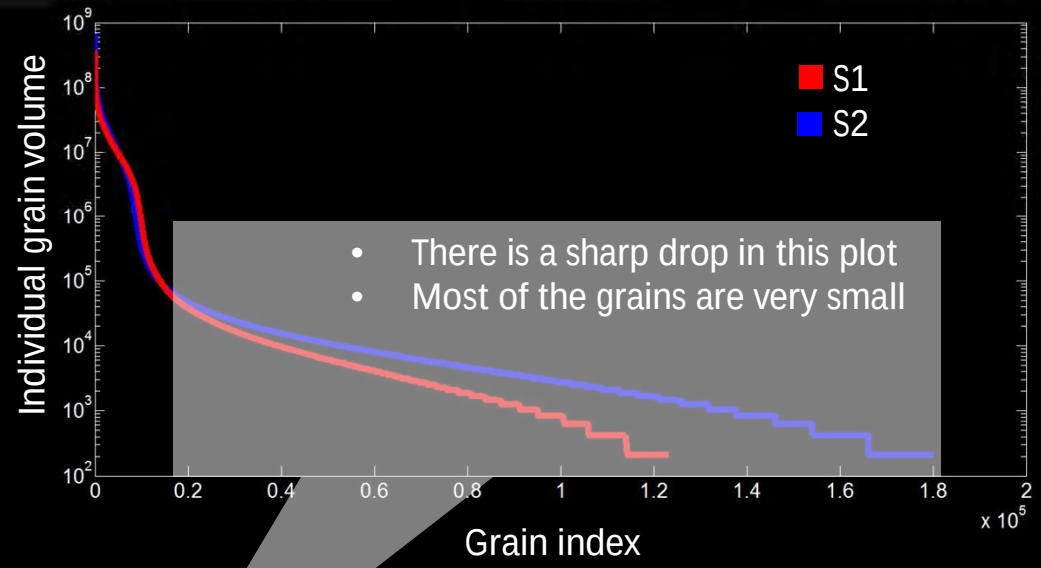
Histogram helps for identifying different minerals



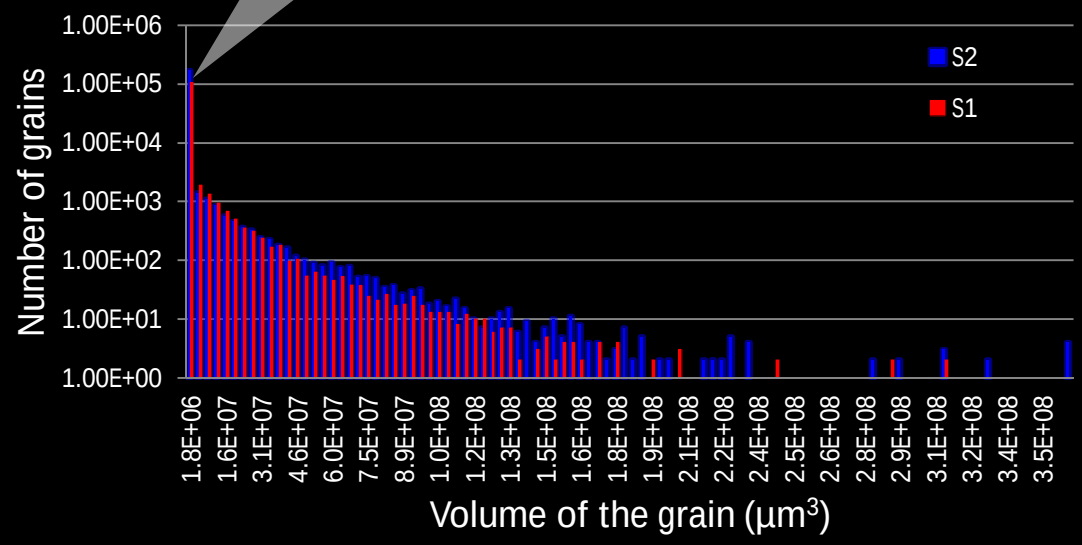
The size distribution of all the grains in S1 and S2

index	$V_{S1_particle}$ (µm³)	$V_{S2_particle}$ (µm³)
1	3.65E+08	6.56E+08
2	3.57E+08	3.94E+08
3	3.12E+08	3.79E+08
4	3.12E+08	3.78E+08
5	2.90E+08	3.57E+08
6	2.88E+08	3.37E+08
…	…	…
…	…	…
…	…	…
124733	207	1.45E+03
124734	207	1.45E+03
124735	207	1.45E+03
…		…
…		…
…		…
180220		207
180221		207
180222		207

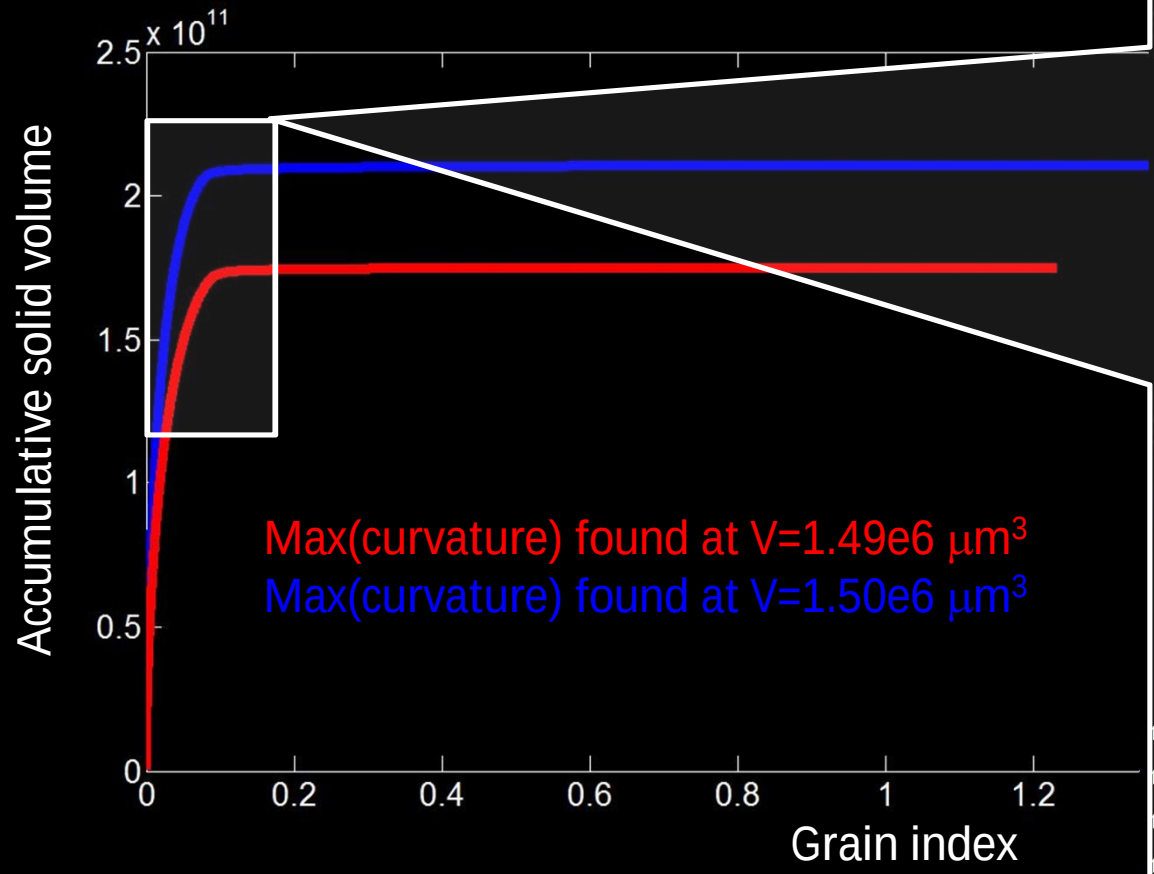
(Smallest : 8 voxels, 207µm³)

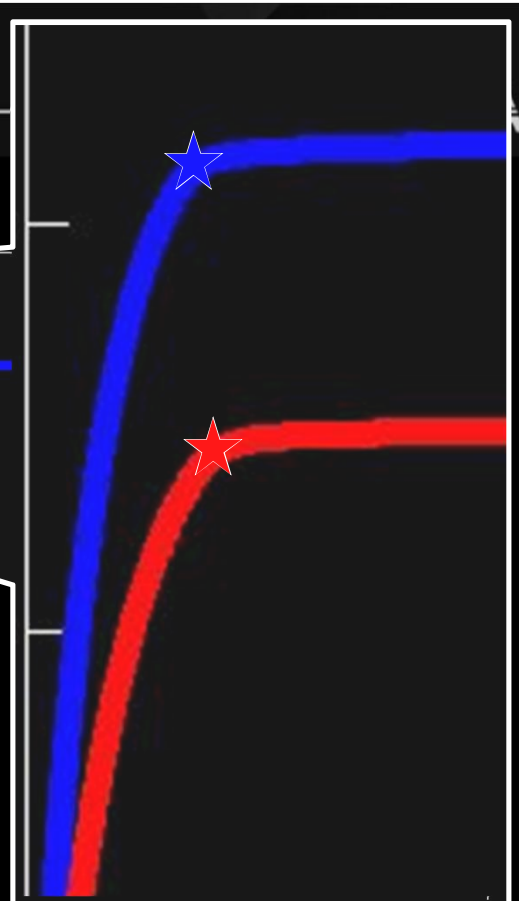


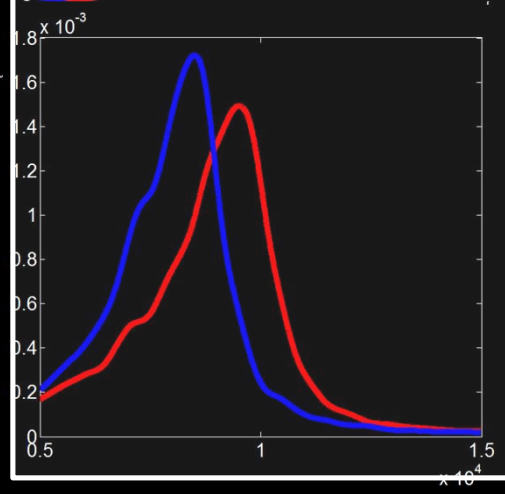
Histogram of the particle size



We group the grains into two categories







First few thousand big grains made up the most volume of the solid phase.
Both turning points (defined as the maximum of the curvature) are found at V ≈ 1.5 e6 μm^3.
The particles are thus grouped into two categories: the "big" and the "small".

The characteristics of the samples we studied

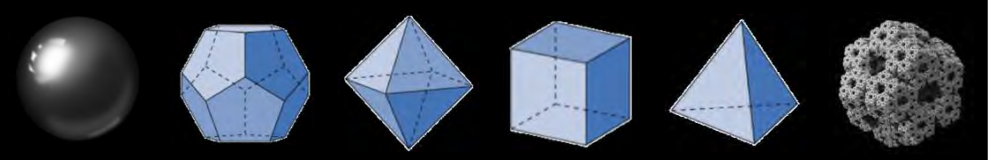
There are 36 representative sub-boxes for S1 and another 36 for S2.
We choose these 9 parameters to describe their characteristics.

- $Porosity_{total}$
- $Porosity_{connected}$
- $Porosity_{connected}/Porosity_{total}$
- $S_{connected_pore}$
- Shape factor: $\varepsilon_{connected_pore}$
- N_{big}
- N_{small}
- V_{small}/V_{total}
- Average V_{big}

$Porosity_{total}=N_{pore_voxels}/N_{all_voxels}$

$Porosity_{connected}=N_{connected_pore_voxels}/N_{all_voxels}$

$\varepsilon_{connected_pore}=V_{connected_pore}^{1/3} / S_{connected_pore}^{1/2}$

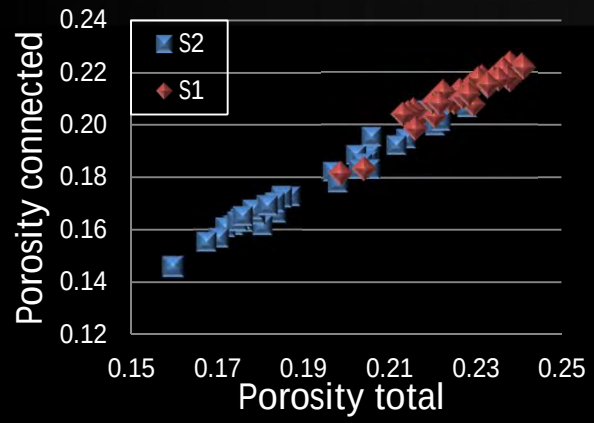


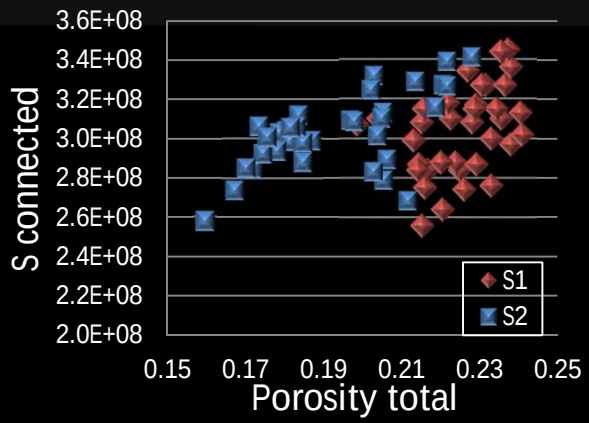
ε= 0.4547 0.4339 0.4182 0.4082 0.3725 ~0

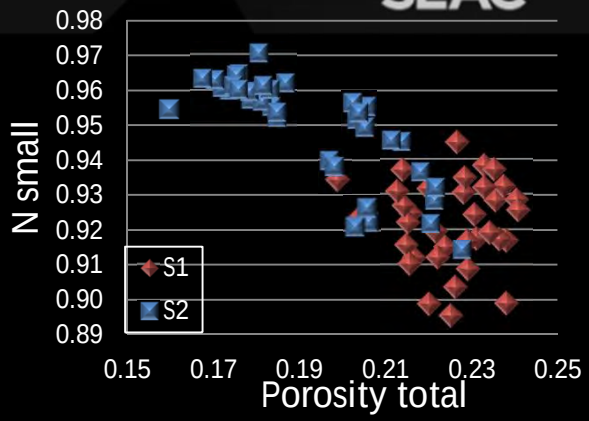
A measurement of the morphological complexity.

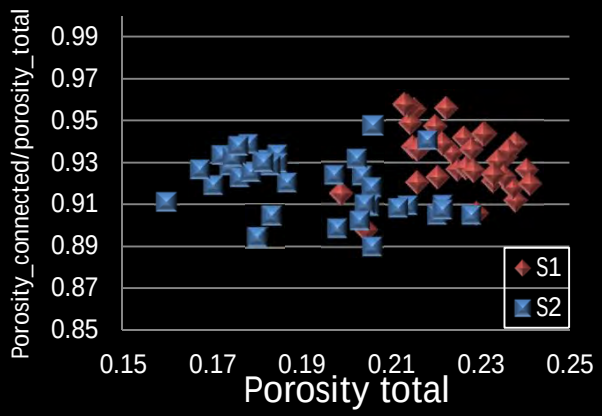
More can be introduced as needed...

The correlation of different parameters

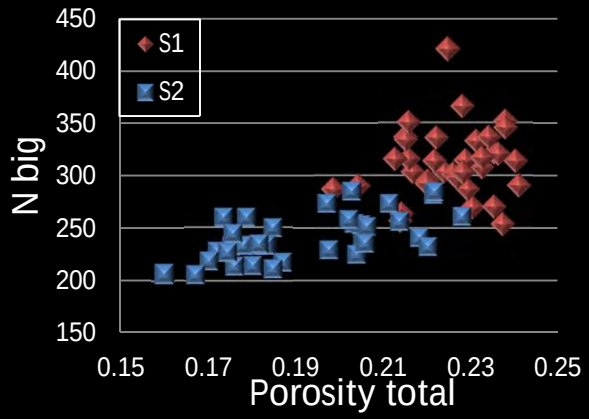


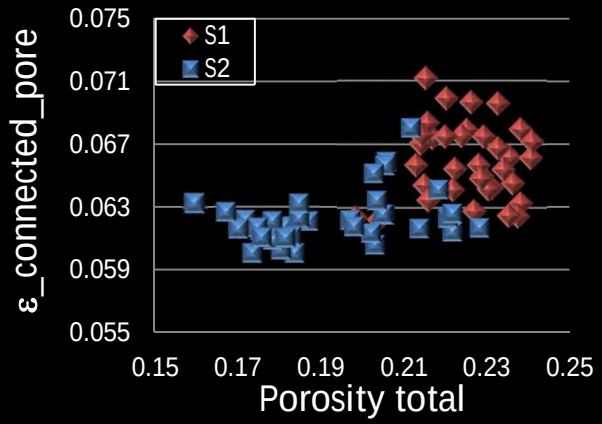


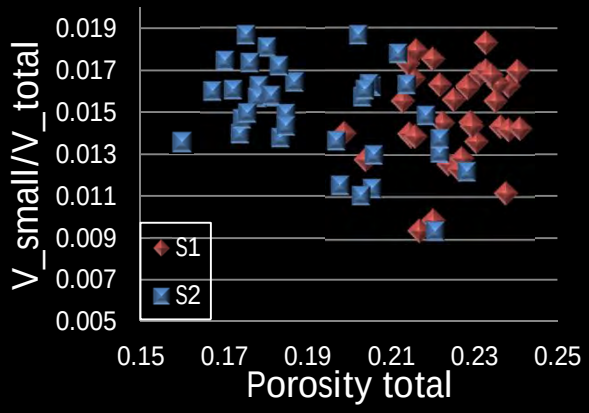


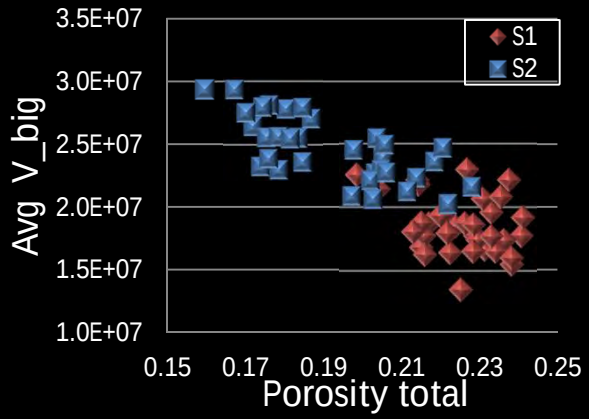


S1 and S2 Separate into two clouds in these plots indicating significant difference in morphology



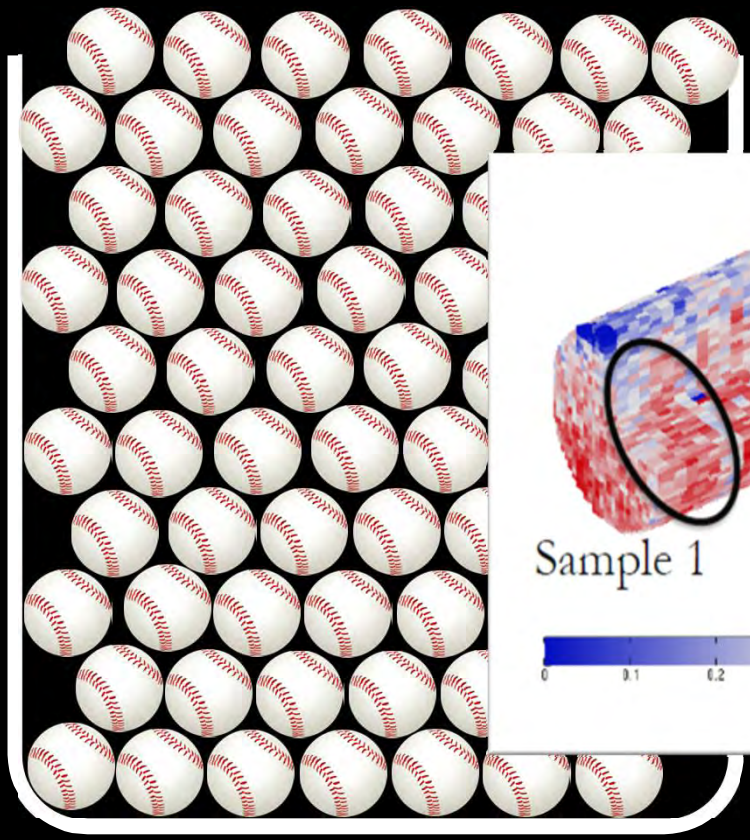




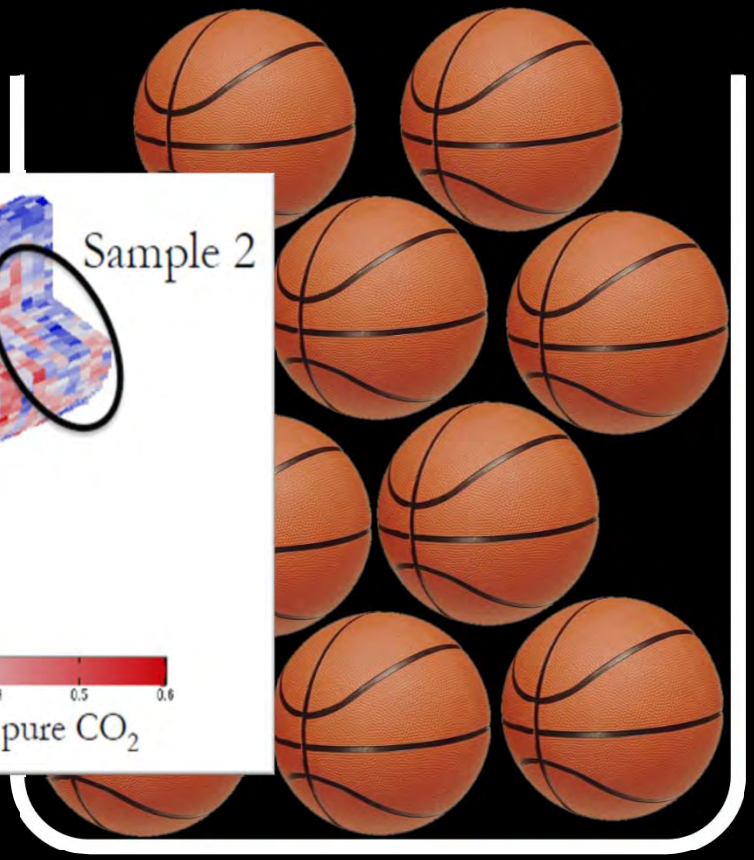


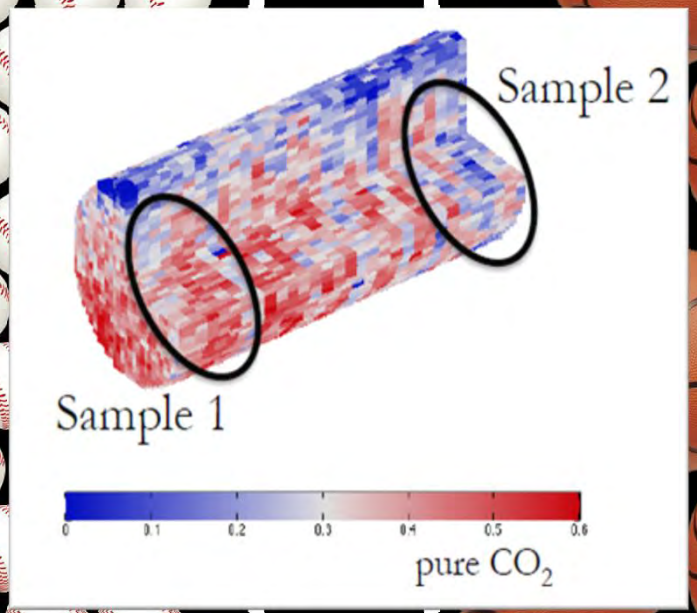
What we normally think

S1



S2



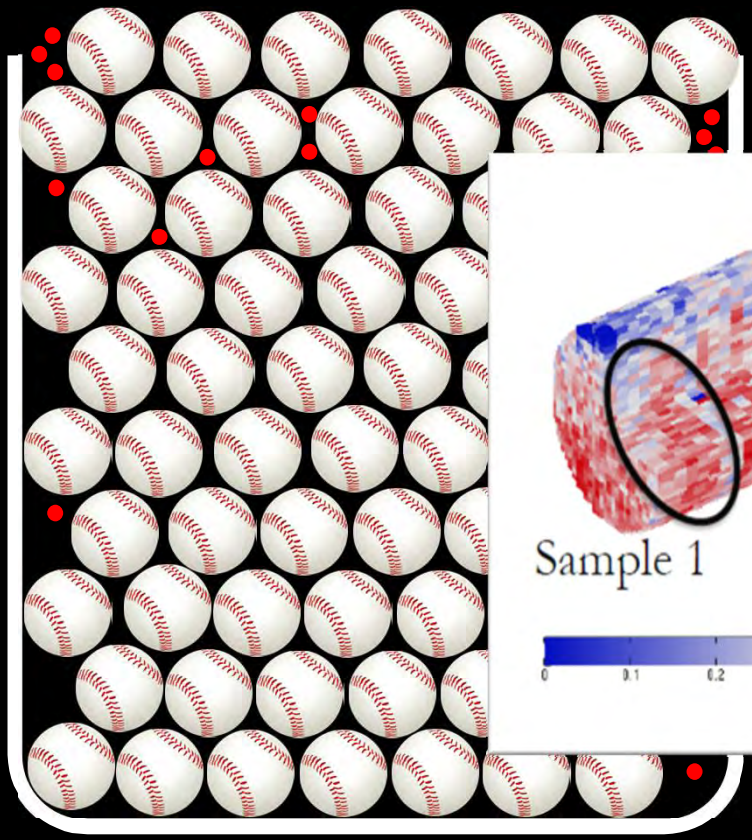


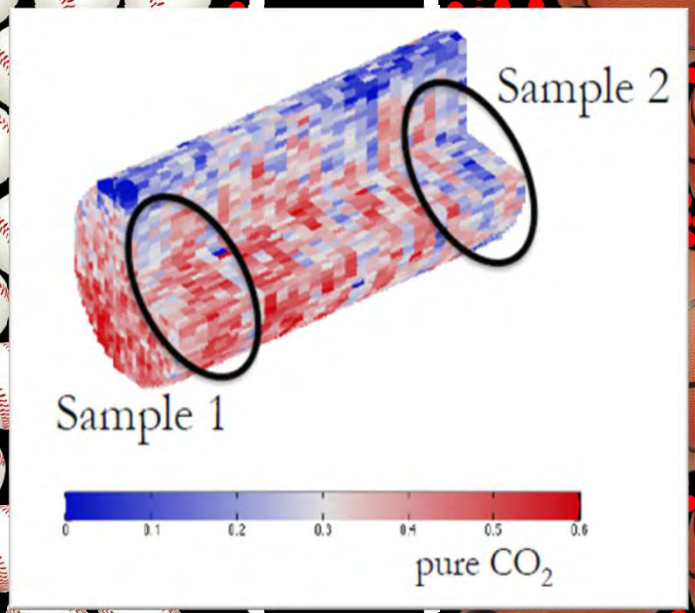
- More and smaller skeleton grains
-
-
- Less space left, smaller porosity
-

- Less and larger skeleton grains
-
-
- More space left, larger porosity
-

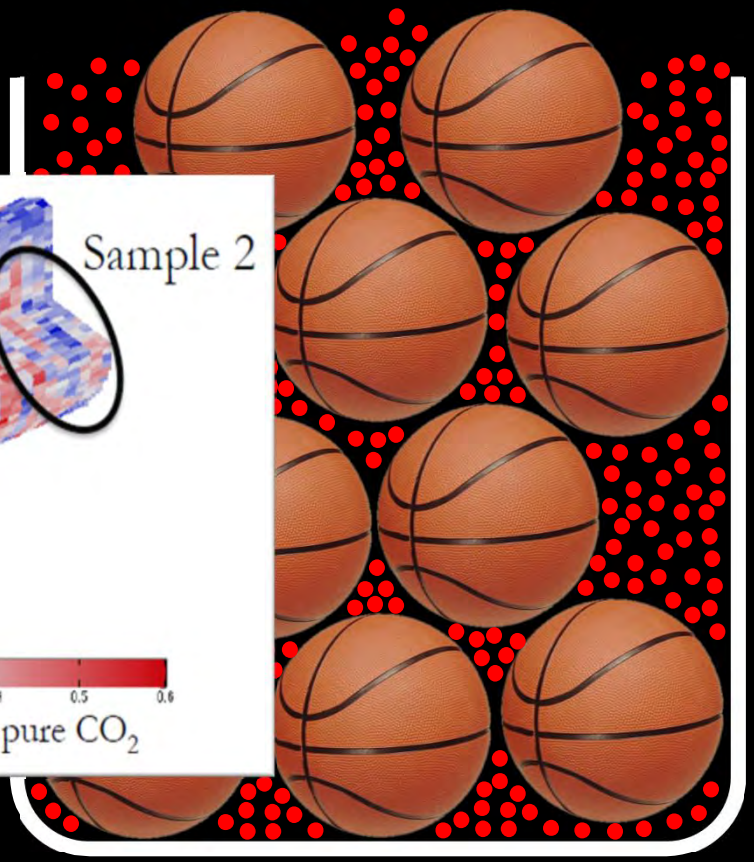
The fact that “small grains” exist has changed the picture

S1





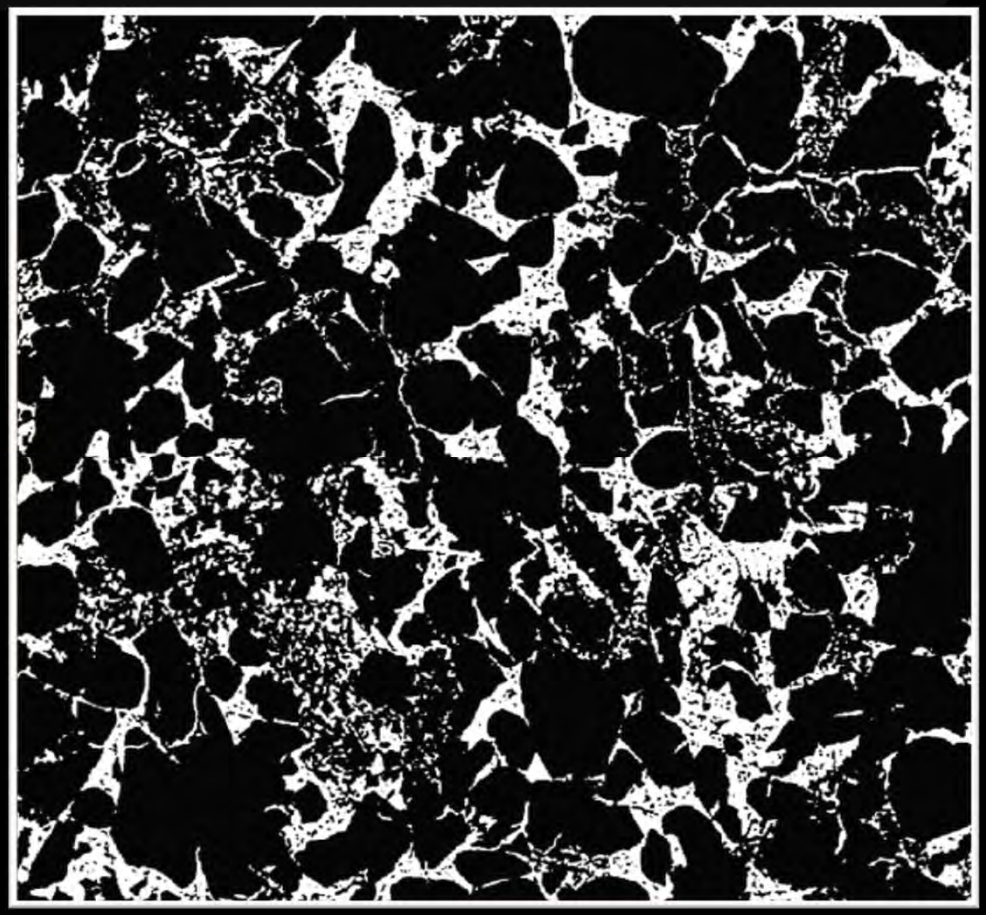
S2



- More and smaller skeleton grains
- “Harder“ for “small grains” to penetrate ,
- Less “small grains”
- More space left, larger porosity
- Less complex the connected pore structure

- Less and larger skeleton grains
- “Easier “ for “small grains” to penetrate,
- More “small grains”
- Less space left, smaller porosity
- More complex the connected pore structure

The pore throats

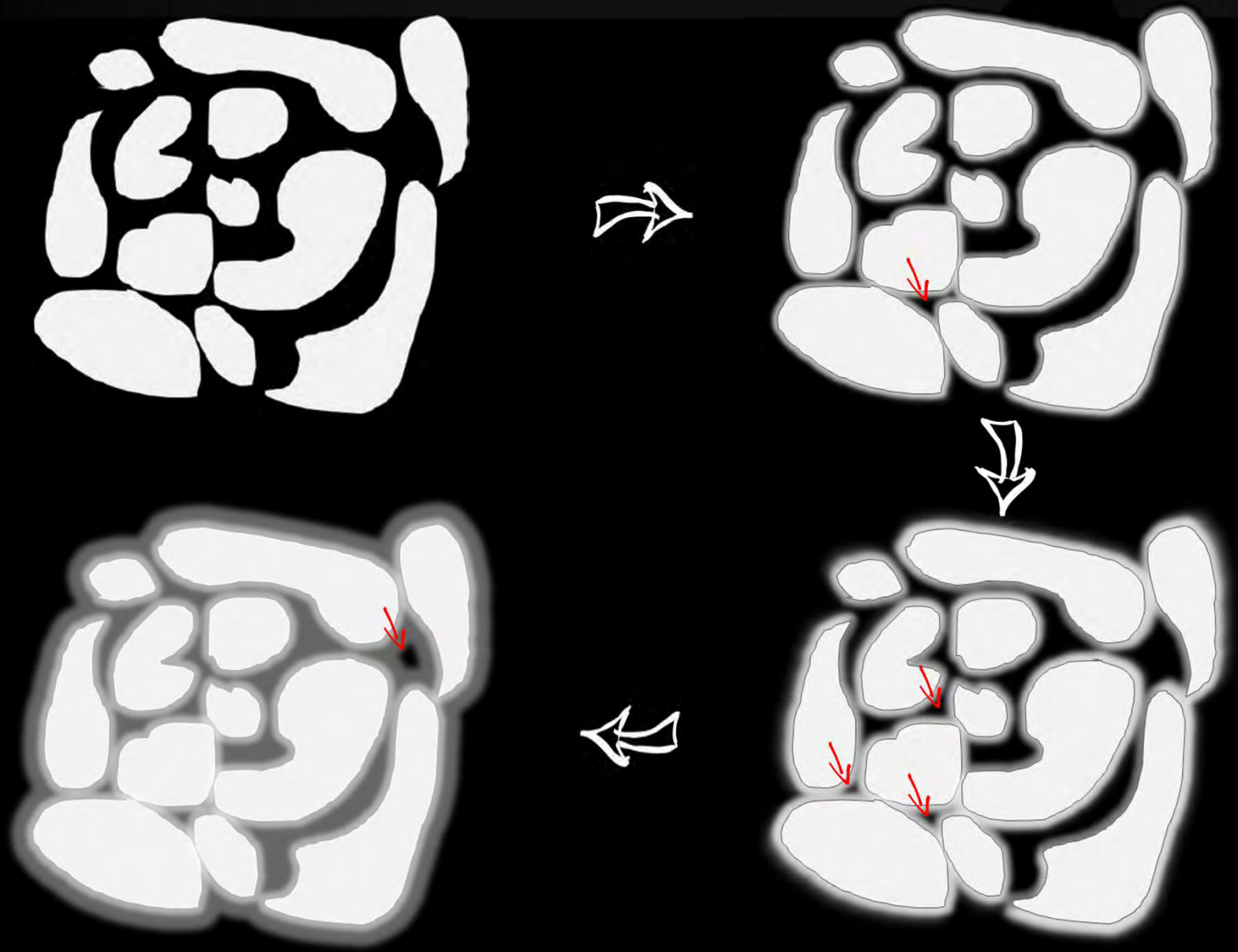


Black: solid; White: connected pore

Pore throat: Narrow part in the connected pore. Traditionally, the pore throat size is experimentally measured by performing Hg injection into dry sample.

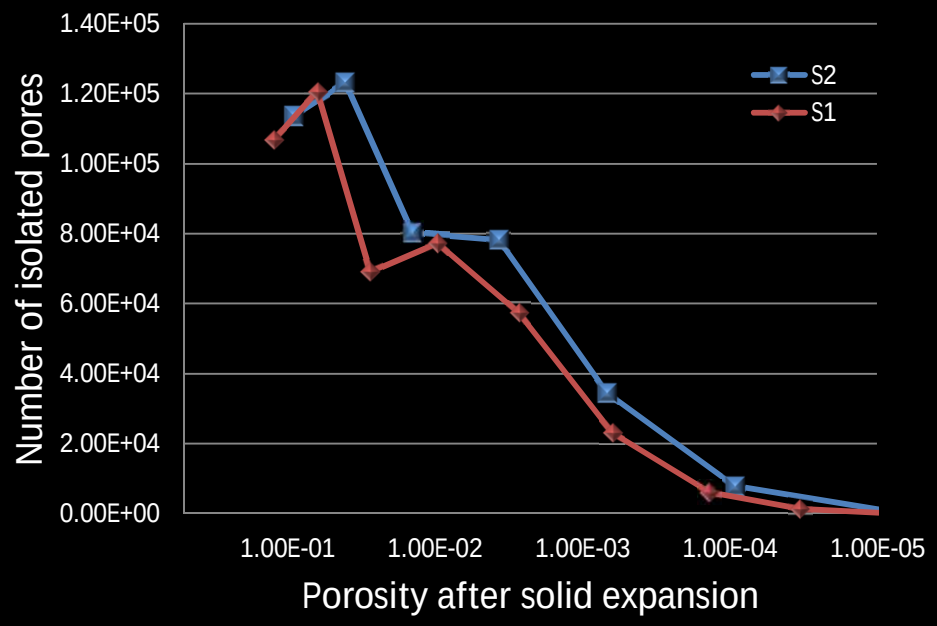
We use 3D imaging of the sample to provide a direct measurement of the pore throat.

Our strategy to measure the pore throats: numerically expand the solid



We propose to evaluate “number of isolated pores” upon “numerical solid expansion”

Number of isolated pores vs. the corresponding Porosity at solid expansion



n	Porosity		Num of isolated pores	
	S1	S2	S1	S2
0	0.200500	0.156770	1	1
1	0.122330	0.089381	106870	113595
2	0.062714	0.040293	120526	123107
3	0.027310	0.014172	69016	80238
4	0.009576	0.003653	77212	78071
5	2.67E-03	6.75E-04	57318	34484
6	6.22E-04	9.19E-05	23126	7883
7	1.36E-04	9.65E-06	6113	1183
8	3.30E-05	8.42E-07	1413	136
9	9.81E-06	4.10E-08	313	9
10	3.69E-06	1.00E-09	72	1
11	1.65E-06	0	21	0
12	7.14E-07		5	
13	2.39E-07		4	
14	4.80E-08		3	
15	4.00E-09		1	
16	0		0	

This plot tells us two things:

1. Red is below Blue
   At the same porosity (In the same amount of solid), S1(red) has less throats.
2. Both curves have two peaks
   There are two 'types' of throats (will show in the next slide)

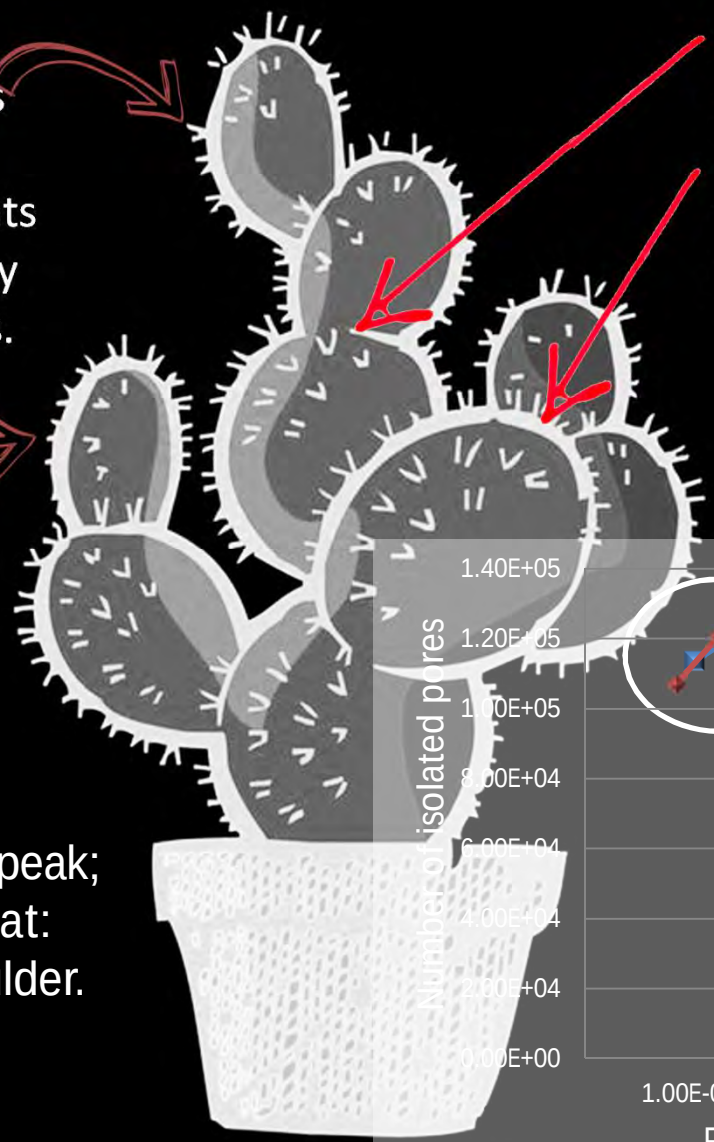
n: expanded pixels (expanded layers)
V: 1000^3 voxels (2.96^3 mm^3)

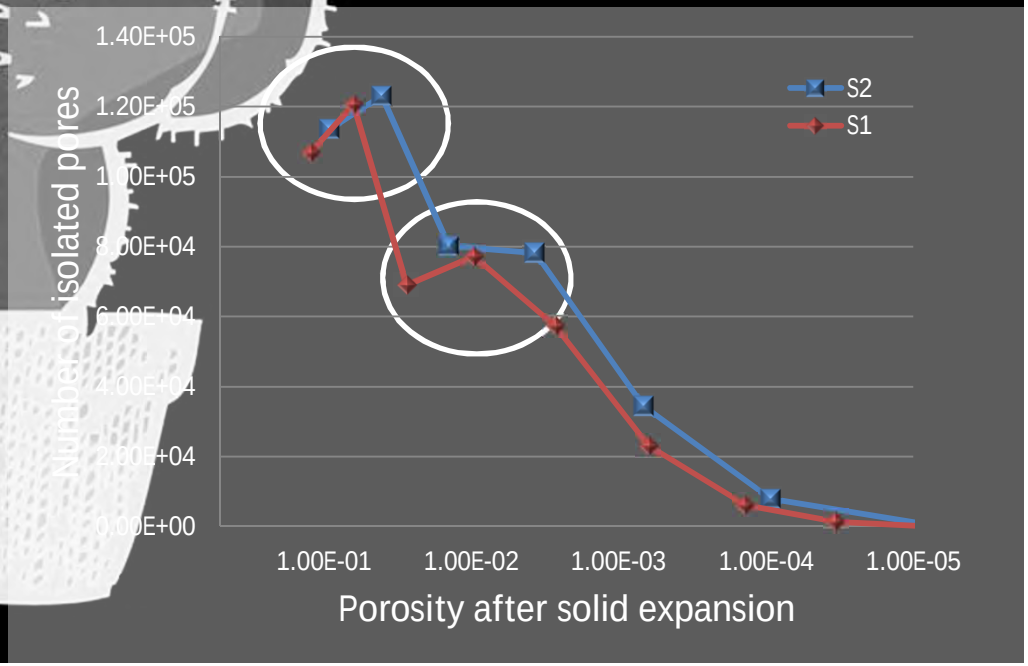
There are two types of pore throats

In this picture, the cactus is the pore.

The fine throat,
which connects the Cactus thorns.
In our sample, those throats connected pores caused by rough surface of the solids.
(≤2 pixels)

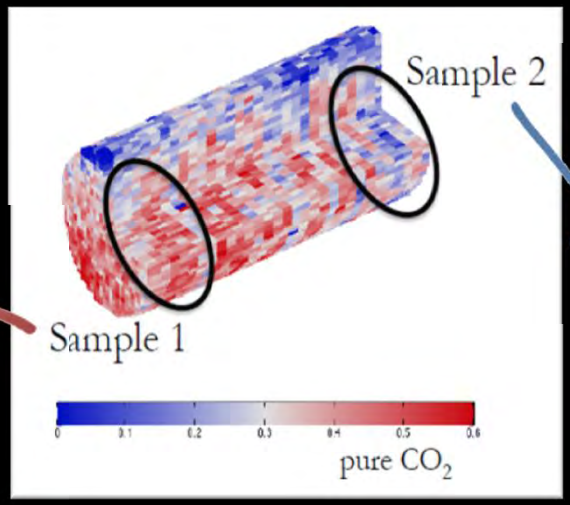
The secondary throat,
which connects the Cactus bodies.
In our sample, those secondary throats connected the space between the solid particles.
(bigger diameter: 6-8 pixels)





The fine pore throat:
Responsible for the first peak;
the secondary pore throat:
Responsible for the shoulder.

What we have learned from synchrotron μ-CT



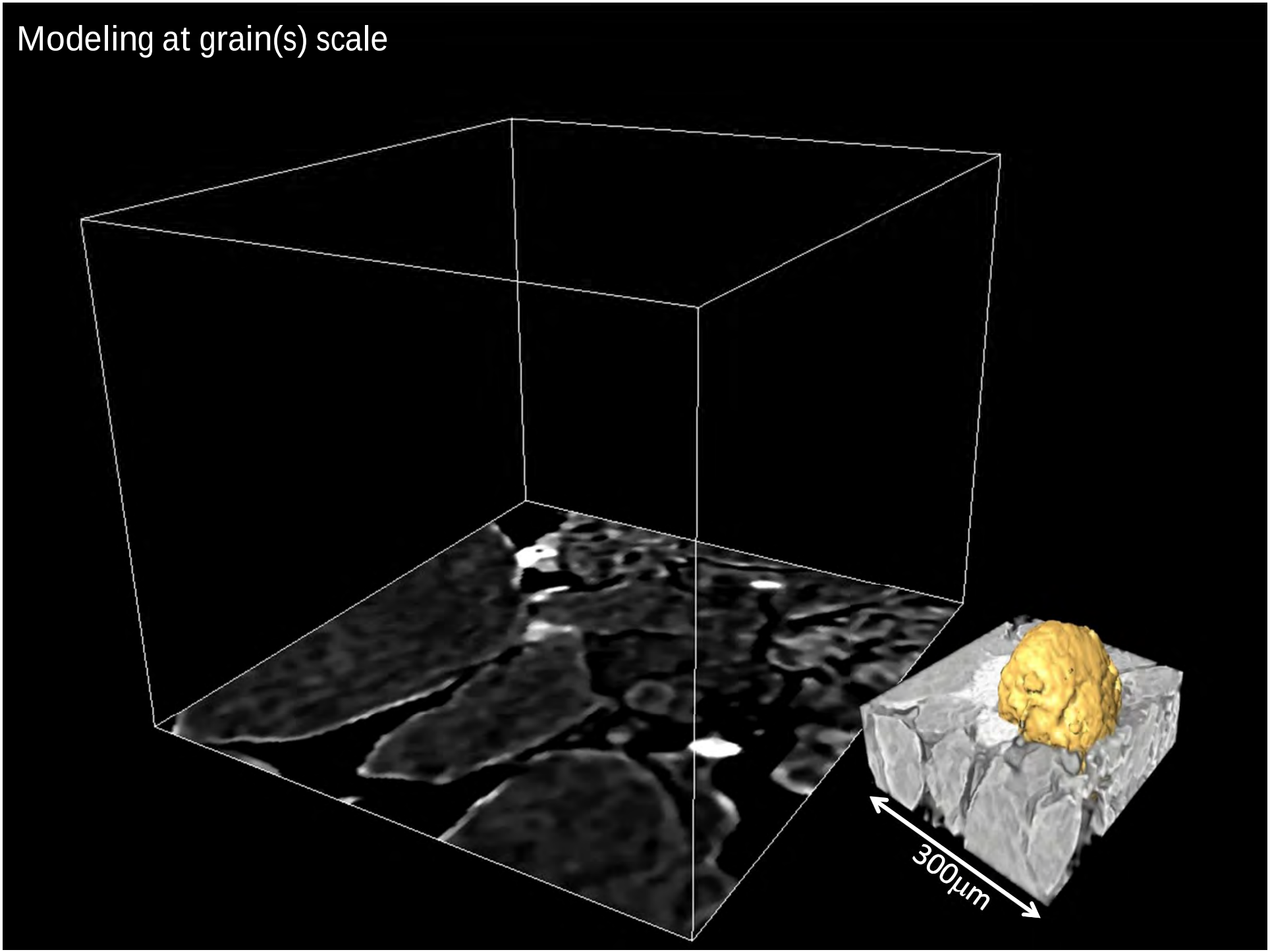
- More and Smaller skeleton grains
- Harder for small grains to penetrate
- Less small grains
- Larger porosity
- Smaller complexity in the connected pore structure
- Less pore throats
- Wider secondary throats

High concentration of CO_2 in CO_2 saturation experiment

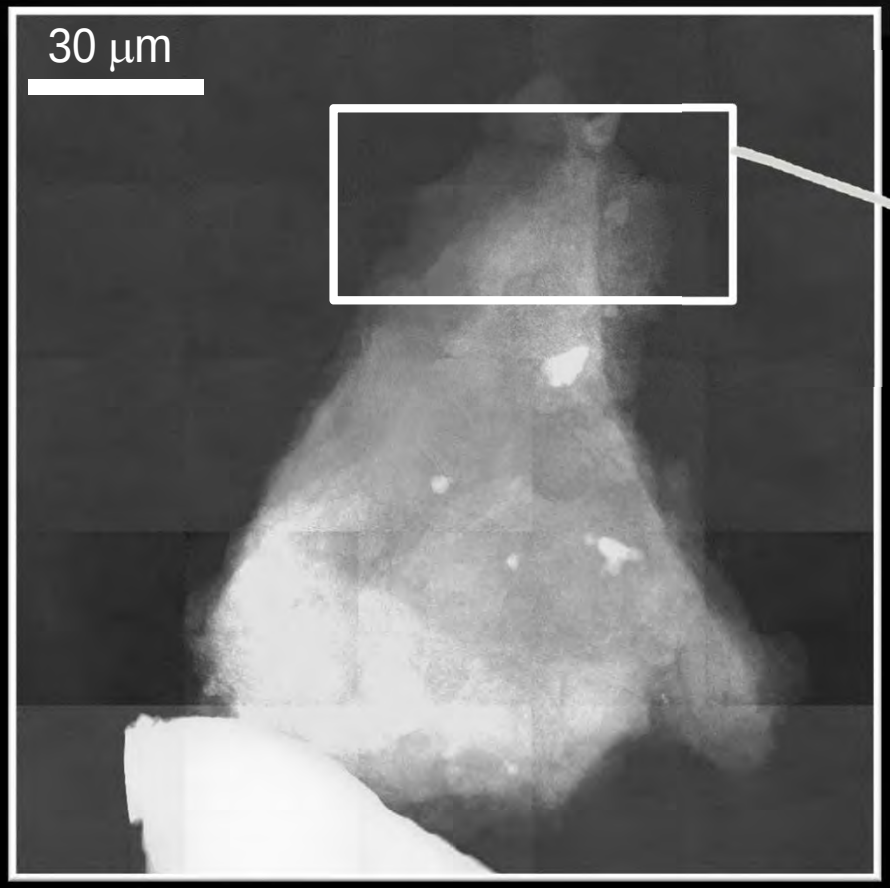
- Less and larger skeleton grains
- Easier for small grains to penetrate
- More small grains
- Smaller porosity
- Larger complexity in the connected pore structure
- More pore throats
- Tighter secondary throats

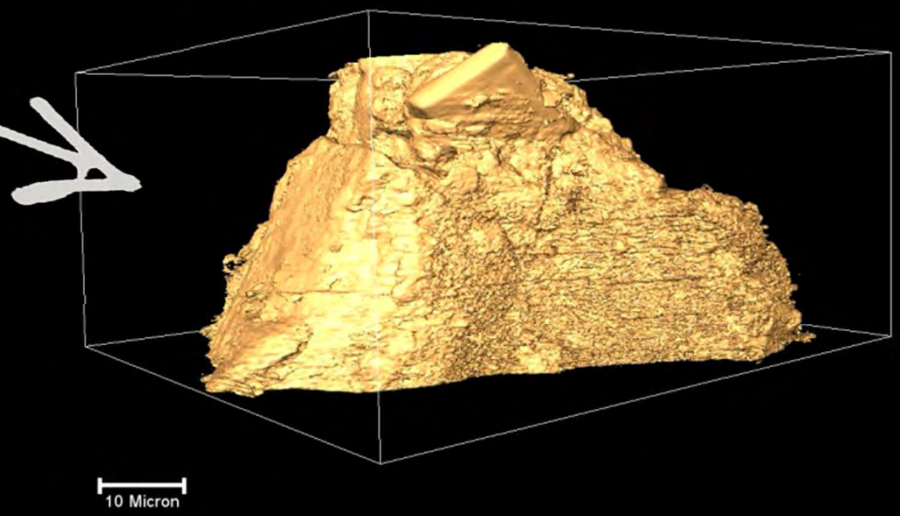
Low concentration of CO_2 in CO_2 saturation experiment

Modeling at grain(s) scale

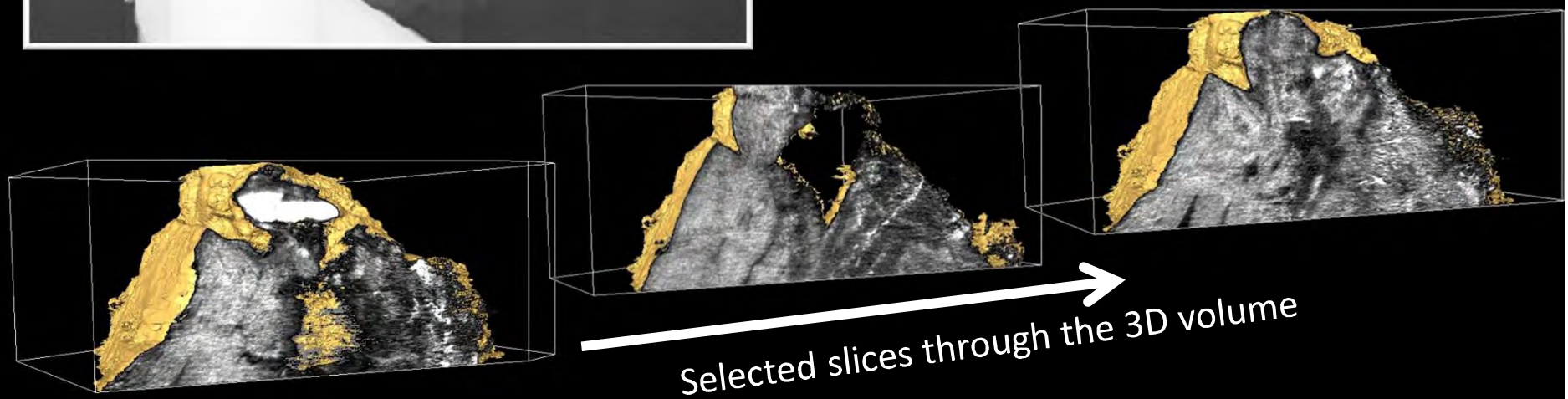


Morphology at sub-grain scale





Single grain mounted on a needle for nano-CT investigation



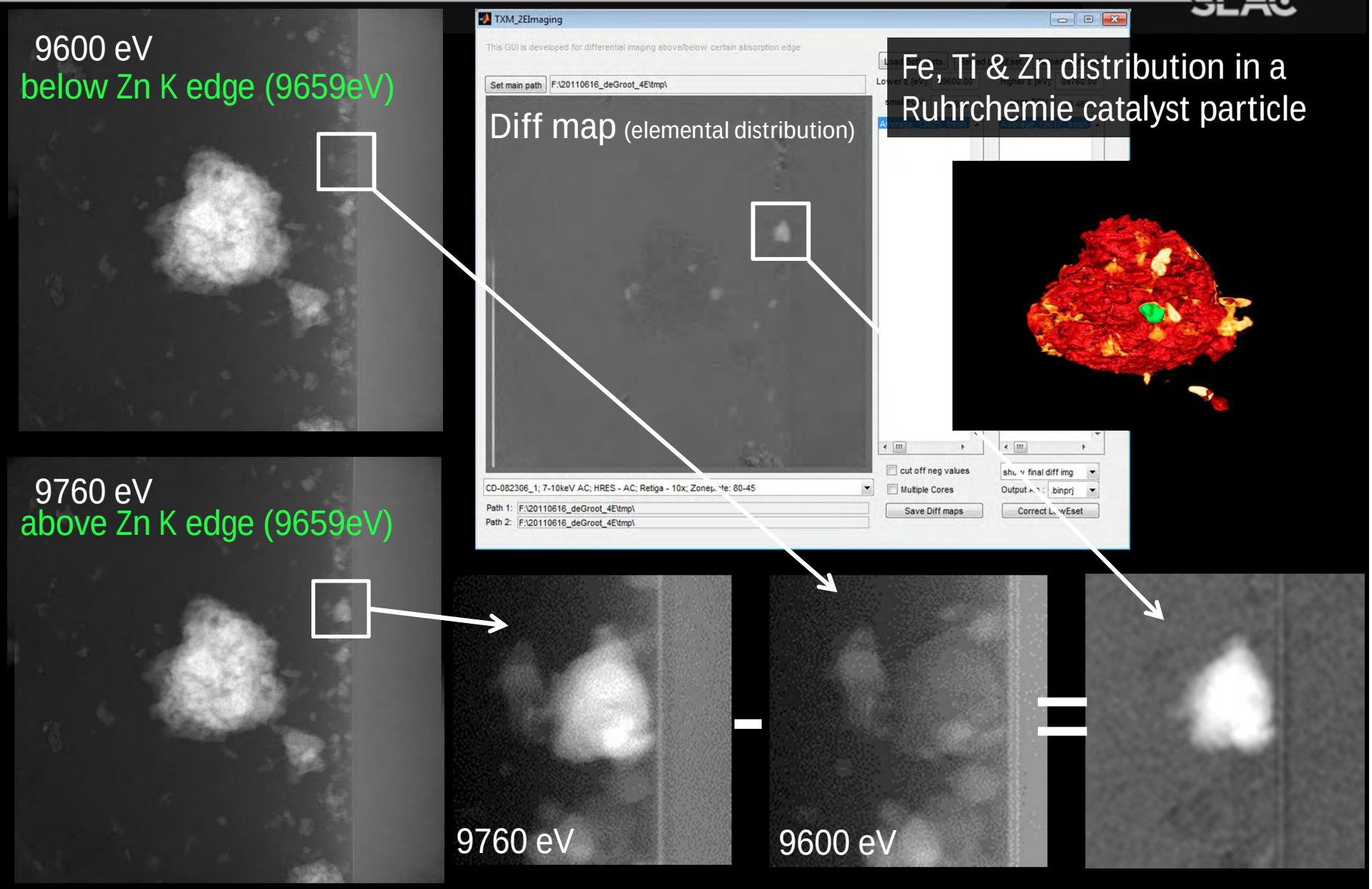
Selected slices through the 3D volume

We care about more than just morphology

SLAC

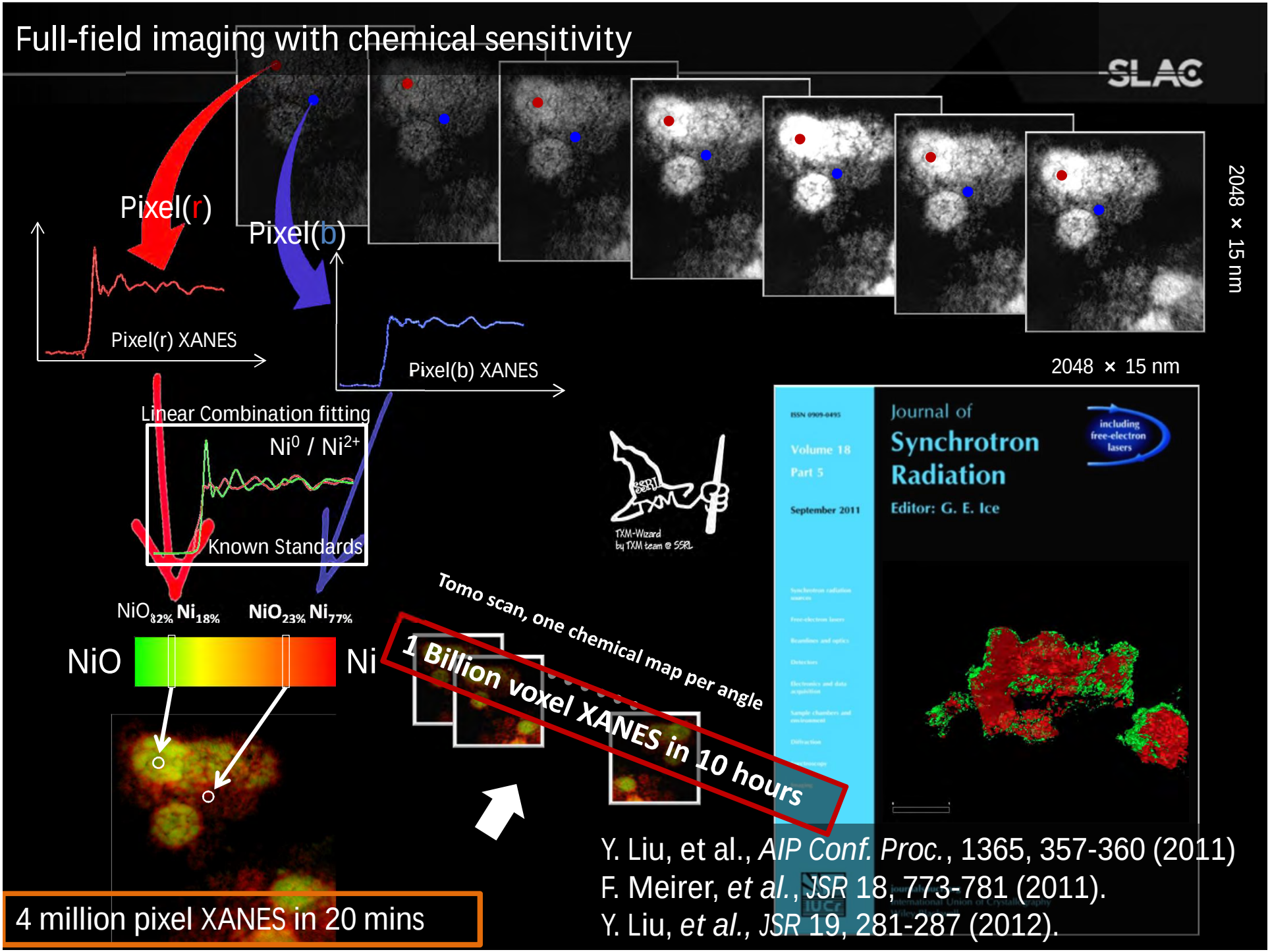
- So far, I have only talked about morphological studies.
- The chemistry (elemental associations, chemical species, interface dynamic and etc.) plays an critical role in the real world.
- What we really want is a technique to provide the information of spatially resolved chemistry, and we want this technique to work under controlled sample environment (temperature, pressure, and etc.)
- How do we do this? We need to make full use of the capabilities enabled by the existing X-ray sources and the future ones.

Full-field imaging with elemental sensitivity



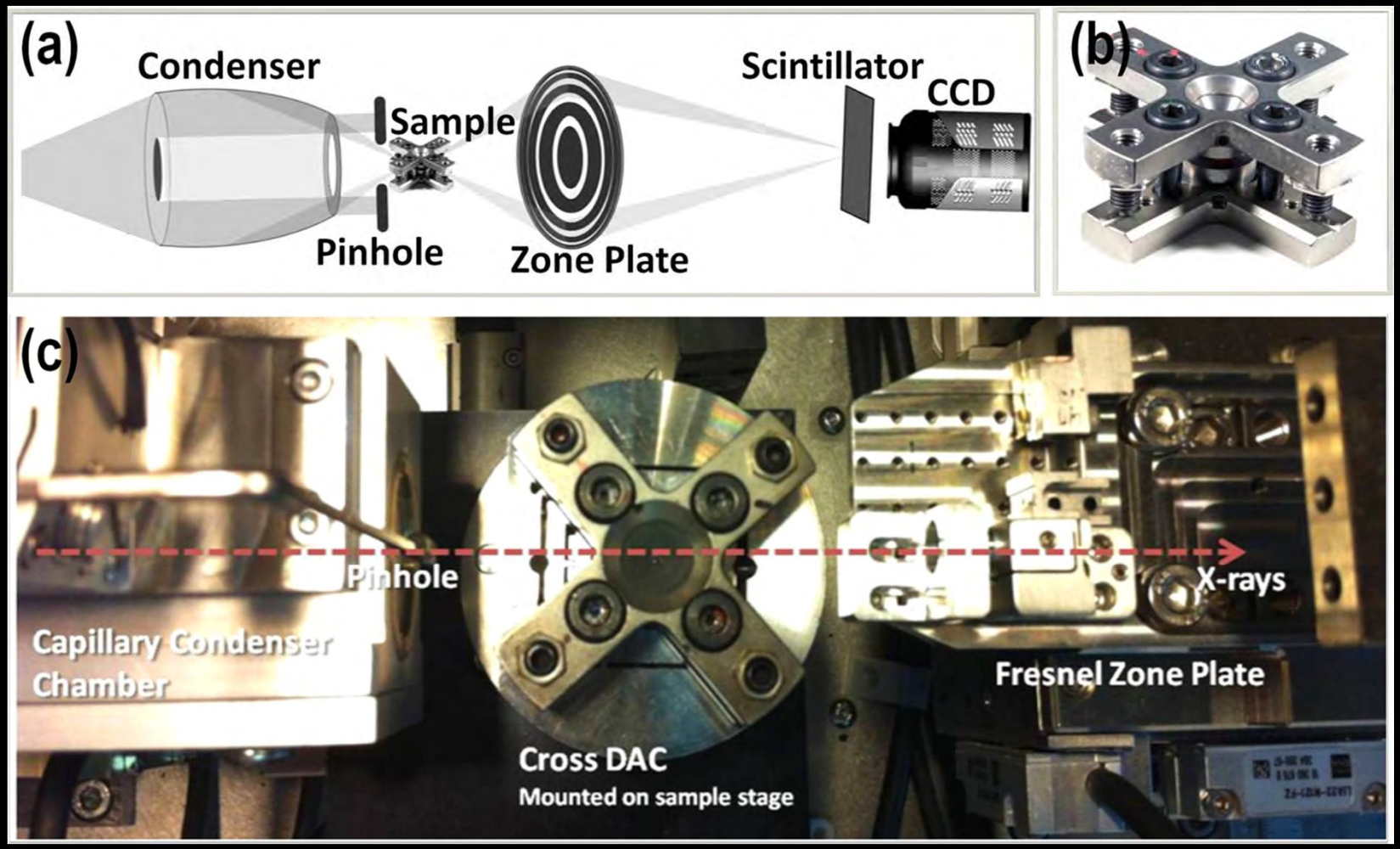
Y. Liu *et al.*, *Anal. Bioanal. Chem.* 404, 1297-1301 (2012).
I. Gonzalez-Jimenez *et al.*, *Angew. Chem. Int. Ed.* 51. 11986-11990 (2012).

Full-field imaging with chemical sensitivity



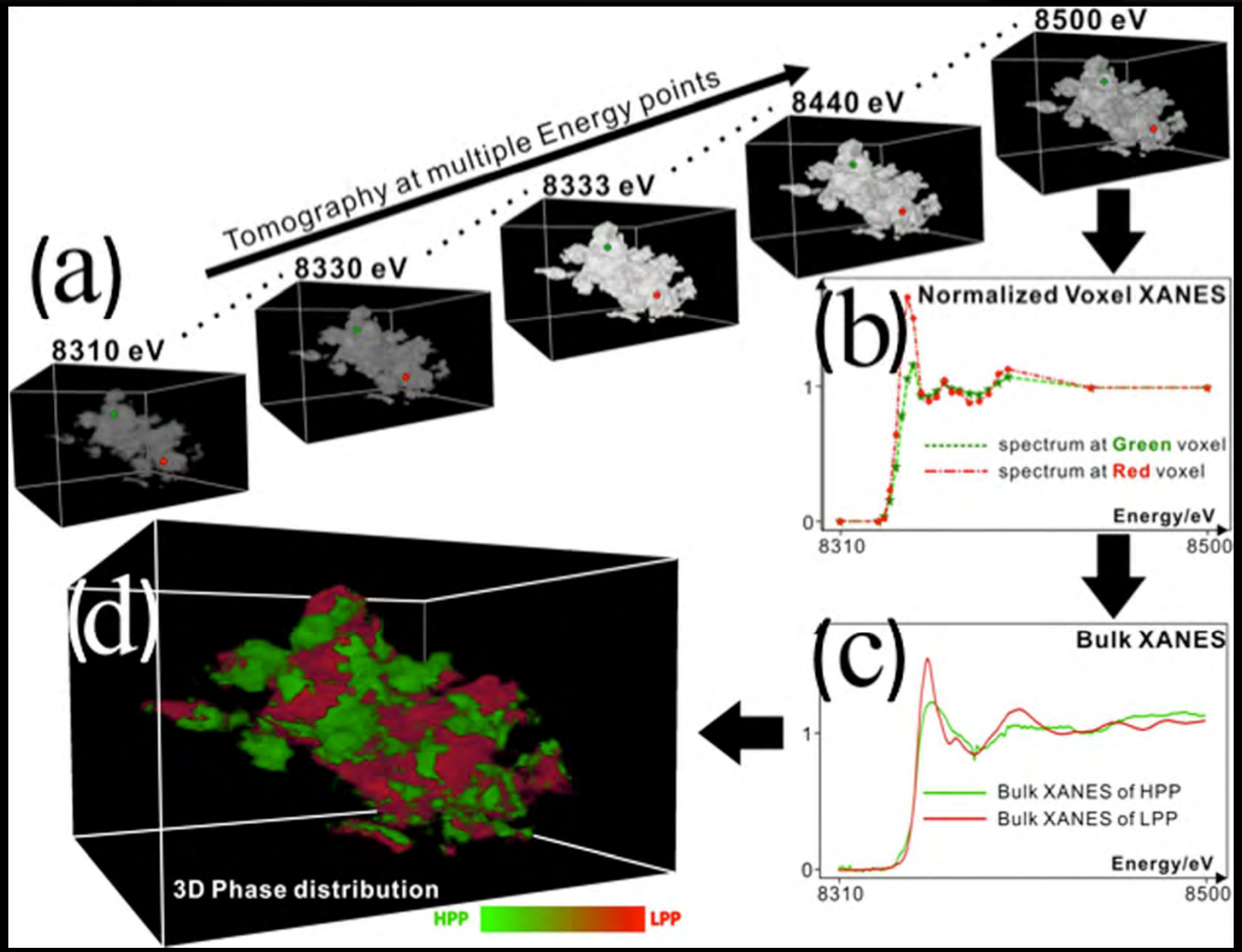
Y. Liu, et al., *AIP Conf. Proc.*, 1365, 357-360 (2011)
F. Meirer, *et al.*, *JSR* 18, 773-781 (2011).
Y. Liu, *et al.*, *JSR* 19, 281-287 (2012).

One example: visualization of pressure induced phase transition in BiNiO3



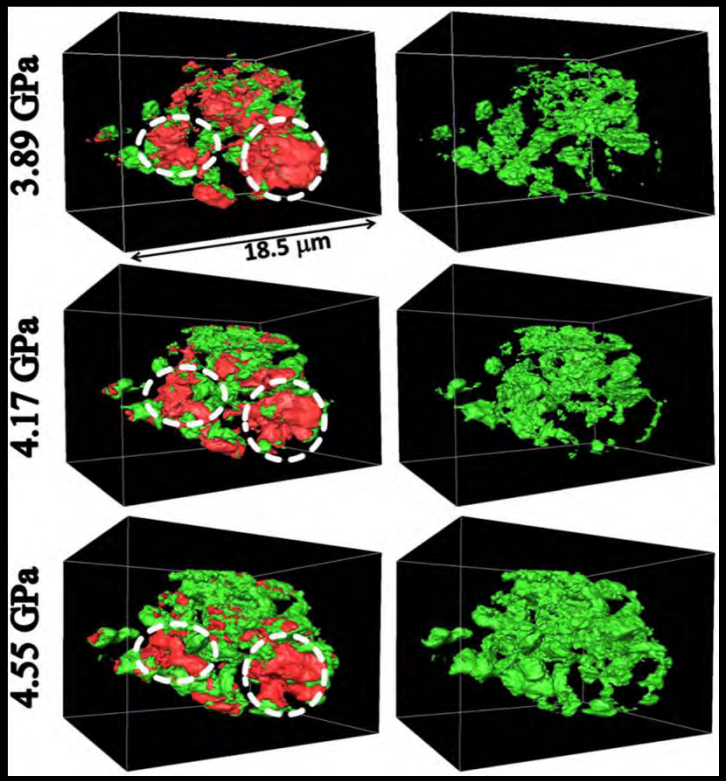
Liu *et al.*, *Appl. Phys. Lett.* 104, 043108, (2014)

Visualization of chemical phases at nanometer resolution

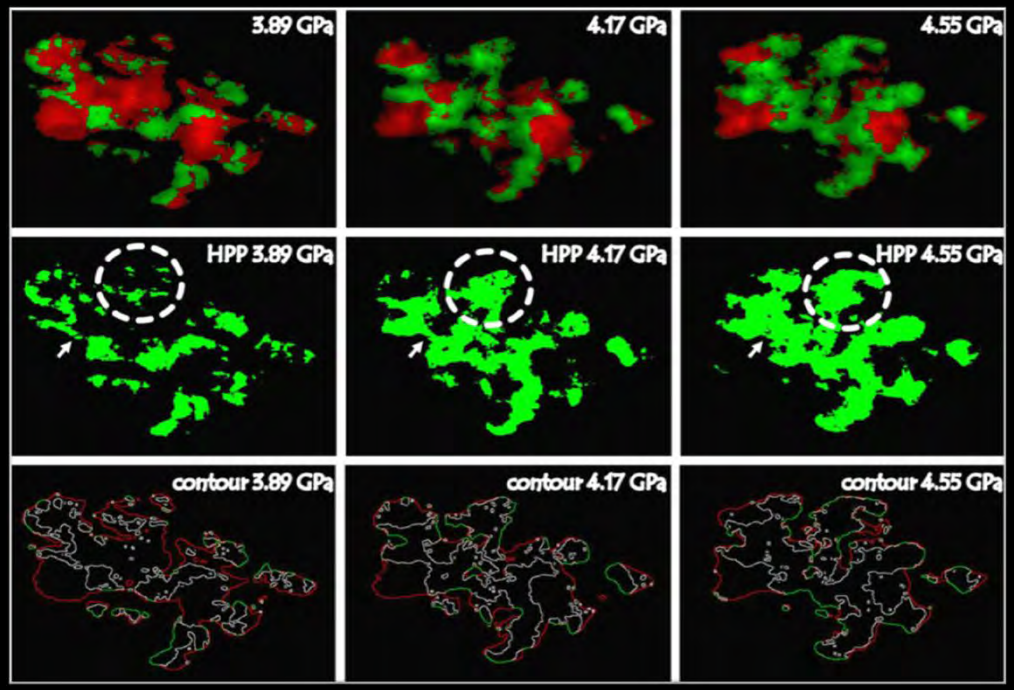


Liu *et al.*, *Appl. Phys. Lett.* 104, 043108, (2014)

5D visualization of pressure induced phase transition in BiNiO3



The 5D (x, y, z, Energy, Pressure) visualization of the phase transition upon compression.



The phase transition pathway visualized over a virtual slice

Liu *et al.*, *Appl. Phys. Lett.* 104, 043108, (2014)

Conclusion

X-ray microscopy is capable of providing very useful information
at different length scales
with elemental/chemical sensitivity
under controlled sample environments.

Scientific case studies, including investigation of under ground formation for CO2 sequestration and material under extreme pressures, have shown the strength of X-ray microscopy.

We expect future development in instrumentation and methodology will open even more scientific opportunities in many research fields.

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Thank you for your attention