Applications of Neutron Scattering in the Geosciences

Lawrence M. Anovitz

Geochemistry and Interfacial Sciences Group

Chemical Sciences Division

Oak Ridge National Laboratory

April 27, 2023

Department of Energy
Division of Chemical Sciences,
Geosciences and Biosciences

Acknowledgments

ORNL Collaborators:

M. Cheshire, V. DeStefano, G. Ehlers, B. Hamilton, A. Ievlev, A. Kolesnikov, K. Littrell, E. Mamontov, A. Podlesnyak, T. Prisk, A.G. Stack, V. Starchenko, J. Weber, D. Wesolowski, R Zhang

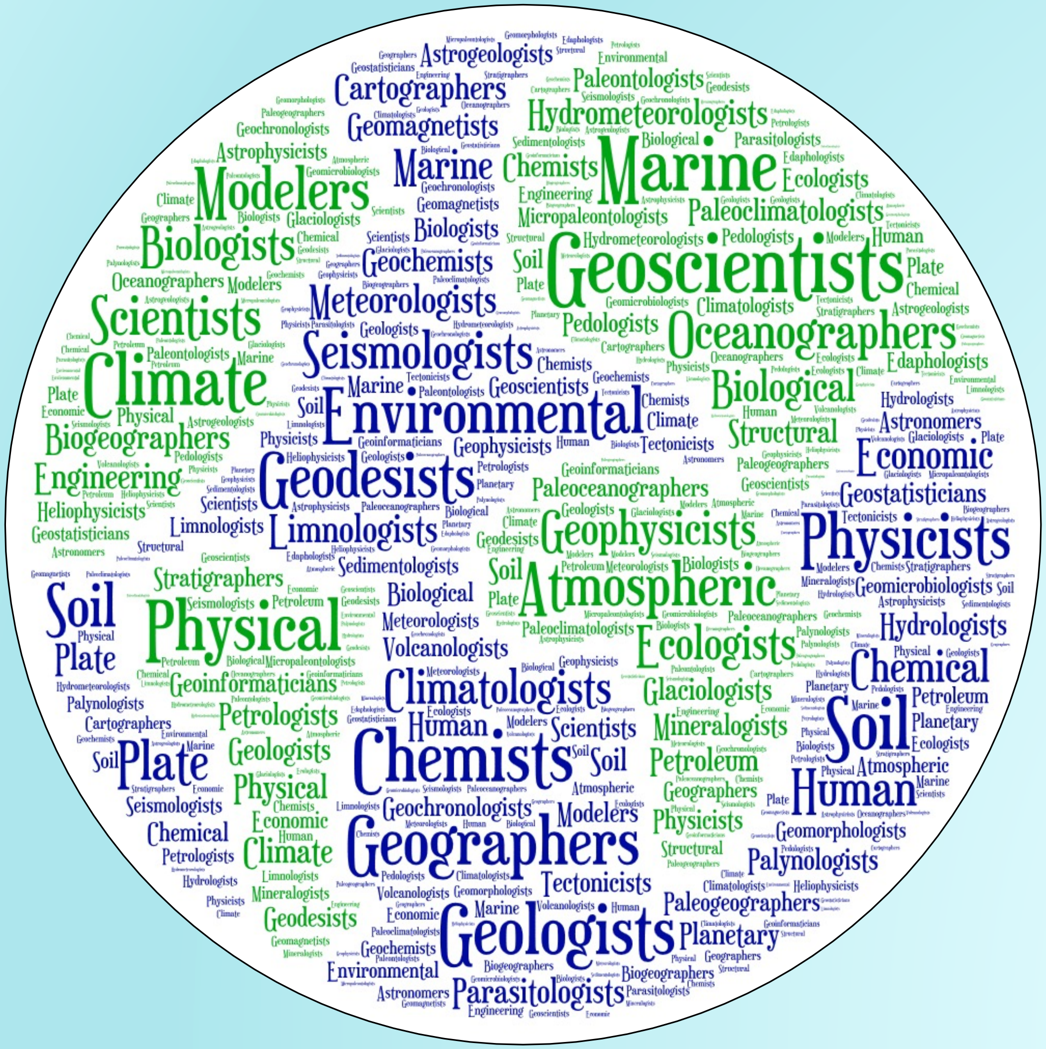
External Collaborators:

M. Bleuel, D. Cole. P. ben Ishai, J. Bozell-Schmidt , Y-J. Chang, N. Choudhury, S. Emmanuel, R. Helm, D. Hussey, I. Ilavsky, K. Littrell, J. LaManna, D. Mildner, A. Patchen, T. Prisk, G. F. Reiter, M. Rivers, A. Seel, A, Treiman, R. Zhang.

Research sponsored by:
Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy

A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.
Neutron Analyses shown were performed at: the Spallation Neutron Source and High-Flux Isotope Reactor, ORNL, the NIST Center for Neutron Research, and the ISIS Facility, Rutherford Appleton Laboratory
X-ray scattering was performed at the Advanced Photon Source, Argonne National Lab

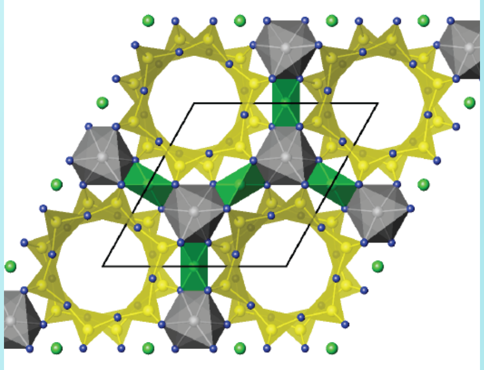
How Geoscientists See Themselves

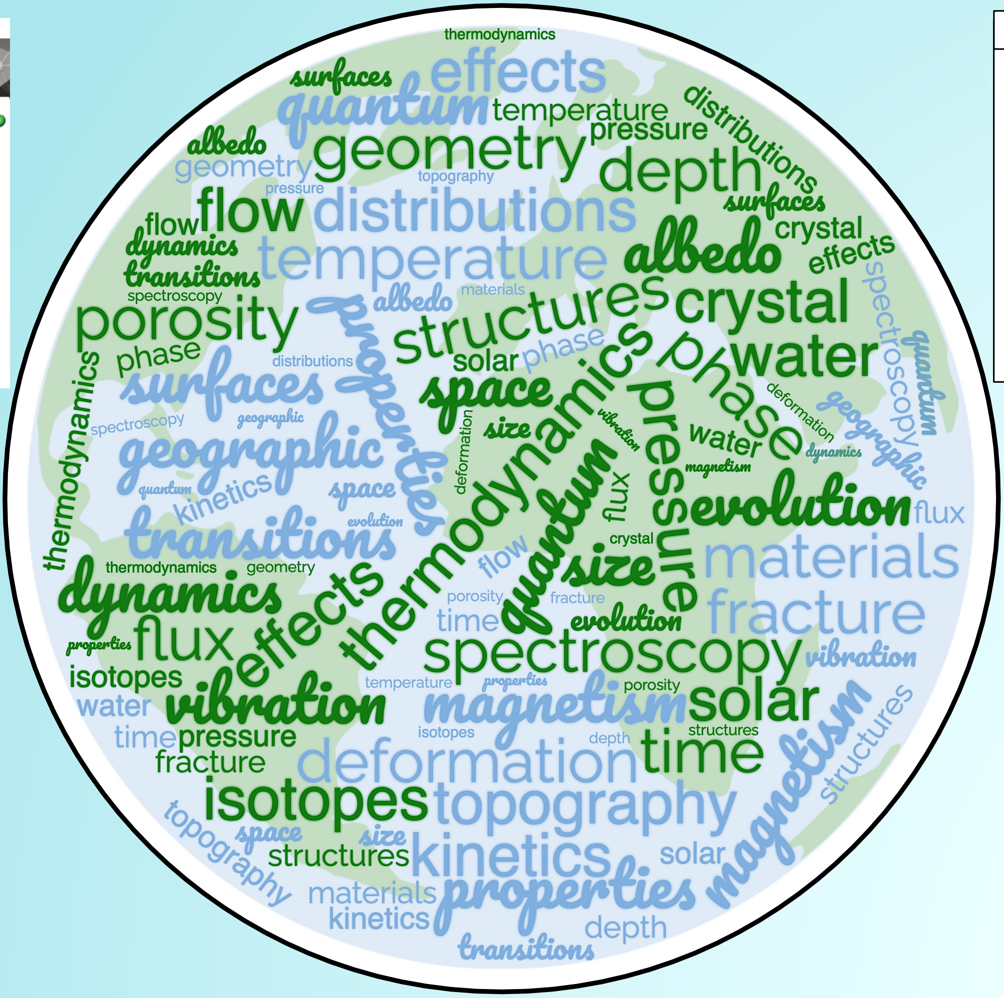


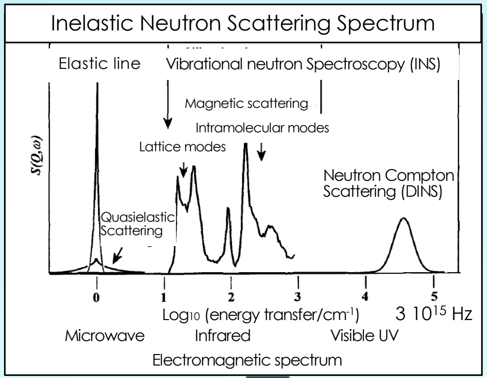
Science Fields
Subdisciplines of "at least"

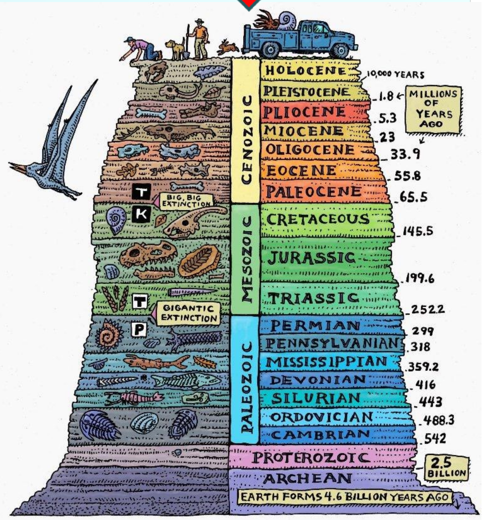
Physics
Chemistry
Biology
Pre-history/History
Mathematics

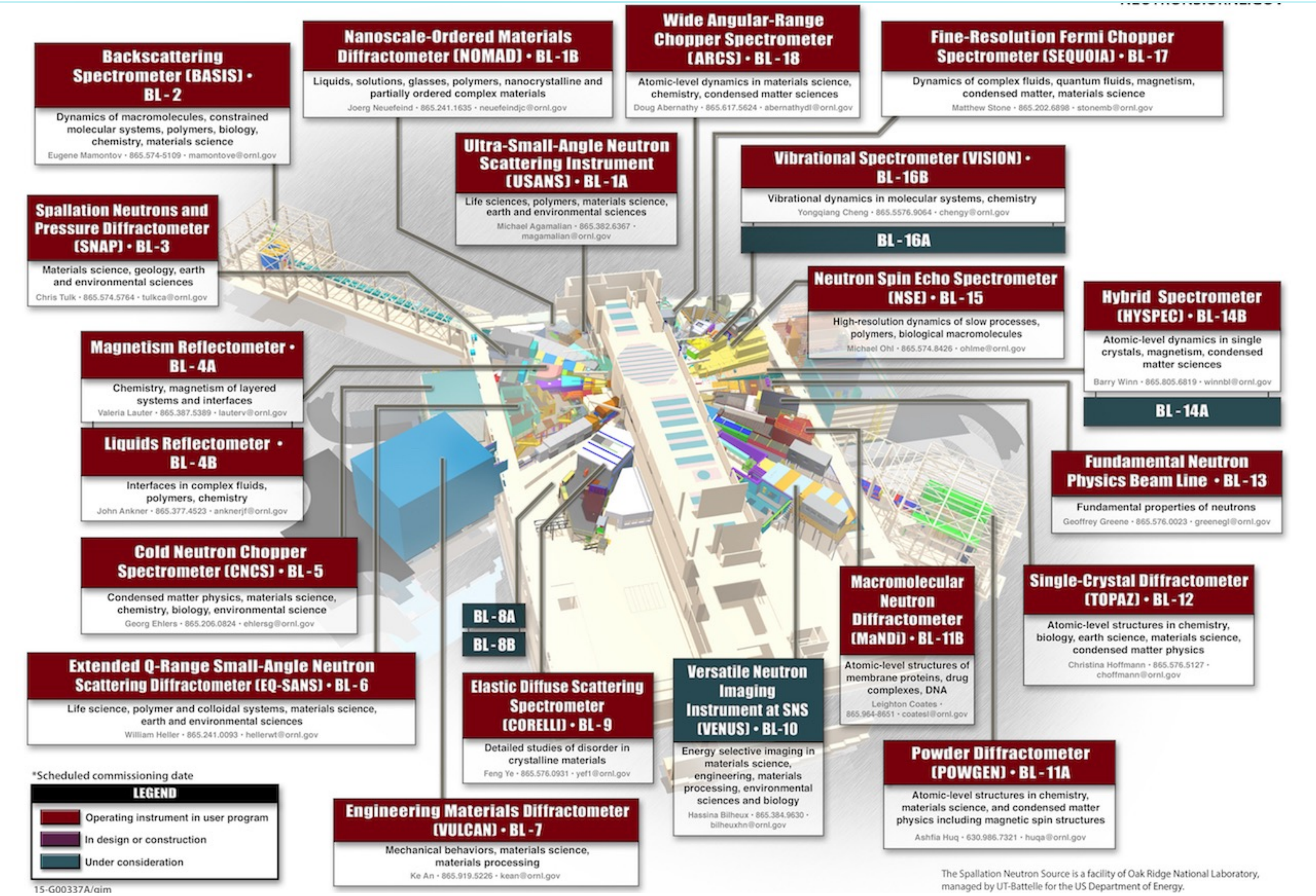
What Geoscientists Actually Measure






Inelastic Neutron Scattering Spectrum





Backscattering Spectrometer (BASIS) • BL-2
Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
Eugene Mamontov • 865.574-5109 • mamontove@ornl.gov

Nanoscale-Ordered Materials Diffractometer (NOMAD) • BL-1B
Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
Joerg Neuefeind • 865.241.1635 • neuefeindjc@ornl.gov

Wide Angular-Range Chopper Spectrometer (ARCS) • BL-18
Atomic-level dynamics in materials science, chemistry, condensed matter sciences
Doug Abernathy • 865.617.5624 • abernathydl@ornl.gov

Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) • BL-17
Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
Matthew Stone • 865.202.6898 • stonemb@ornl.gov

Ultra-Small-Angle Neutron Scattering Instrument (USANS) • BL-1A
Life sciences, polymers, materials science, earth and environmental sciences
Michael Agamalian • 865.382.6367 • magamalian@ornl.gov

Vibrational Spectrometer (VISION) • BL-16B
Vibrational dynamics in molecular systems, chemistry
Yongqiang Cheng • 865.5576.9064 • chengy@ornl.gov

BL-16A

Spallation Neutrons and Pressure Diffractometer (SNAP) • BL-3
Materials science, geology, earth and environmental sciences
Chris Tulk • 865.574.5764 • tulkca@ornl.gov

Neutron Spin Echo Spectrometer (NSE) • BL-15
High-resolution dynamics of slow processes, polymers, biological macromolecules
Michael Ohl • 865.574.8426 • ohlme@ornl.gov

Hybrid Spectrometer (HYSPEC) • BL-14B
Atomic-level dynamics in single crystals, magnetism, condensed matter sciences
Barry Winn • 865.805.6819 • winnbl@ornl.gov

BL-14A

Magnetism Reflectometer • BL-4A
Chemistry, magnetism of layered systems and interfaces
Valeria Lauter • 865.387.5389 • lauterv@ornl.gov

Liquids Reflectometer • BL-4B
Interfaces in complex fluids, polymers, chemistry
John Ankner • 865.377.4523 • anknerjf@ornl.gov

Fundamental Neutron Physics Beam Line • BL-13
Fundamental properties of neutrons
Geoffrey Greene • 865.576.0023 • greenegl@ornl.gov

Cold Neutron Chopper Spectrometer (CNCS) • BL-5
Condensed matter physics, materials science, chemistry, biology, environmental science
Georg Ehlers • 865.206.0824 • ehlersg@ornl.gov

BL-8A

BL-8B

Macromolecular Neutron Diffractometer (MaNDi) • BL-11B
Atomic-level structures of membrane proteins, drug complexes, DNA
Leighton Coates • 865.964-8651 • coatesl@ornl.gov

Single-Crystal Diffractometer (TOPAZ) • BL-12
Atomic-level structures in chemistry, biology, earth science, materials science, condensed matter physics
Christina Hoffmann • 865.576.5127 • choffmann@ornl.gov

Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) • BL-6
Life science, polymer and colloidal systems, materials science, earth and environmental sciences
William Heller • 865.241.0093 • hellerwt@ornl.gov

Elastic Diffuse Scattering Spectrometer (CORELLI) • BL-9
Detailed studies of disorder in crystalline materials
Feng Ye • 865.576.0931 • yef1@ornl.gov

Versatile Neutron Imaging Instrument at SNS (VENUS) • BL-10
Energy selective imaging in materials science, engineering, materials processing, environmental sciences and biology
Hassina Bilheux • 865.384.9630 • bilheuxhn@ornl.gov

Powder Diffractometer (POWGEN) • BL-11A
Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
Ashfia Huq • 630.986.7321 • huqa@ornl.gov

Engineering Materials Diffractometer (VULCAN) • BL-7
Mechanical behaviors, materials science, materials processing
Ke An • 865.919.5226 • kean@ornl.gov

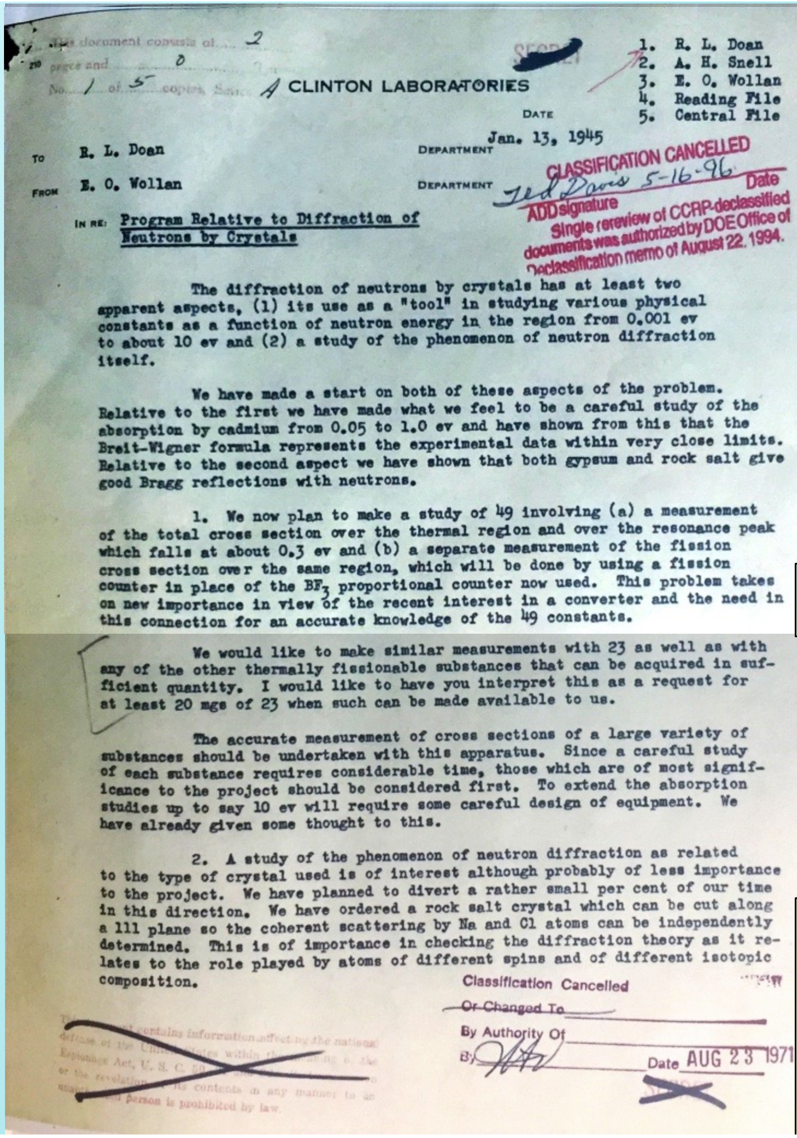
*Scheduled commissioning date

LEGEND

- 🟥 Operating instrument in user program
- 🟪 In design or construction
- 🟦 Under consideration

15-G00337A/gim

The Spallation Neutron Source is a facility of Oak Ridge National Laboratory, managed by UT-Battelle for the US Department of Energy.



This document consists of 2 pages and 0 figures.
No. 1 of 5 copies, Series A

CLINTON LABORATORIES

[redacted]

1. R. L. Doan
2. A. H. Snell
3. E. O. Wollan
4. Reading File
5. Central File

DATE Jan. 13, 1945

TO R. L. Doan DEPARTMENT

FROM E. O. Wollan DEPARTMENT

IN RE: Program Relative to Diffraction of Neutrons by Crystals

CLASSIFICATION CANCELLED
Ted Davis 5-16-96
ADD signature Date
Single rereview of CCRP-declassified documents was authorized by DOE Office of Declassification memo of August 22, 1994.

The diffraction of neutrons by crystals has at least two apparent aspects, (1) its use as a "tool" in studying various physical constants as a function of neutron energy in the region from 0.001 ev to about 10 ev and (2) a study of the phenomenon of neutron diffraction itself.

We have made a start on both of these aspects of the problem. Relative to the first we have made what we feel to be a careful study of the absorption by cadmium from 0.05 to 1.0 ev and have shown from this that the Breit-Wigner formula represents the experimental data within very close limits. Relative to the second aspect we have shown that both gypsum and rock salt give good Bragg reflections with neutrons.

1. We now plan to make a study of 49 involving (a) a measurement of the total cross section over the thermal region and over the resonance peak which falls at about 0.3 ev and (b) a separate measurement of the fission cross section over the same region, which will be done by using a fission counter in place of the BF_3 proportional counter now used. This problem takes on new importance in view of the recent interest in a converter and the need in this connection for an accurate knowledge of the 49 constants.

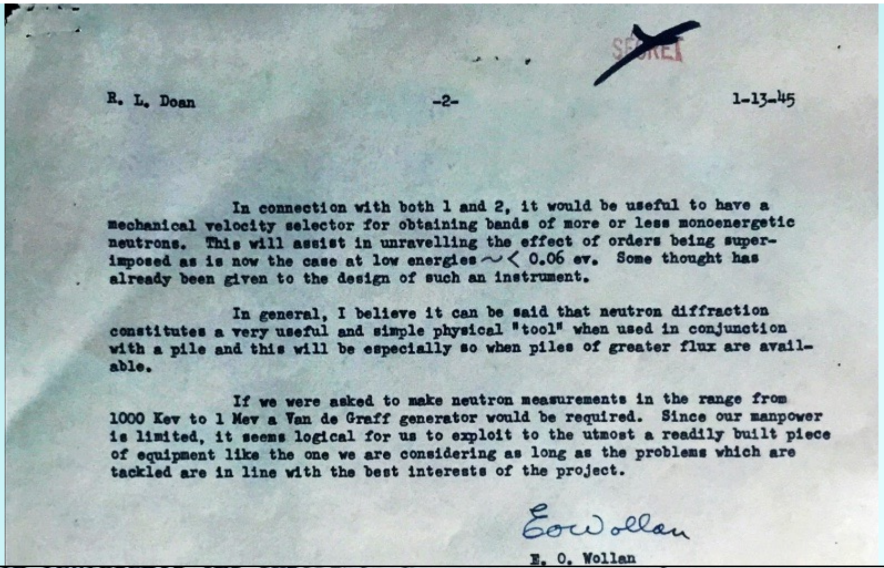
We would like to make similar measurements with 23 as well as with any of the other thermally fissionable substances that can be acquired in sufficient quantity. I would like to have you interpret this as a request for at least 20 mgs of 23 when such can be made available to us.

The accurate measurement of cross sections of a large variety of substances should be undertaken with this apparatus. Since a careful study of each substance requires considerable time, those which are of most significance to the project should be considered first. To extend the absorption studies up to say 10 ev will require some careful design of equipment. We have already given some thought to this.

2. A study of the phenomenon of neutron diffraction as related to the type of crystal used is of interest although probably of less importance to the project. We have planned to divert a rather small per cent of our time in this direction. We have ordered a rock salt crystal which can be cut along a 111 plane so the coherent scattering by Na and Cl atoms can be independently determined. This is of importance in checking the diffraction theory as it relates to the role played by atoms of different spins and of different isotopic composition.

~~This [illegible] contains information affecting the national defense of the [illegible] States within the meaning of the Espionage Act, U. S. C. 50 [illegible] or the revelation [illegible] its contents in any manner to an [illegible] person is prohibited by law.~~

Classification Cancelled
~~Or Changed To~~
By Authority Of
By
Date AUG 23 1971



~~SECRET~~

R. L. Doan -2- 1-13-45

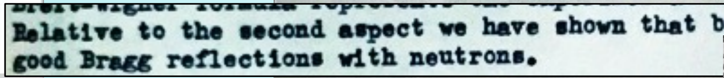
In connection with both 1 and 2, it would be useful to have a mechanical velocity selector for obtaining bands of more or less monoenergetic neutrons. This will assist in unravelling the effect of orders being superimposed as is now the case at low energies $\sim< 0.06$ ev. Some thought has already been given to the design of such an instrument.

In general, I believe it can be said that neutron diffraction constitutes a very useful and simple physical "tool" when used in conjunction with a pile and this will be especially so when piles of greater flux are available.

If we were asked to make neutron measurements in the range from 1000 Kev to 1 Mev a Van de Graff generator would be required. Since our manpower is limited, it seems logical for us to exploit to the utmost a readily built piece of equipment like the one we are considering as long as the problems which are tackled are in line with the best interests of the project.

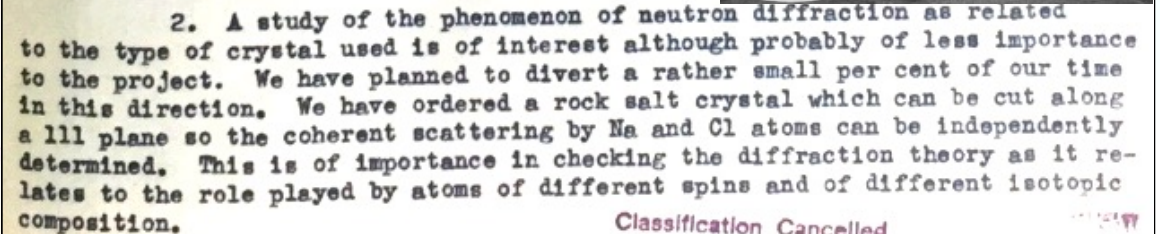
E O Wollan
E. O. Wollan

EOW:H



Relative to the second aspect we have shown that both gypsum and rock salt give good Bragg reflections with neutrons.

1949



2. A study of the phenomenon of neutron diffraction as related to the type of crystal used is of interest although probably of less importance to the project. We have planned to divert a rather small per cent of our time in this direction. We have ordered a rock salt crystal which can be cut along a 111 plane so the coherent scattering by Na and Cl atoms can be independently determined. This is of importance in checking the diffraction theory as it relates to the role played by atoms of different spins and of different isotopic composition.

Classification Cancelled

The largest growth includes the topics of instrumentation and archeology/geology since they were almost non-existing in the 2006–2010 time period

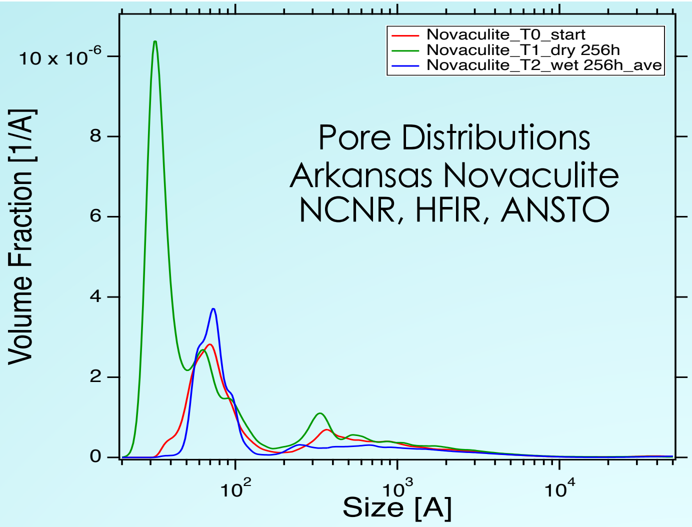
Barriga et al., (2021) A Bibliometric Study on Swedish Neutron Users For the Period 2006–2020. 2020, Neutron News, 32:4, 28-33. DOI:10.1080/10448632.2021.1999147

There are a LOT of Neutron Techniques Applicable to Geologic Problems
A Few Quick Examples

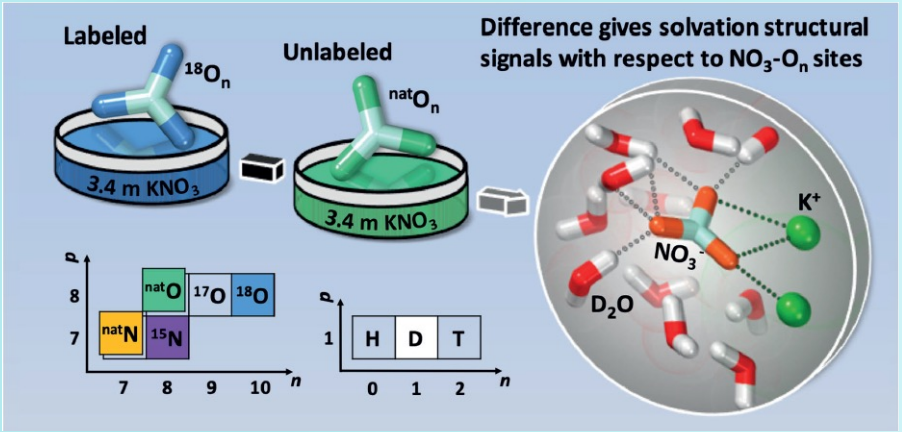
Anovitz, L. M., Lynn, G. W., Cole, D. R., Rother, G., Allard, L. F., Hamilton, W. A. et al. (2009) A new approach to quantification of metamorphism using ultra-small and small angle neutron scattering. *Geochimica et Cosmochimica Acta*, *73*(24), 7303-7324.

Geological Questions: (U)SANS, PDF, Strain Mapping

- Multiscale porosity
  - Changes with Space, Time, Mineralogy, Reaction
  - Accessible porosity
- Disordered material structures
- Strain fields INSIDE rocks

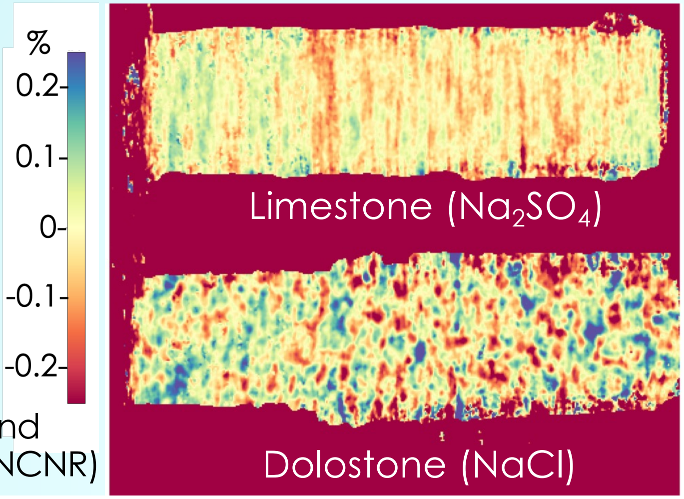


Pore Distributions
Arkansas Novaculite
NCNR, HFIR, ANSTO



NDIS determination of KNO_3 structure In solution NOMAD. SNS (Stack et al., 2021)

Calcite (113) Strain Mapping using Neutron Transmission Bragg Edge Imaging

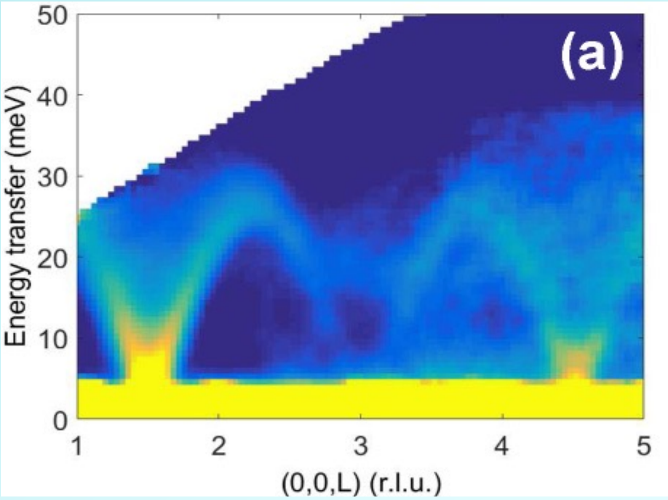


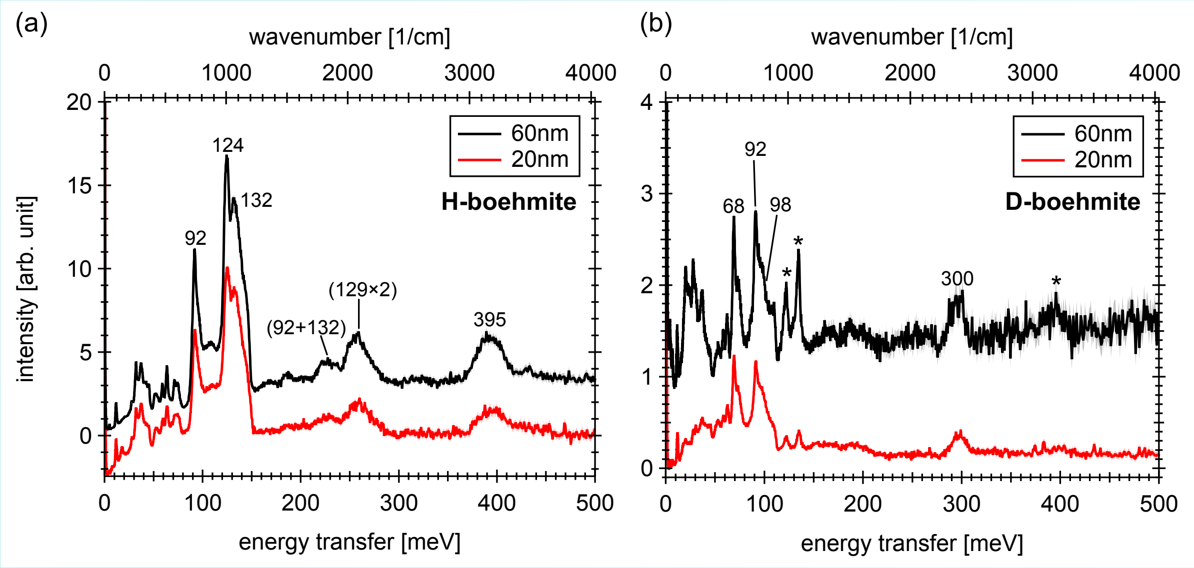
With Dan Hussey and Cyrus Daugherty (NCNR)

Geological Questions: INS and QENS

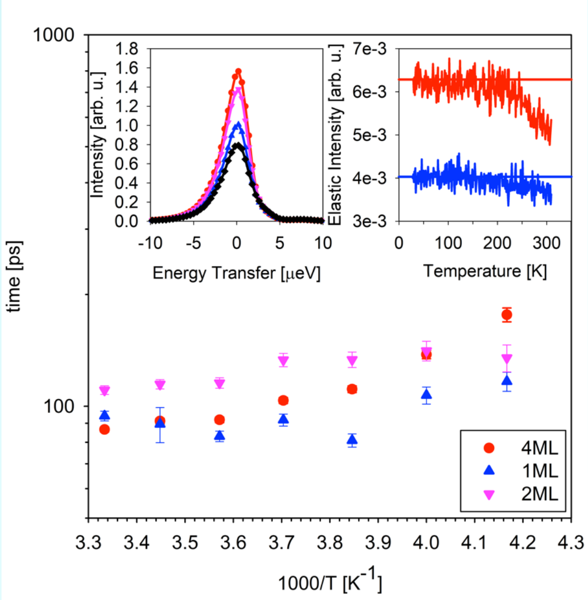
- Rock and mineral magnetism
- Surface Chemistry

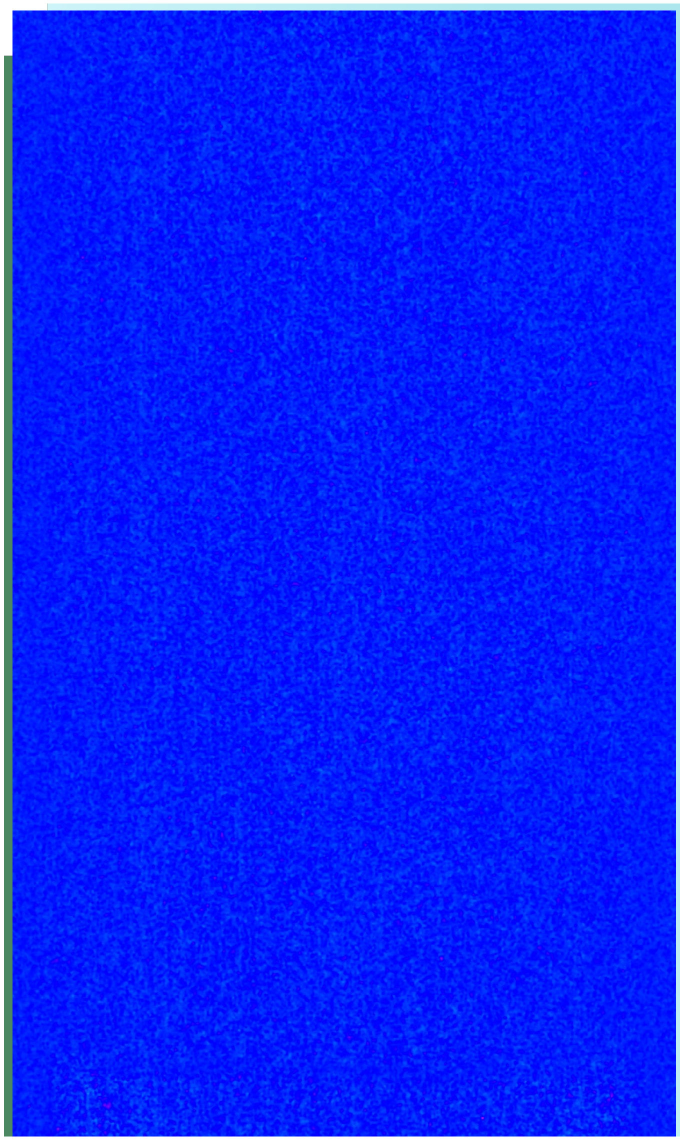
Magnetic Excitation Spectrum (INS)
Black Dioptase ($CuSiO_3$)
CNCS, SNS
Podlesnyak et al. (2019)





Water Layers on Boehmite (AlOOH) surfaces, BASIS





Geological Questions: Neutron Imaging

- Fluid Flow
  - Dynamic radiography
- 3D Phase Distributions
  - X/N Tomographic Imaging

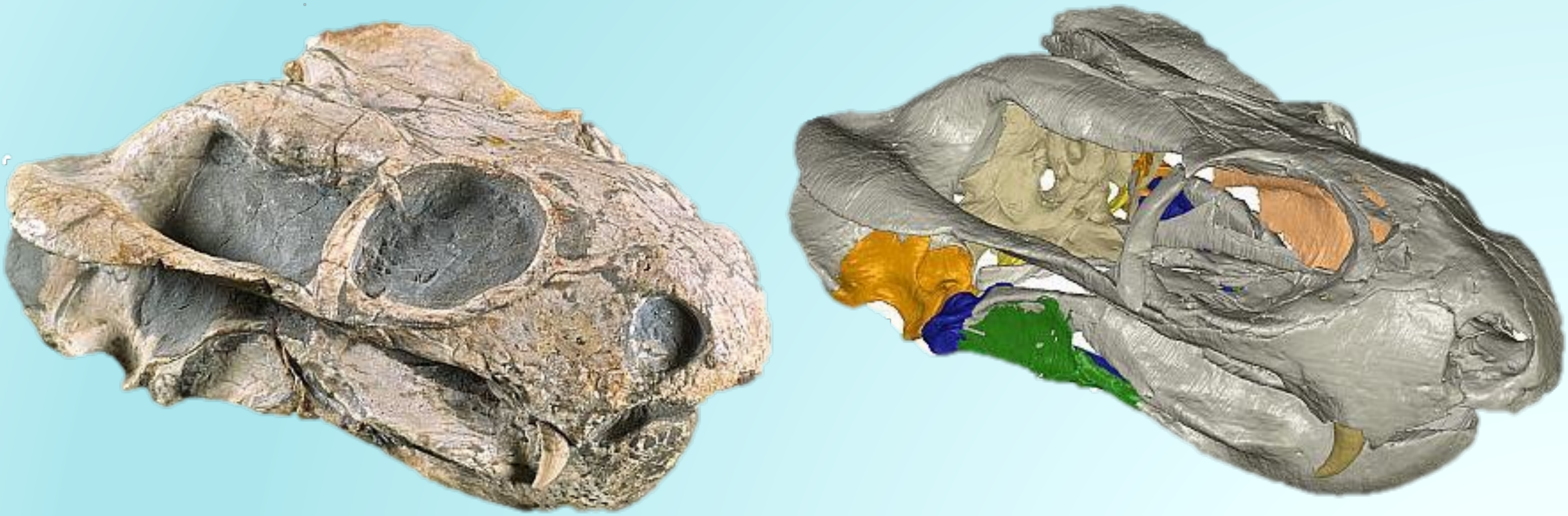
Neutron/X-ray Tomography

Wormhole formation
2-4 mD
Indiana Limestone
pH 0 HCl, 10 cc/min

Howardite Meteorite

Treiman et al. (2022)

Neutron Imaging in Paleontology



Skull of non-mammalian synapsid ***Pristerodon mackayi***, Late Permian, Biesjespoort, South Africa
Neutron Tomography at Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland. ICON cold neutron beamline.

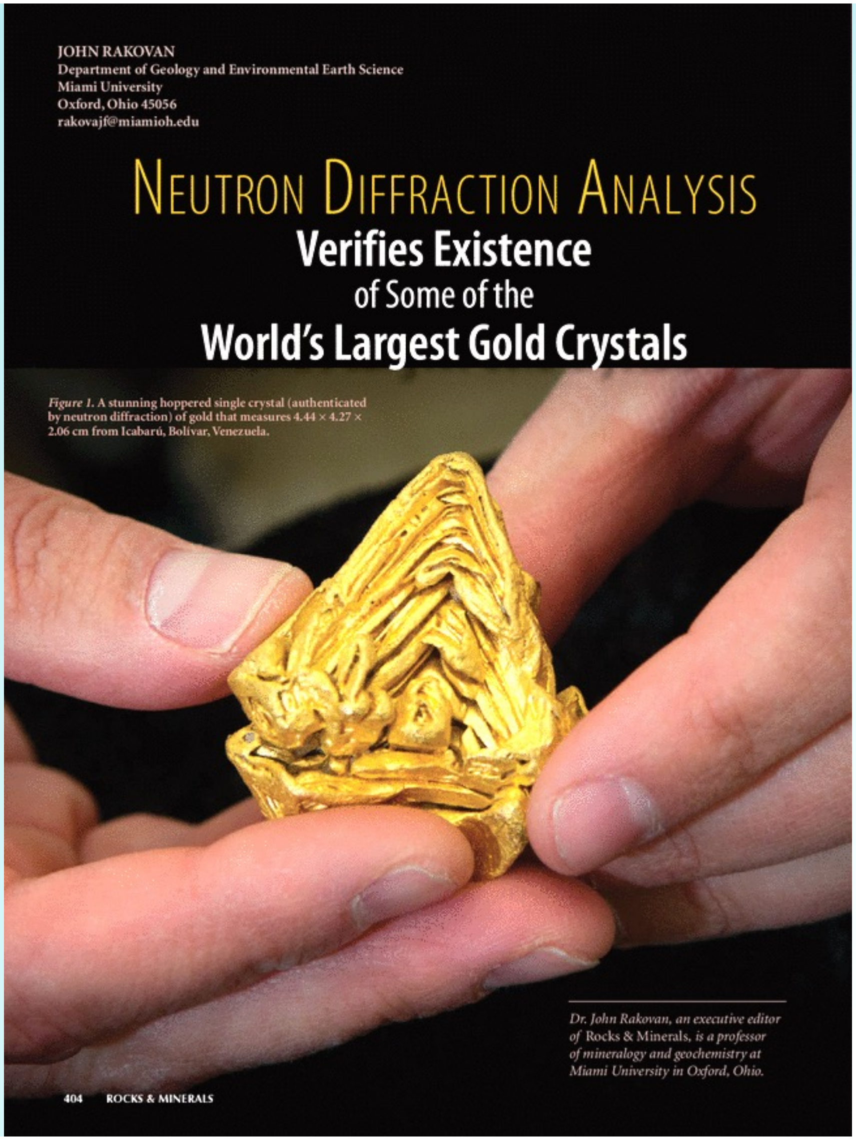
Laass, M (2016) *Acta Palaeontologica Polonica 61 (2): 267–280*

Testing the "naturalness" of Purported Huge Single Crystal Gold Specimens – Neutron Diffraction

" There was no doubt that they were gold; the question was whether Mother Nature was responsible for their beautifully faceted shapes. If they were natural—and we now know that most of them are—there is great scientific interest in the nature of their crystal structures and how they may have formed, which was the second goal of the study.

John Rakovan (2014) Neutron Diffraction Analysis Verifies Existence of Some of the World's Largest Gold Crystals, Rocks & Minerals, 89:5, 404-407, DOI:10.1080/00357529.2014.926175

Single Crystal Diffraction Measurements at
Lujan Center, HIPPO Diffractometer
Los Alamos National Laboratory



JOHN RAKOVAN
Department of Geology and Environmental Earth Science
Miami University
Oxford, Ohio 45056
rakovajf@miamioh.edu

NEUTRON DIFFRACTION ANALYSIS Verifies Existence of Some of the World's Largest Gold Crystals

Figure 1. A stunning hoppered single crystal (authenticated by neutron diffraction) of gold that measures 4.44 × 4.27 × 2.06 cm from Icabarú, Bolívar, Venezuela.

Dr. John Rakovan, an executive editor of Rocks & Minerals, *is a professor of mineralogy and geochemistry at Miami University in Oxford, Ohio.*

404 ROCKS & MINERALS

Plan For the Rest of the Talk

A couple of longer examples

1,2) Porosity: Replacement and Dissolution

3) Ultraconfined Water

EXAMPLE (1)

Porosity: Replacement and Dissolution

(small angle scattering)

Replacement Reactions

Pseudomorphism: Internal structure or chemical composition is changed but external form is preserved

Diffusion:

- ❖Negligibly slow at ambient conditions

Malachite Replacing Azurite (Bizbee, AZ)

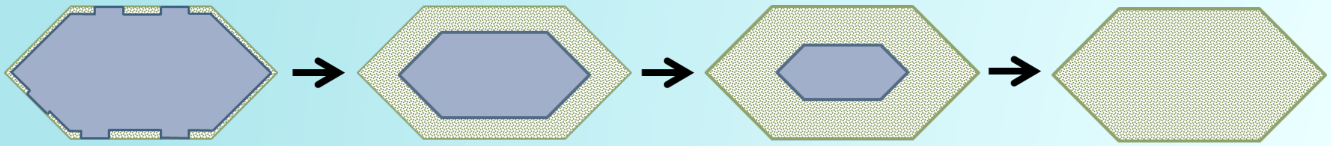
Irocks.com

Limonite after Pyrite

Minerals.net

Gold after Pyrite

Interface coupled dissolution and reprecipitation (ICDR):

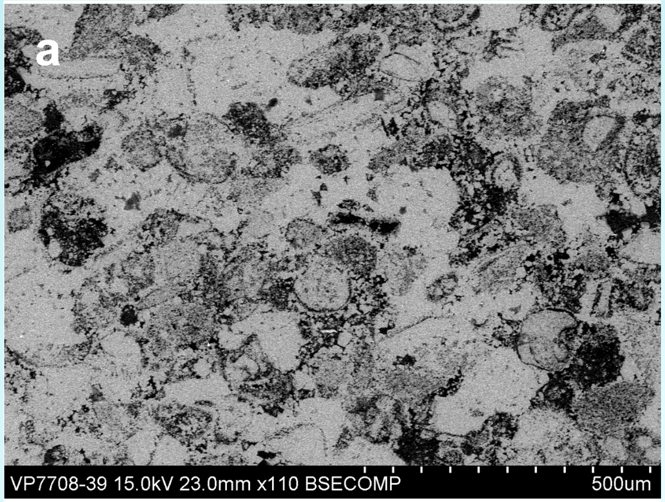


after Ruiz-Agudo et el., 2014

Carthage "Marble" and Texas Cream Limestone

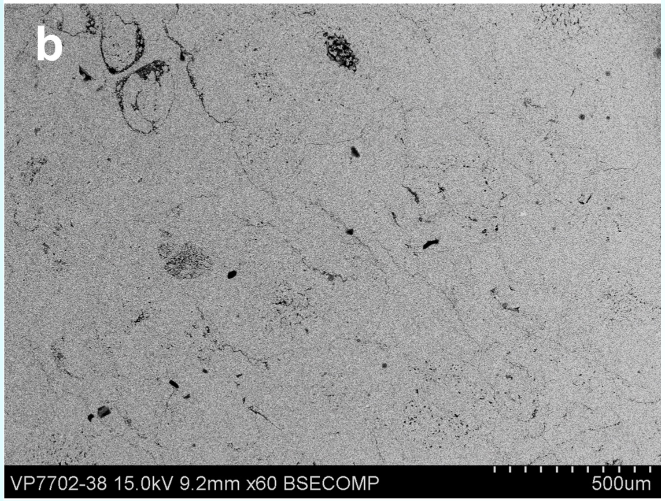
Texas Cream

Edwards Limestone,
Segovia Member,
I10 west of Kerrville, TX
14% porosity
Permeability 2.9-3.9 mD



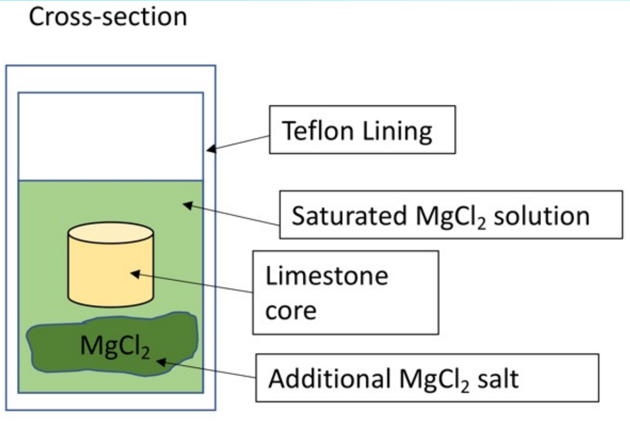
Carthage "Marble"

(Burlington/Keokuk limestone)
East Battlefield Overlook,
Wilson's Creek
National Battlefield, MO
2.5% porosity
Permeability 2 x 10^{-6} mD



Experimental Setup

- Static, saturated replacement experiments
- Dried & Thin section preparation
- Chemical Imaging
- (Ultra)-Small Angle Scattering Porosity analyses



Carthage Marble

Texas Cream

Reaction:

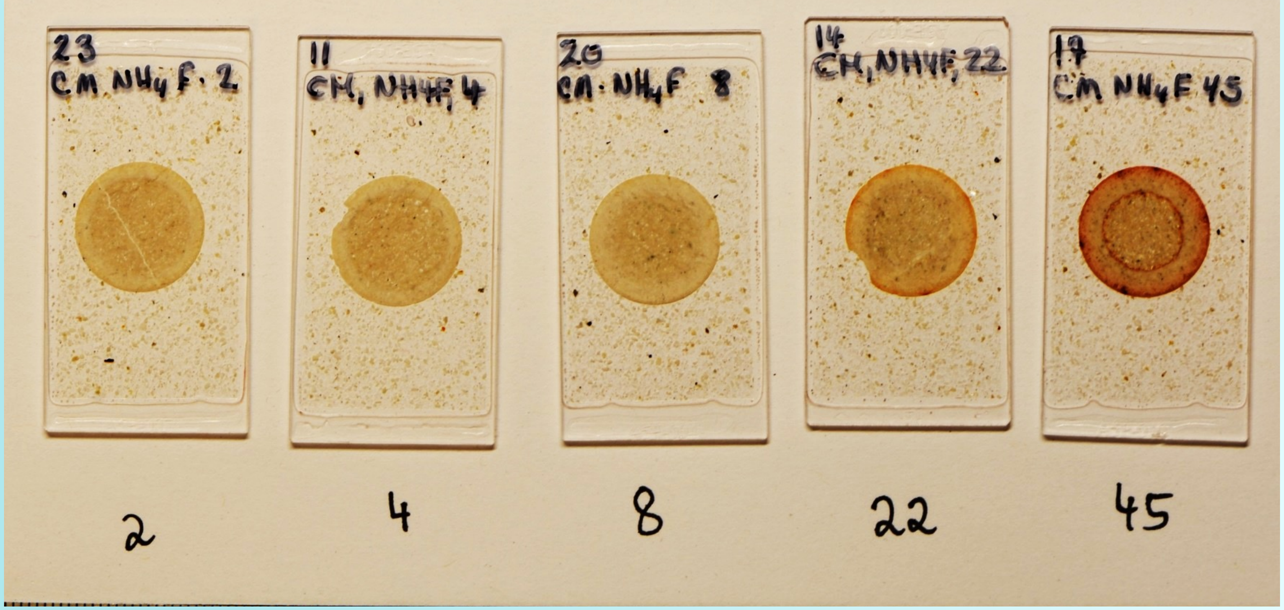
200 °C ($CaCO_3$ + $McCl_2$ = $CaMg(CO_3)_2$) / $MgCO_3$ **ΔV_s = -12.899 vol. % / -12.906 vol. %**

Saturated solutions. Cores 5/8" x 5/8"

Microstructure Characterization

Static, saturated replacement experiments → **Dried & Thin section preparation** → Chemical Imaging → (Ultra)-Small Angle Scattering Porosity analyses

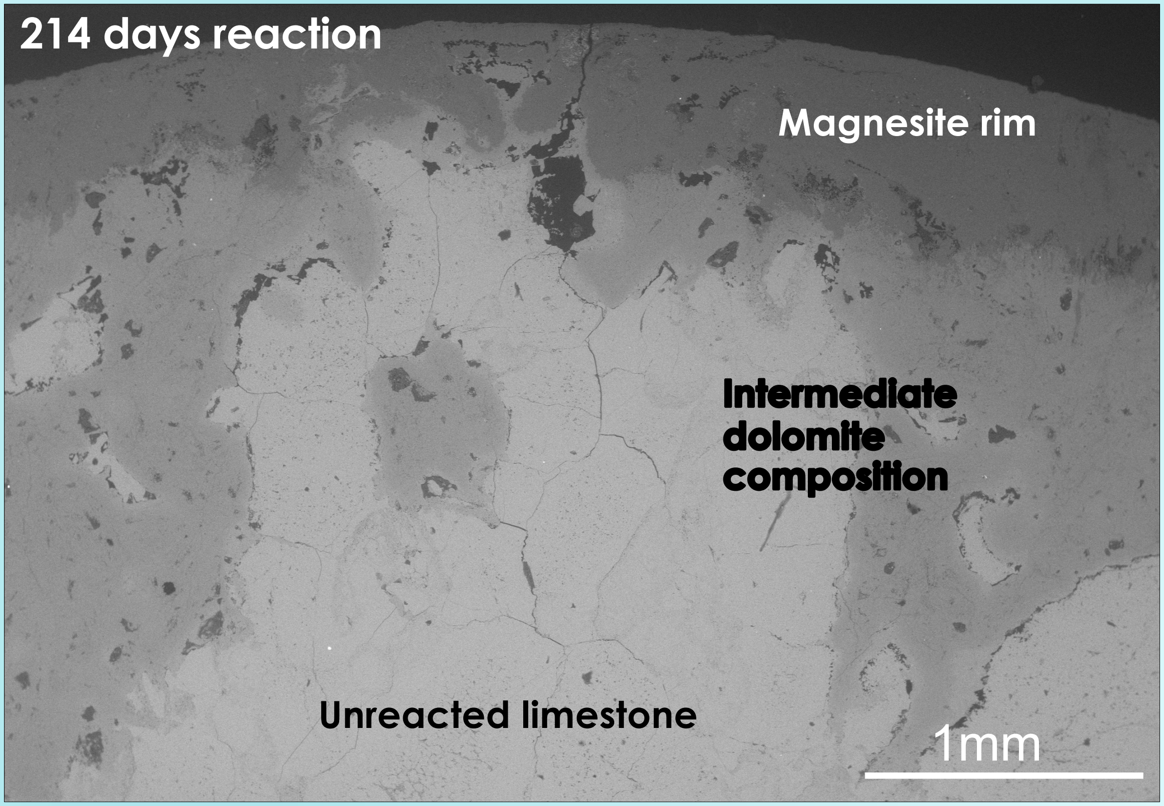
Time series



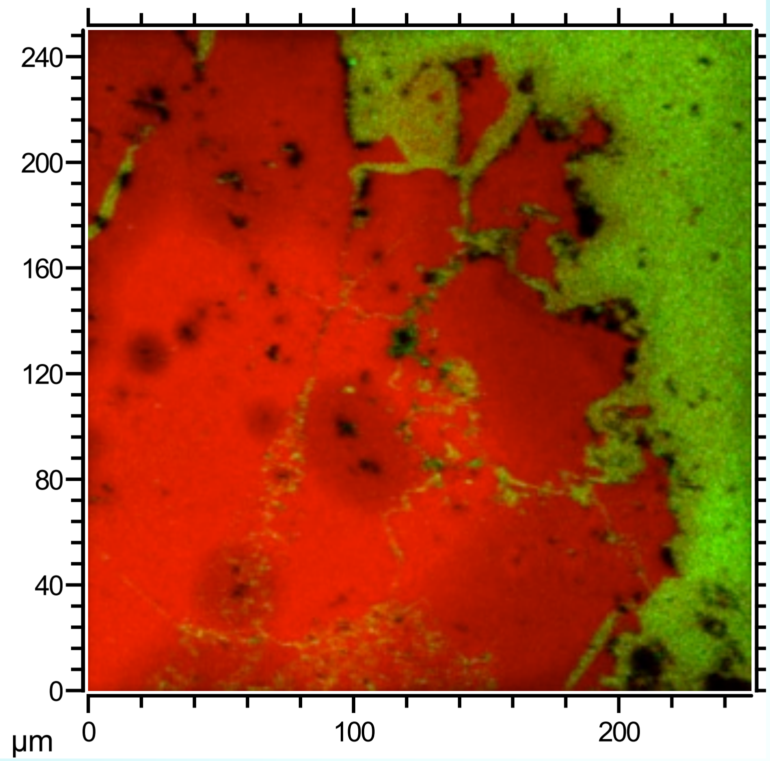
Days

Dolomitization of Limestone – Grain Boundaries?

Carthage marble: Low Porosity Limestone



SEM-BSE – Chemical composition via microprobe



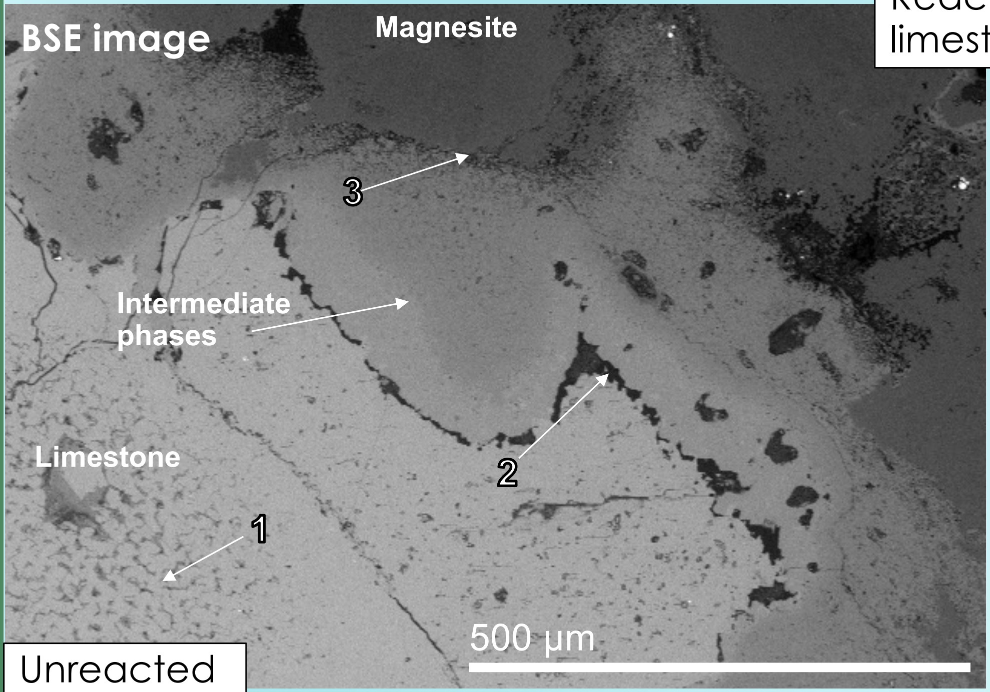
ToF-SIMS

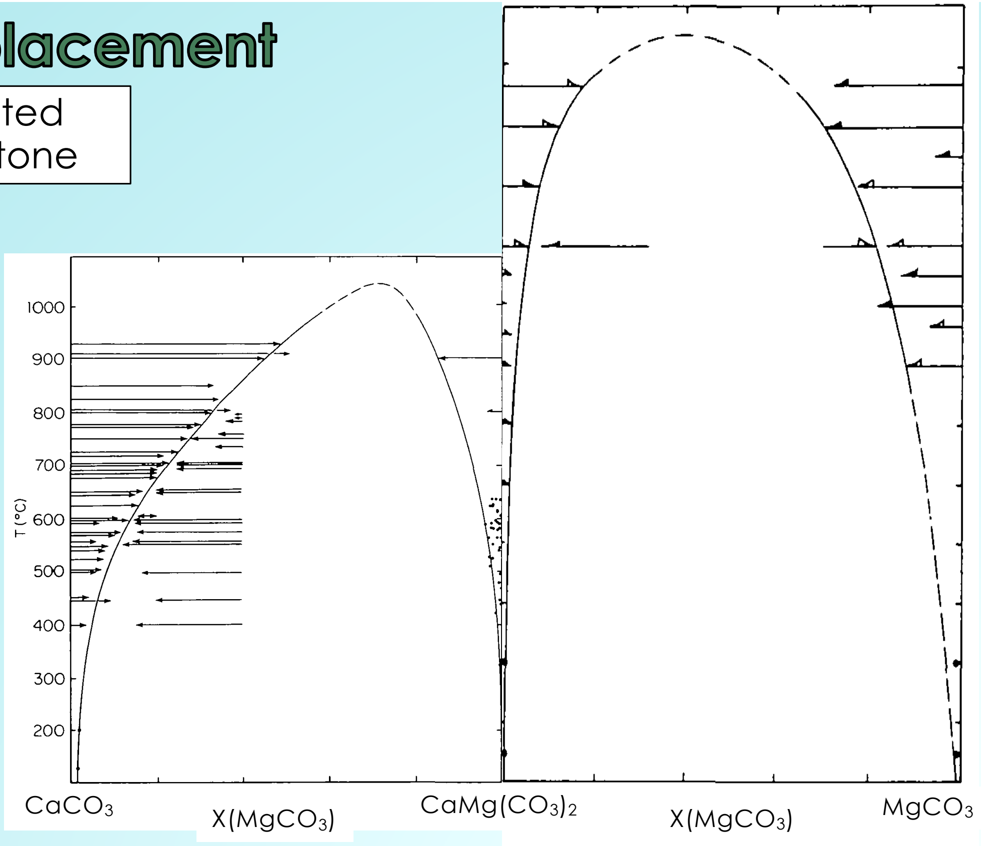
Ca Mg

ICDR model is clearly insufficient – fast Transport Pathways

Weber et al., **2021**

Porosity Development During Replacement





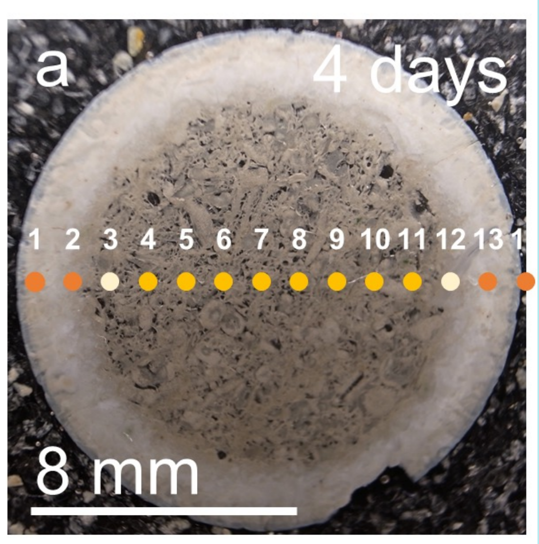
Anovitz and Essene (1987)

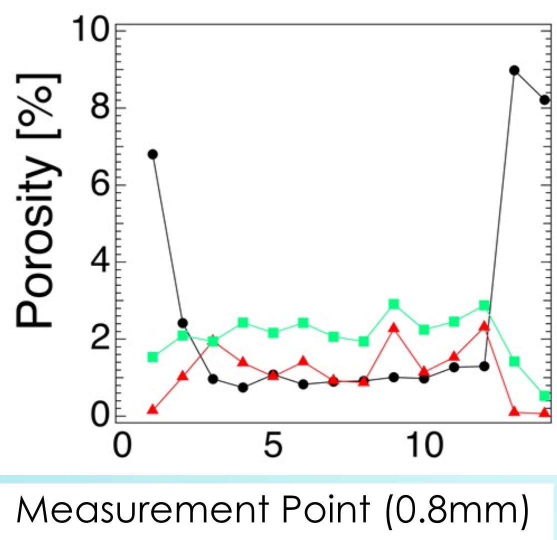
Three kinds of pores:

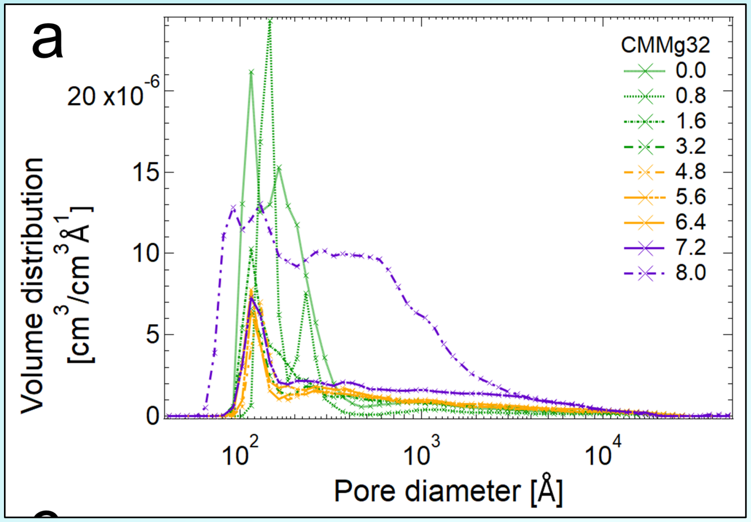
1) Intra-granular porosity in primary calcite
2) Inter-granular pores (several µm) between pristine calcite + replaced material
3) Porosity between magnesite and intermediate phase

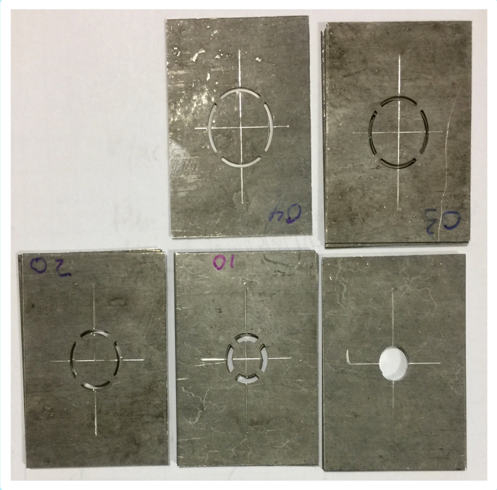
Weber et al., **2021**

Porosity: Low Porosity Limestone (U)(W)SAX(N)S



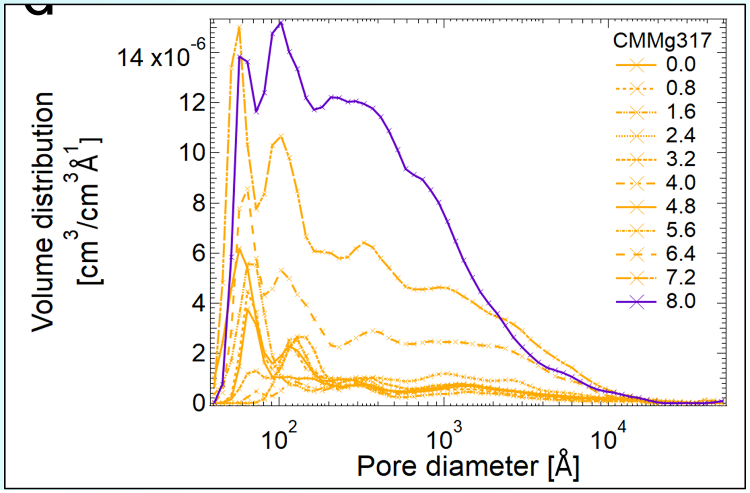




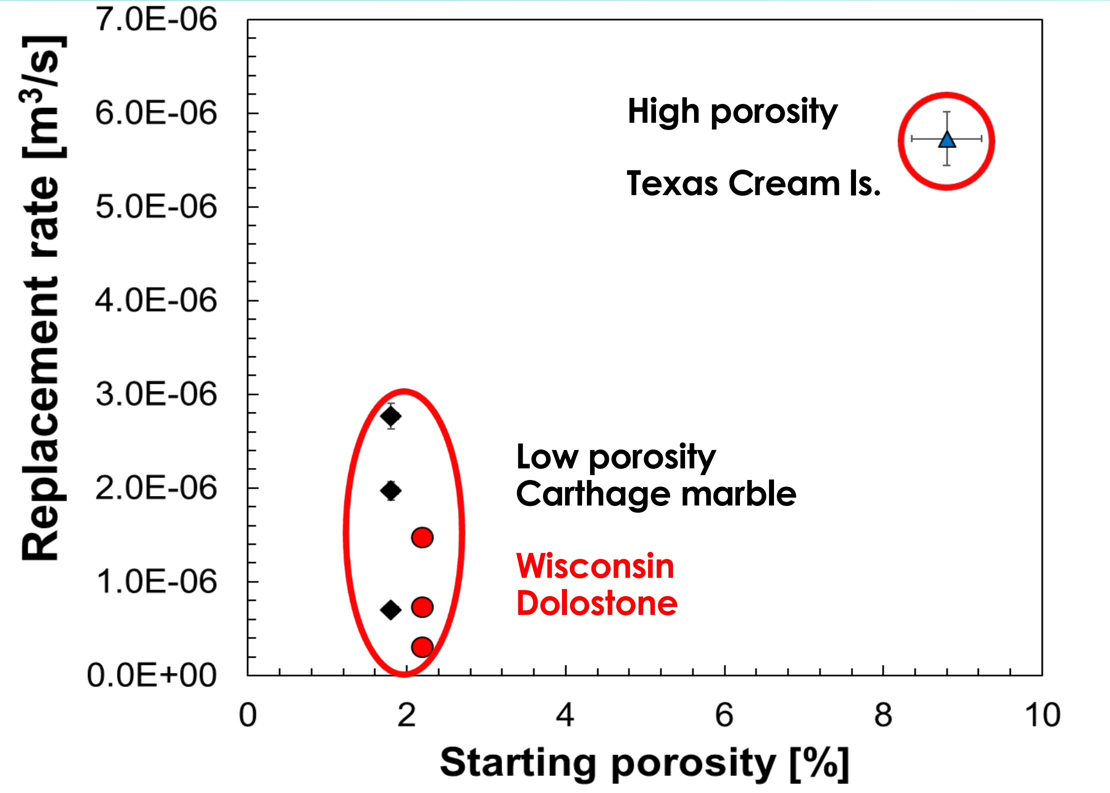


- Replacement rim forms
- Rim porosity is higher
- More nanopores and
  more macropores in rim

Weber et al., **2021**



Microstructure Affects Replacement Rate



Replacement rate
determination by
image analyses

Weber et al., **2019**

- Both low porosity limestone and dolostone show similar replacement rate
- **Grain boundaries are important for replacement reactions**
- **Effect of microstructure is greater than that of chemical reactivity**

Porosity and Dissolution (Weathering)

Chemomechanical Weathering of Carbonates

Weathering rates
Western Wall, Jerusalem

(Emmanuel and Levenson 2014)

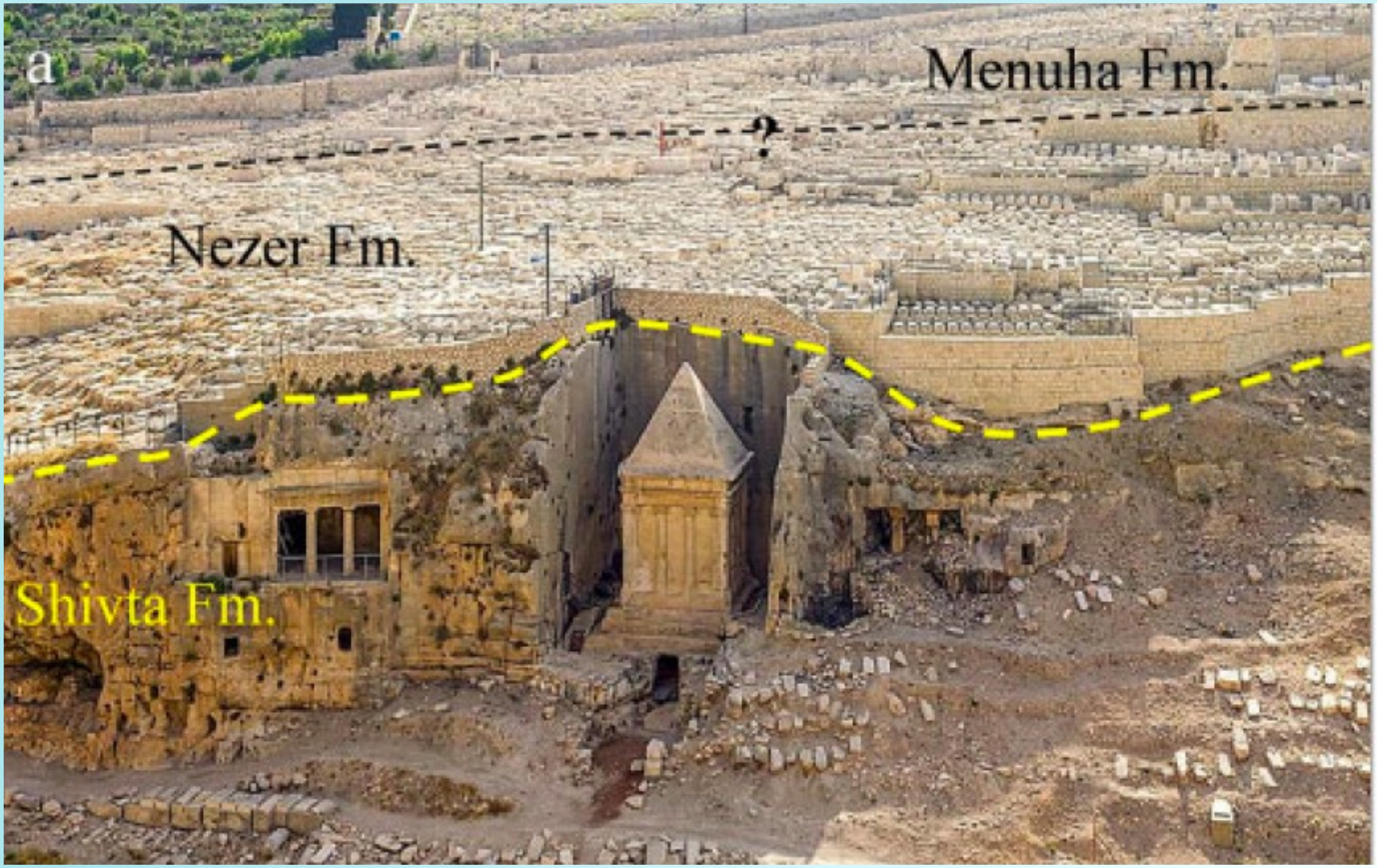
Finer-grained limestone, harder, less porous limestone (Netzer Fm.)

eroded faster than

Coarser-grained, softer, more porous limestone (Shivta Fm.)

Why?

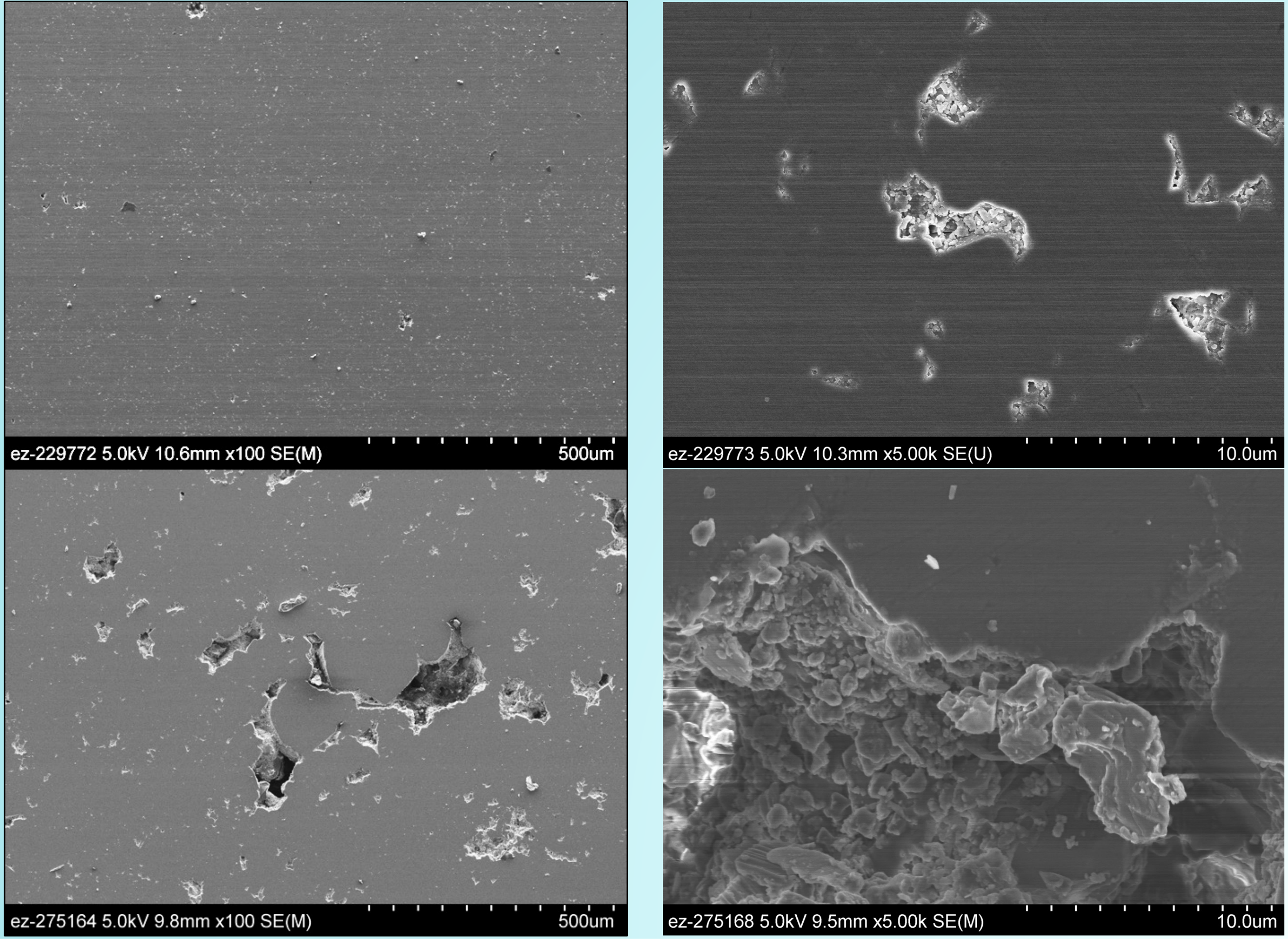
Weathering of Shivta and Netzer



Kidron Valley, Lower slope, Mount of Olives
“Did Herod’s builders cheat him ?”

Shtober-Zisu and Zissu, 2018

Shivta and Netzer Limestones Starting (polished)



Netzer Limestone

1.5%
Porosity

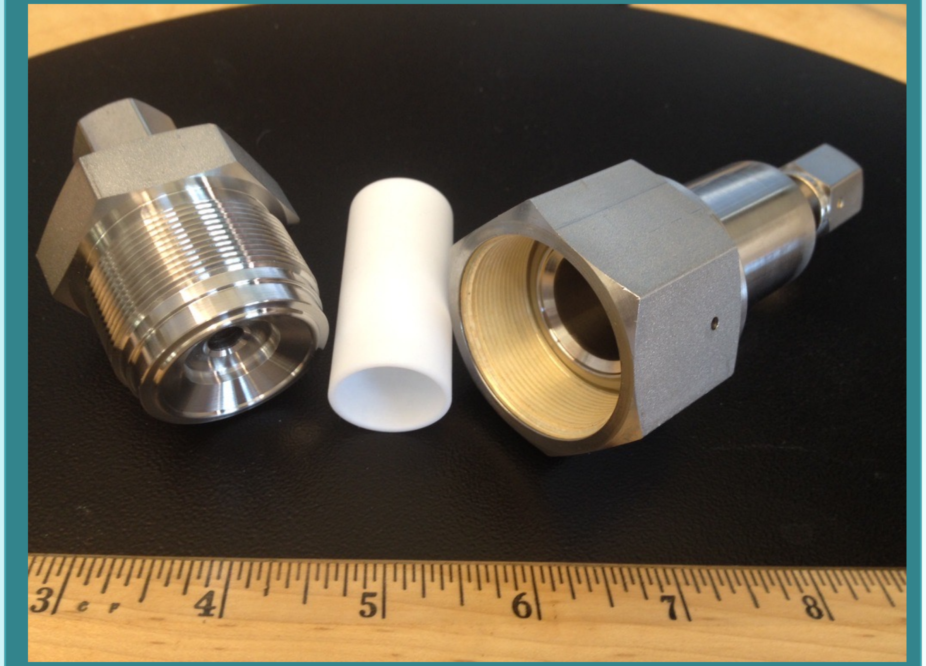
Shivta Limestone

~21%
Porosity

Experimental Conditions

- **Experiment 2**
  - Flow rate: 1.25 cm^3/min
  - Flow time: 958.917 hr.
  - pH: 5.7 (CO_2 from air)
  - Flow amount: 71.92 liters
- **Experiment 3**
  - same total H^+ as Exp. 1, 0.55x Exp. 2
  - Flow rate: 1.25 cm^3/min
  - pH: 3.96
  - Flow amount: 0.72 liters
- **Experiment 4**
  - Flow rate: 1.25 cm^3/min
  - pH: 2
  - Flow amount: 0.75 liters
- 30°C water bath, ~1 atm.
- Samples initially dry
- One end of core polished
- (U)SANS samples cut as cross sections

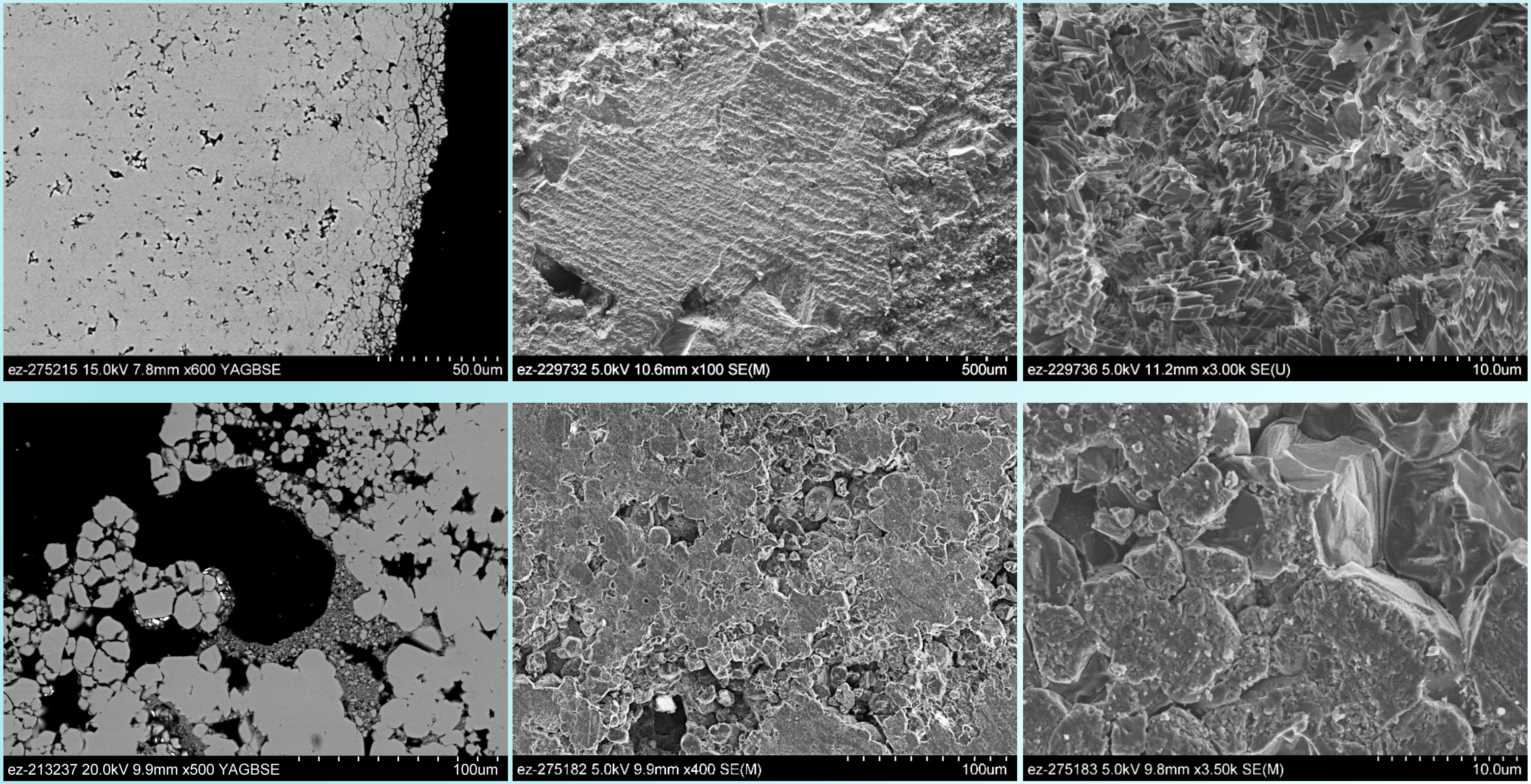
4 limestones, 5 masks, 3 experiments
60 data sets!



Flow vessels

Constructed from VCR fittings
316 steel
Teflon lined

Shivta and Netzer Limestones After Run 2



Netzer Limestone

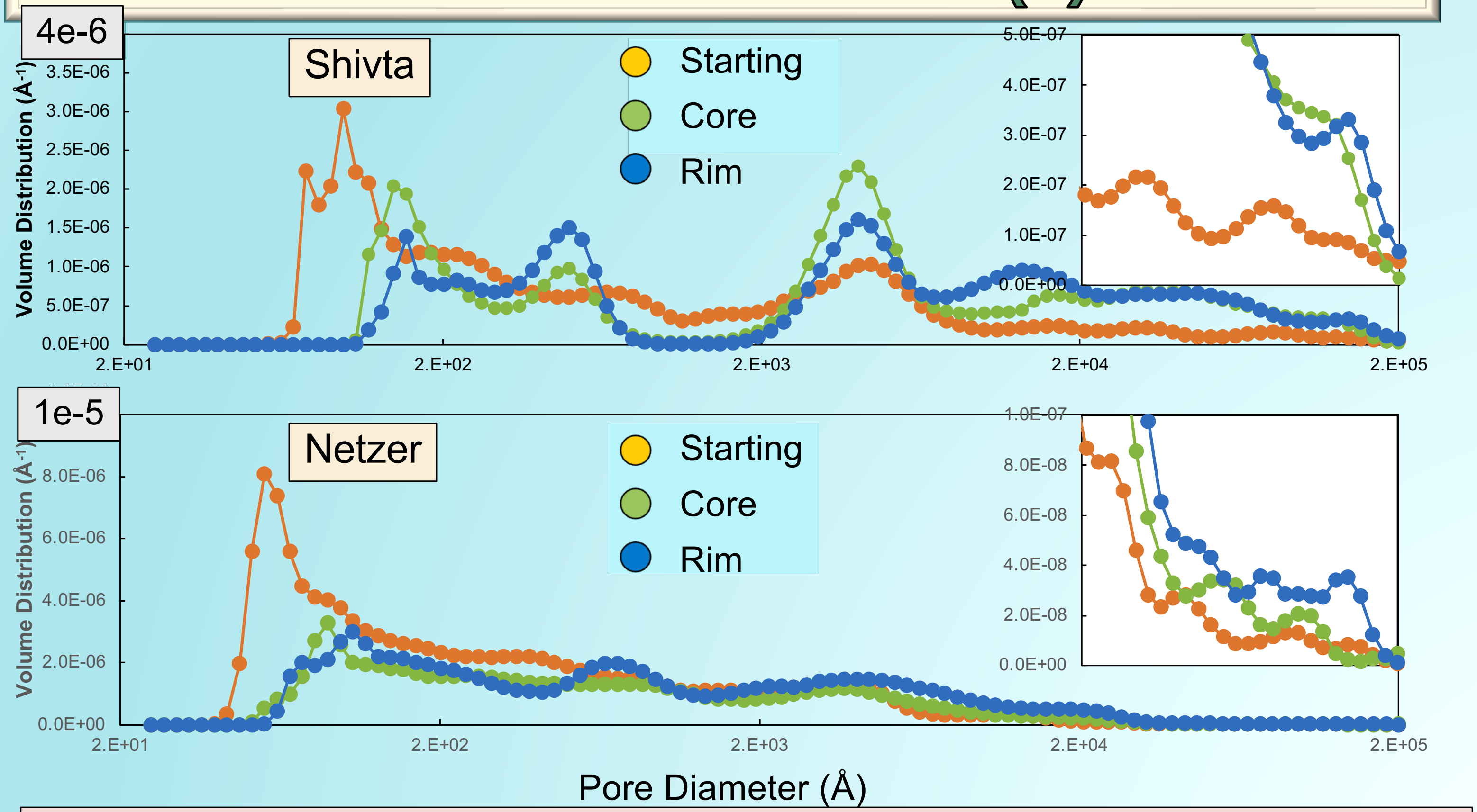
Shivta Limestone

Cross Section

Polished End

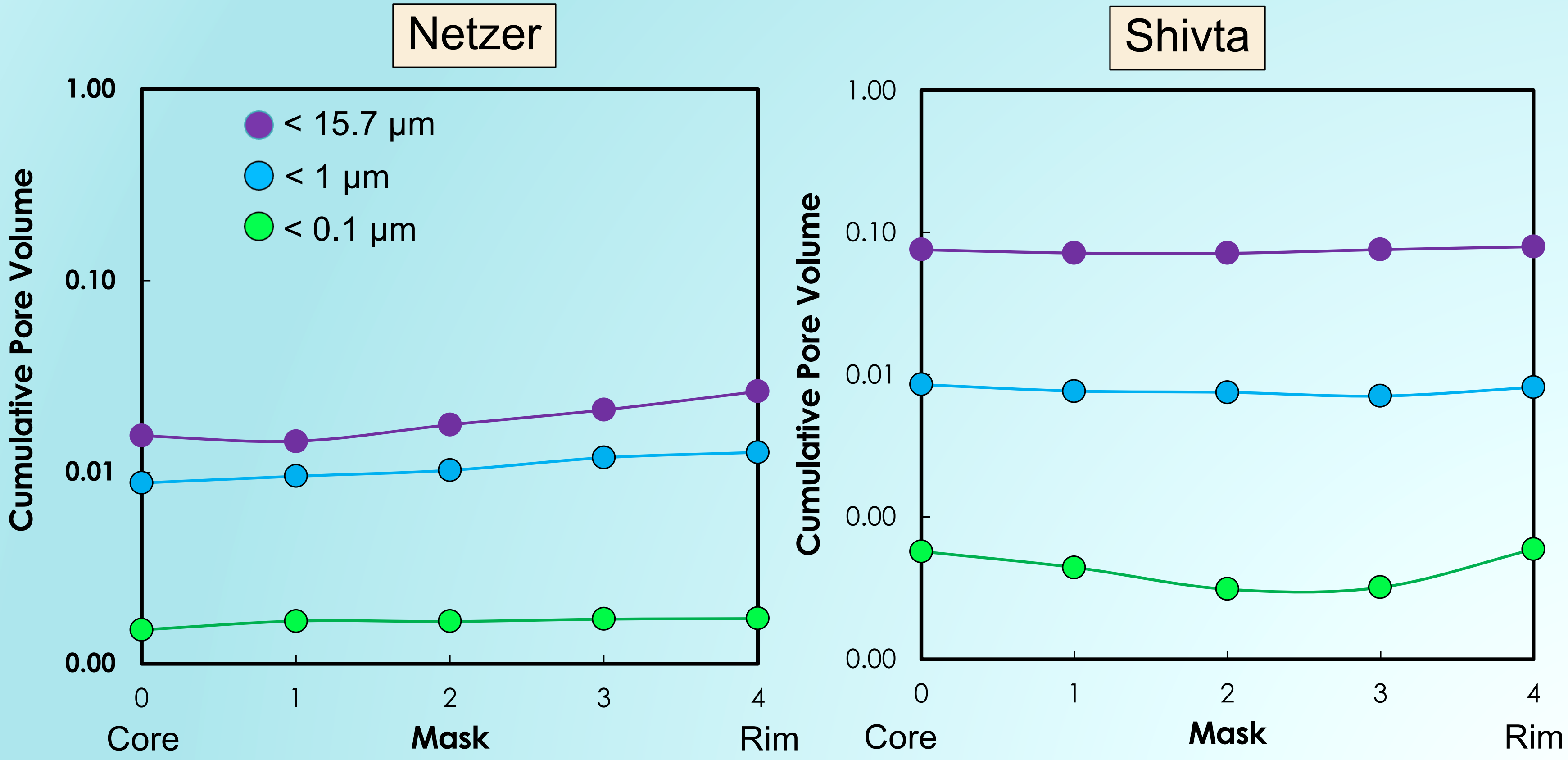
Polished End

Pore Volume Distributions – (U)SANS



1. Apparent loss of smallest pores
2. Netzer has more small-scale porosity, less total porosity
3. Shivta shows much more relative porosity increase core and rim

Cumulative Pore Volume - Core to Rim



Shivta shows larger pervasive changes
Netzer only small changes near the surface

So Far

Everything about these results is, qualitatively, EXACTLY What one would expect

And NOT what really happens

Shivta

naturally, weathers much more **slowly** than Netzer

Remember this?

Weathering rates
Western Wall, Jerusalem

(Emmanuel and Levenson 2014)

In the REAL world

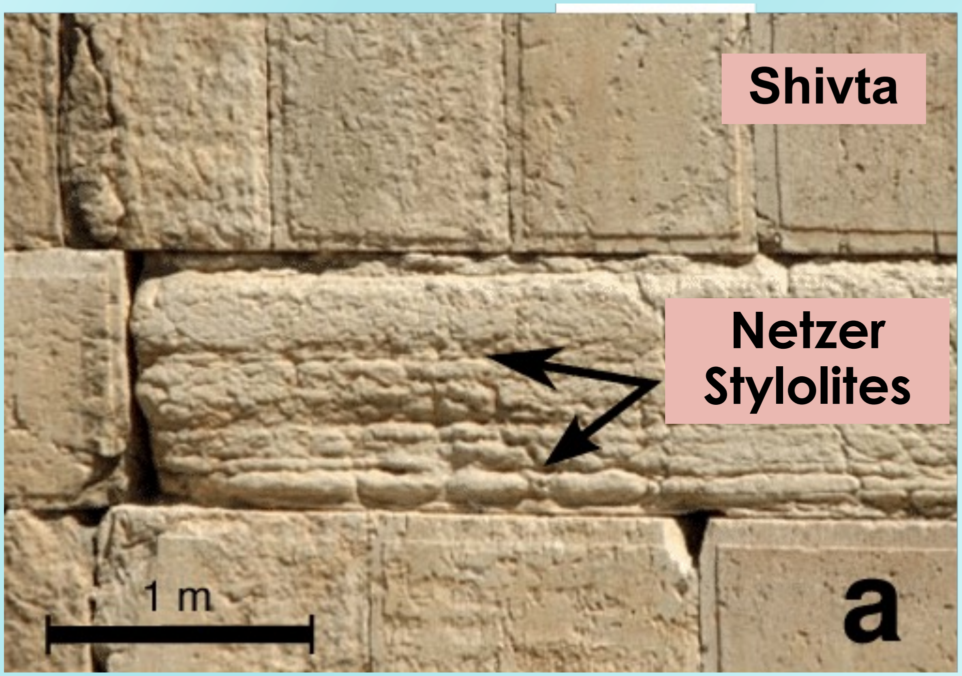
The finer-grained, less porous Netzer weathers faster in than the Shivta

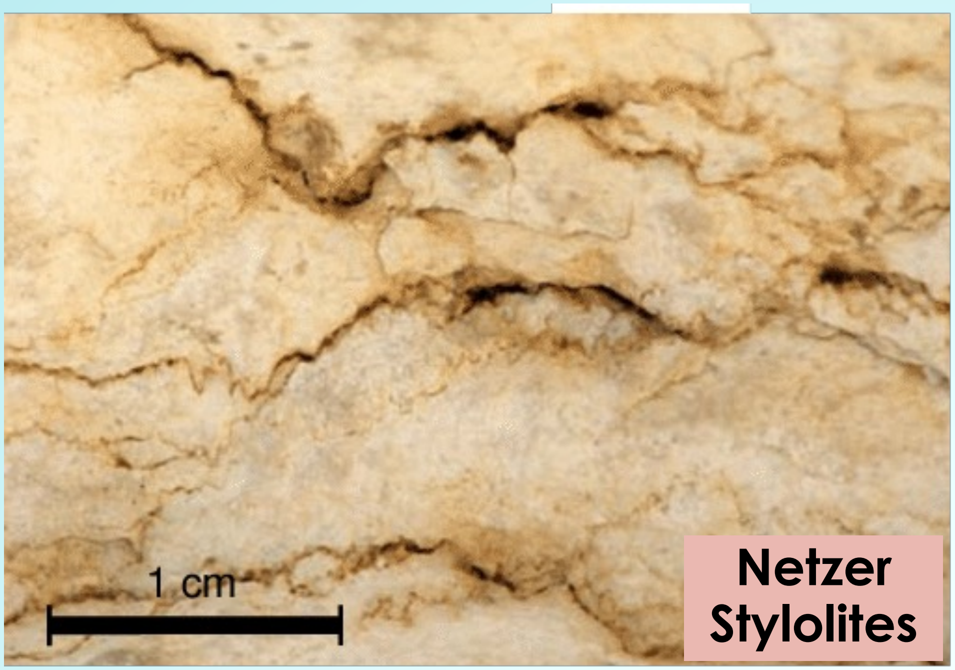
In the LABORATORY

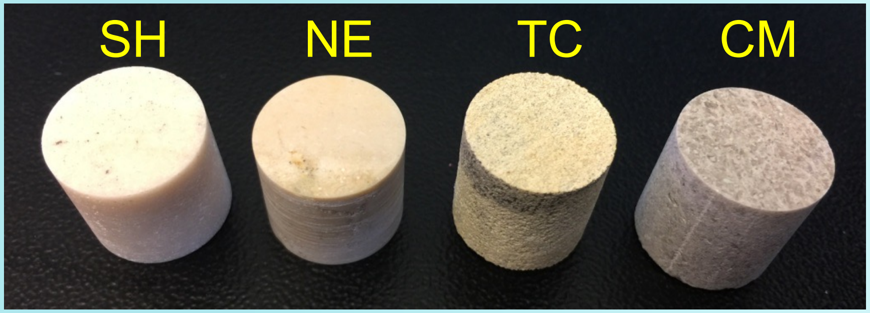
The Shivta weathers faster

Why?

Larger-Scale Features







Stylolites: Pressure solution features

Scale Matters

Parallel to grain boundary effects in replacement

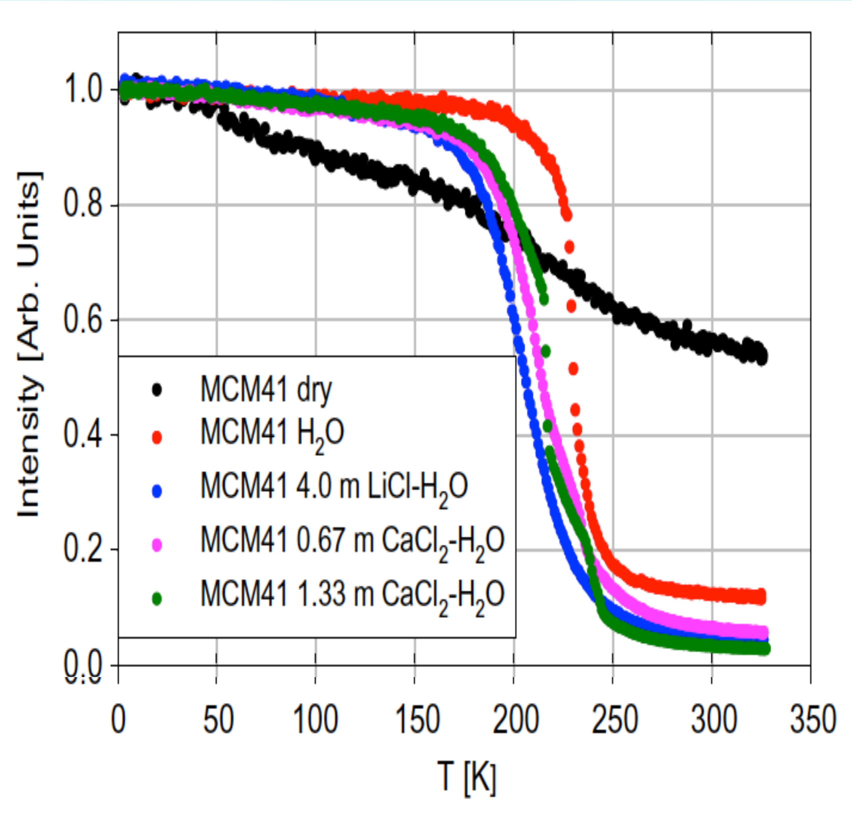
Example (2)

Ultraconfinement

A Multi-Technique Problem

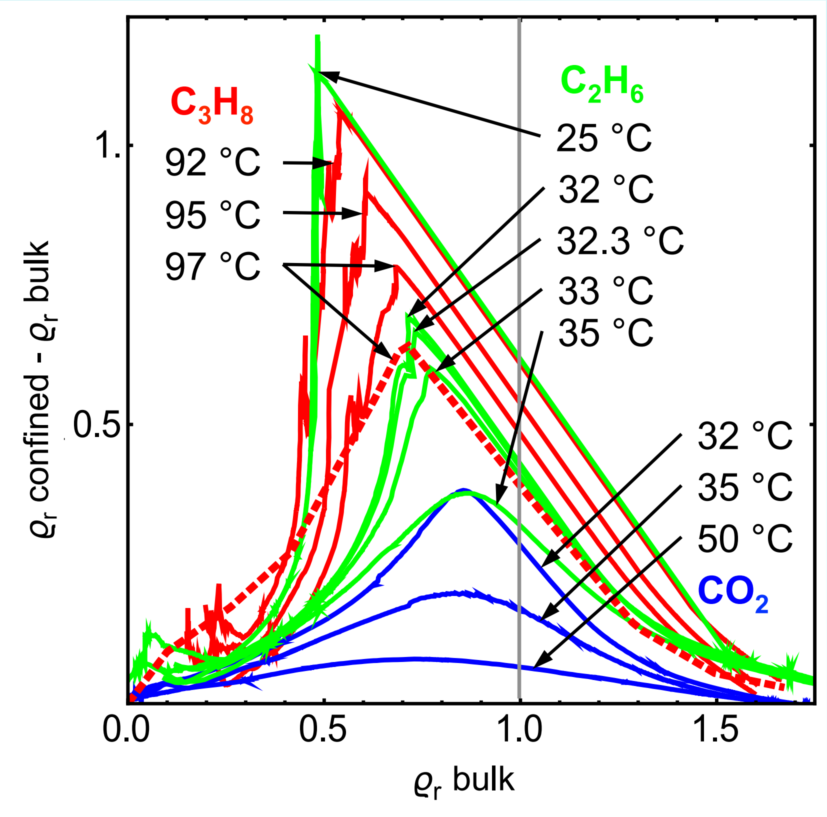
As Pores Get Small, Fluid Properties Change

QENS Elastic Intensity



Depression of freezing points of aqueous fluids in 1.9 nm MCM41 (Mamontov et al., 2008)

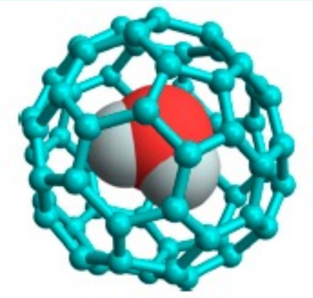
Vibrating Tube Densimetry



Excess densities of pore-confined propane, ethane, and CO_2 in silica aerogel - 7-9 nm (Gruszkiewicz et al., 2012)

ULTRACONFINEMENT

What happens if we take this idea to an end-member extreme
Cage, Channel or Planar-structures
ONLY large enough for a single fluid molecule

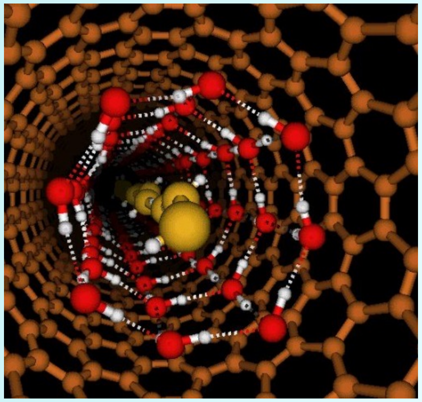

H_2O water in fullerene C_{60}

- Well-defined structure, not “broken” surfaces
- Varying confining chemistry, some are natural minerals
- Large crystals permit oriented measurements

Hemimorphite: planar H-bonds

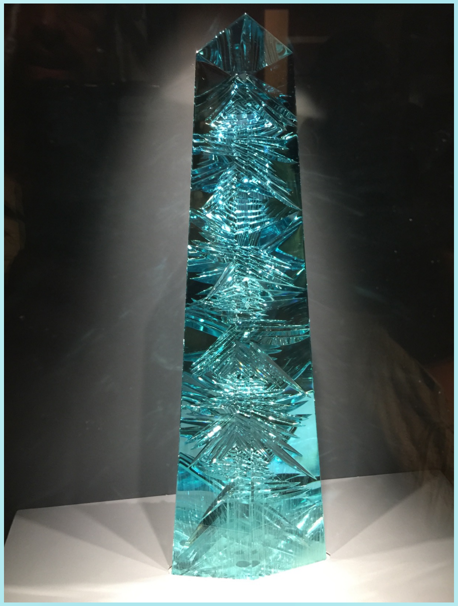
Dioptase: proton ordered

Water in SWNT

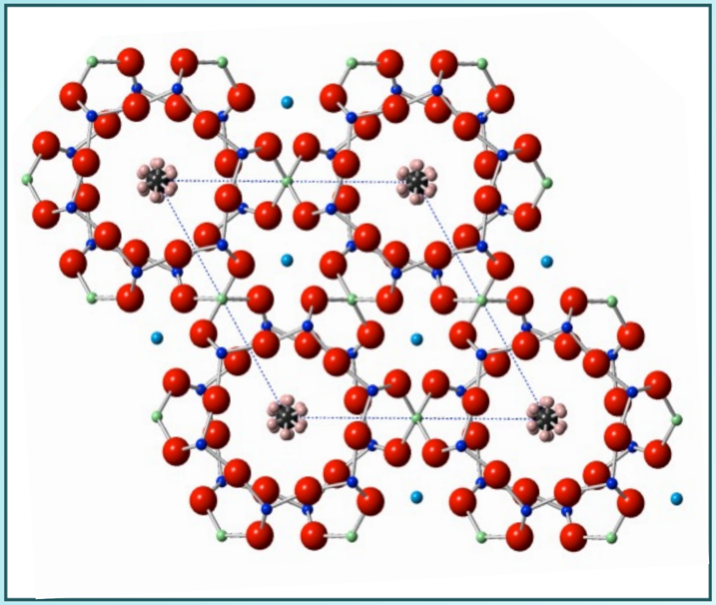


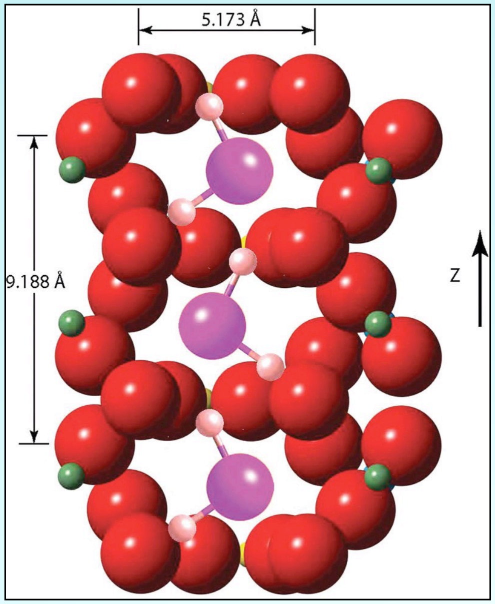
Bassanite (Plaster of Paris)

Beryl



Dom Pedro aquamarine
Smithsonian 10,363 carats



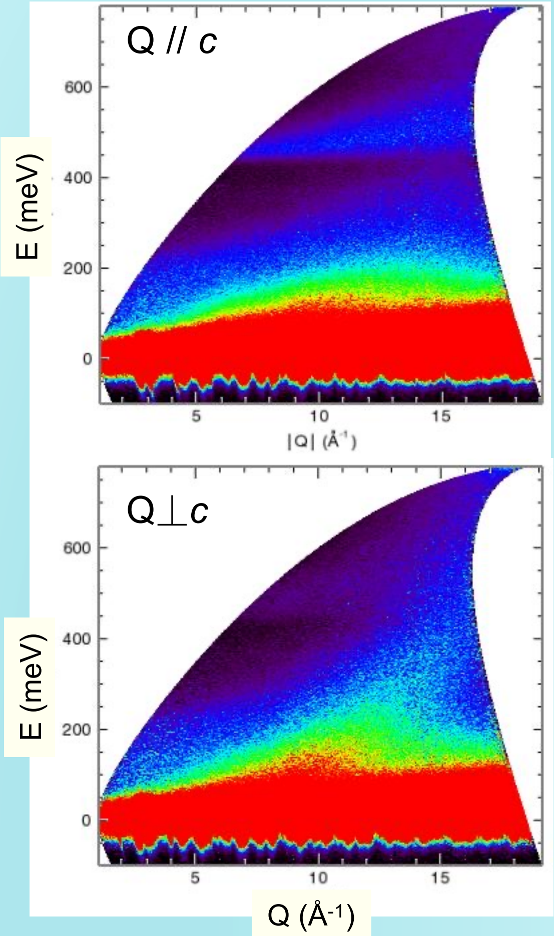


Cage-like Channel

- Hexagonal channel structure 3-5 Å wide
- Type I: water dipole perpendicular to channel
- Type II: water dipole parallel to channel
  - Alkalis in channel
- Gem names depend on color
- INS, QENS, ND, DINS

INS: Single Crystals Allow Measurements in Crystallographic Directions

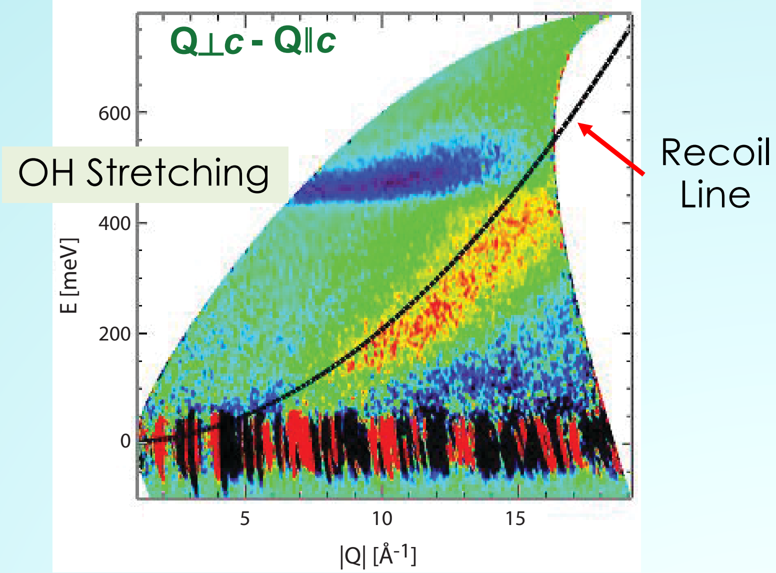
$S(Q,E)$ spectra for beryl at 6 K, E_i = 800meV, for $Q \perp c$,Q||c.



E_i = 800 meV

SEQUOIA Spectrometer
SNS, ORNL

Difference Spectrum

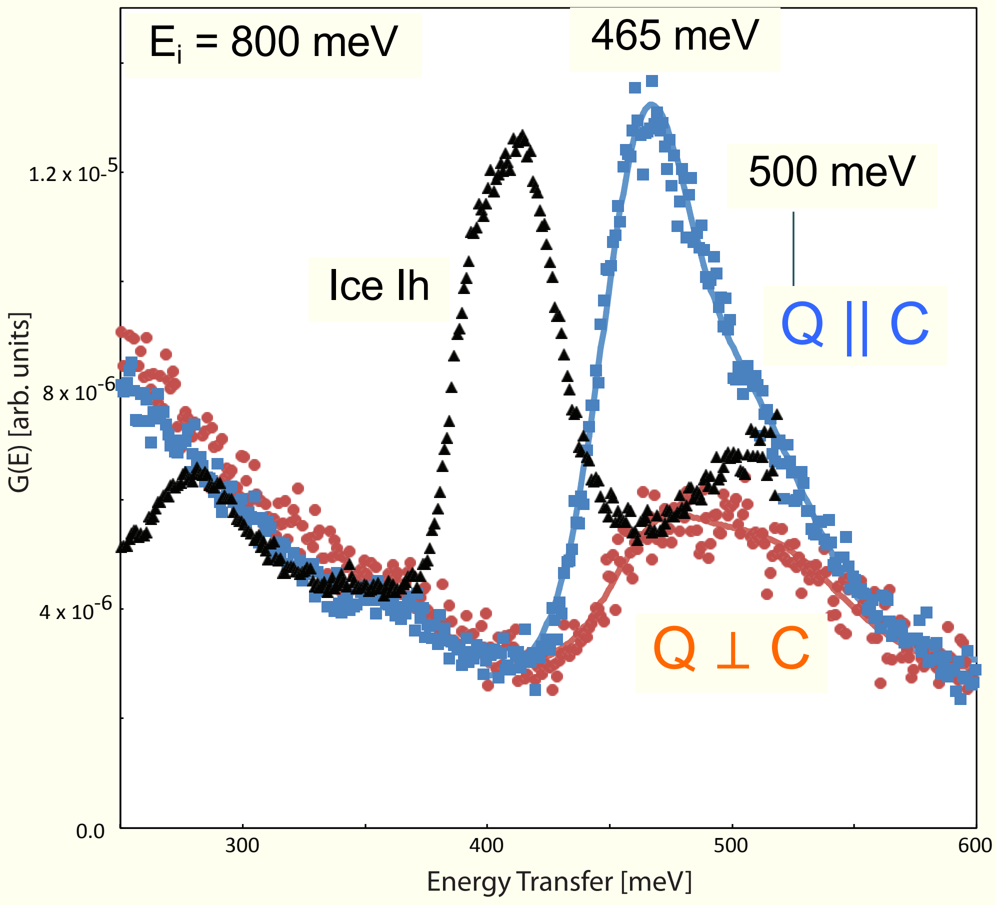


Solid line - neutron recoil spectrum for free particle of mass M = 1 a.u., $E = \hbar^2 Q^2/2m$.

Extra intensity in the $Q \perp c$ closely approximates the recoil line.

Greater ease of motion by water protons perpendicular to c than parallel to it.

OH Stretching Modes



Free water
454 and 466 meV
(symmetrical/asymmetrical stretch)

500 meV - multiphonon combination peak

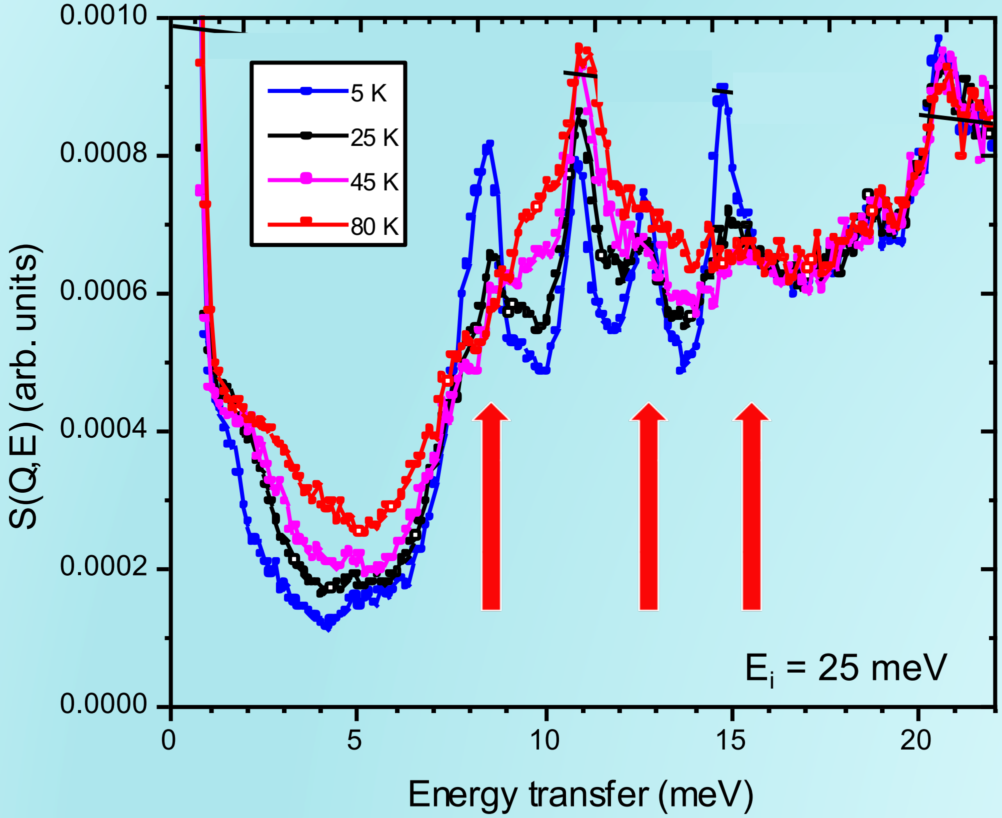
Parallel vs perpendicular
Debye-Waller asymmetry

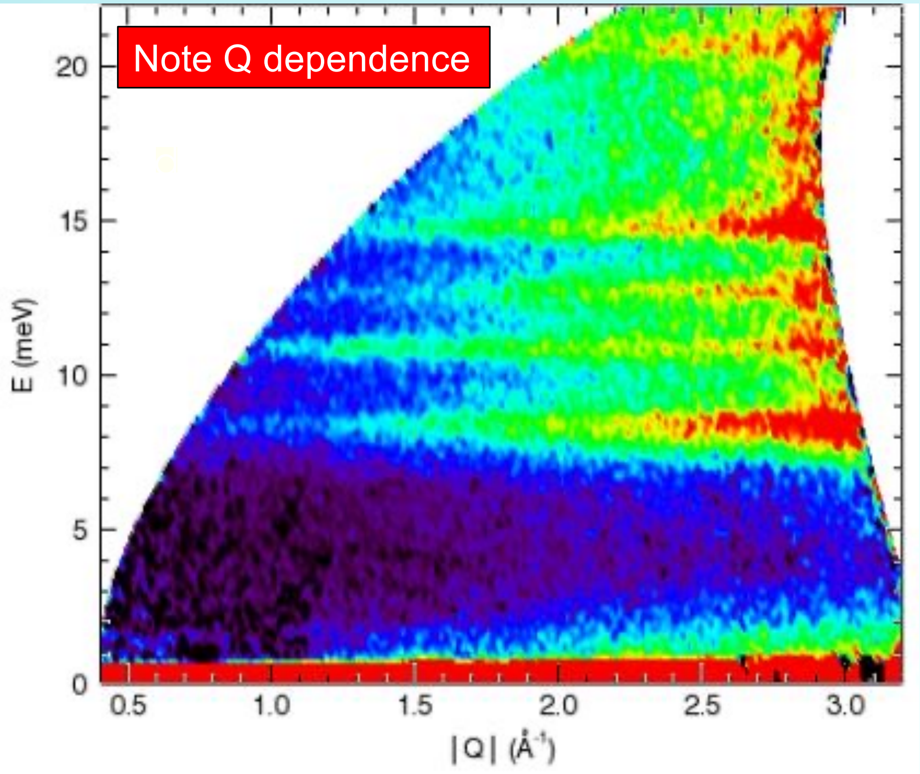
Ice is "red-shifted" (softened) - Hydrogen bonding

Beryl is not
Beryl water is like Free Water

No evidence of hydrogen bonding of water to beryl at 5 K

Temperature Dependence: $Q_{\text{perpendicular}}$ to *c*



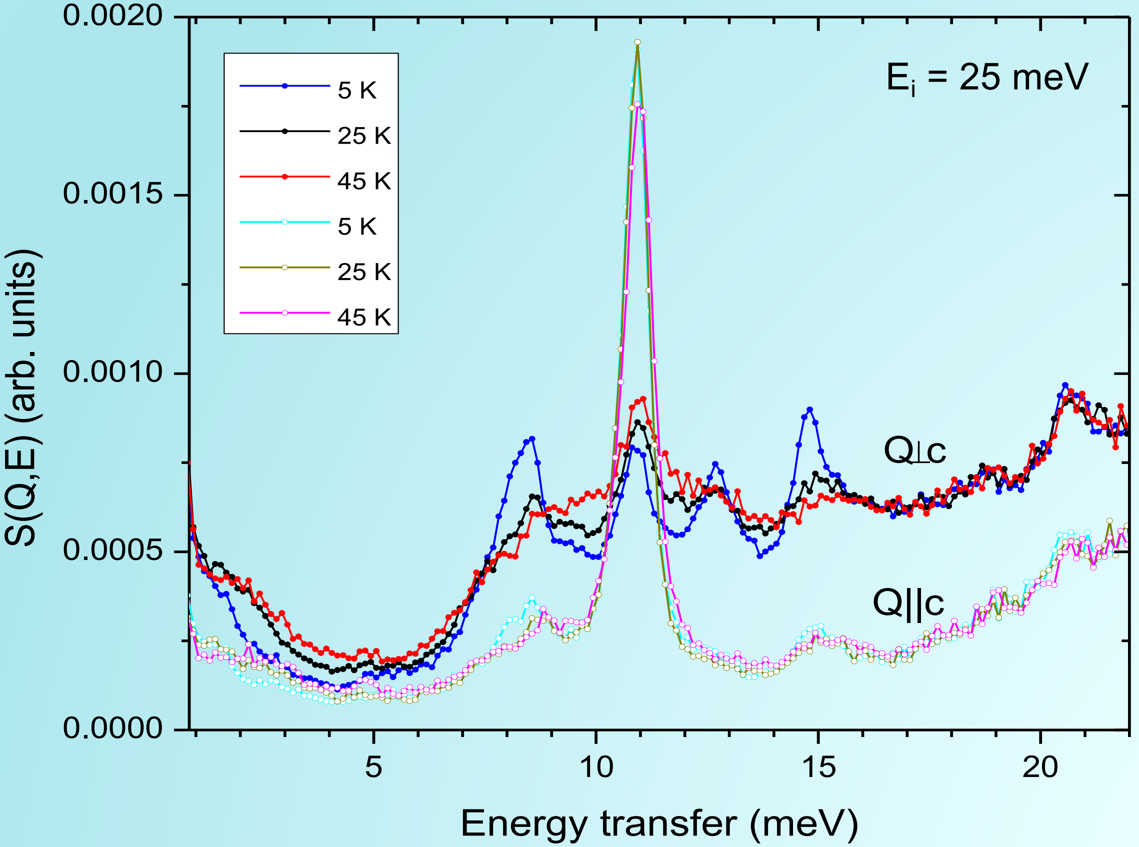

Note Q dependence

Intensities at 8.4, 12.7 and 14.7 meV strongly decrease with temperature

Increase with Q

Disappear at *T* > 25 K.

Direction: Parallel vs. Perpendicular Spectra



INS spectra of water in beryl, E_i=25 meV, comparison of neutron momentum transfer Q perpendicular and parallel to the *c*-axis.

The temperature decreasing peaks are only observed in the orientation perpendicular to c

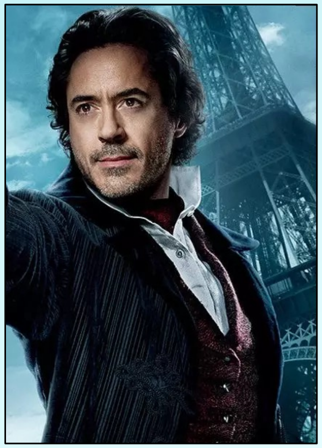
The Sherlock Holmes Argument


Basil Rathbone


Benedict Cumberback

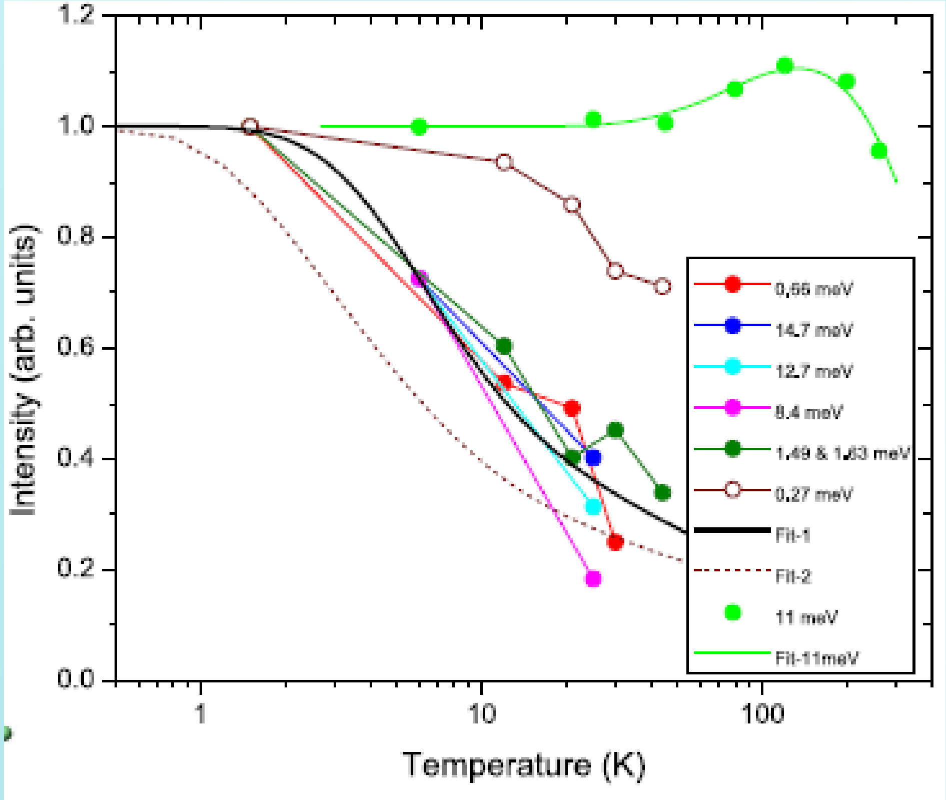
“When you have eliminated the impossible, whatever remains, however improbable, must be the truth.”

Sherlock Holmes
<u>The Sign of the Four</u>, Ch. 6 (1890)


Robert Downey Jr.


Jeremy Brett

Temperature dependence



Vibrational modes obey Bose statistics (increase with T) (number of particles in an energy state):

$$n(E,T) = \frac{1}{e^{E/k_B T} - 1}$$

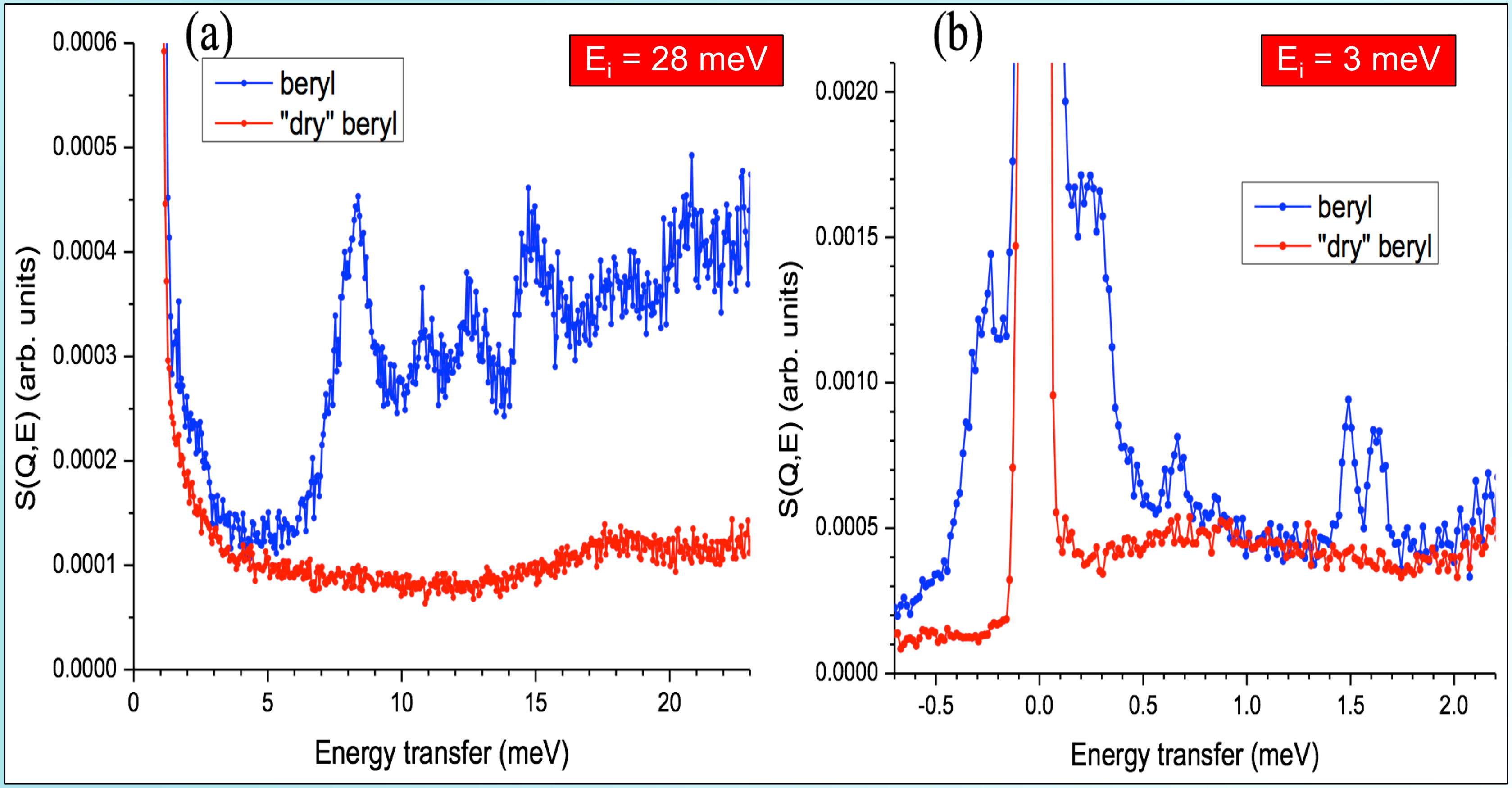
Tunneling modes exhibit distinctive temperature dependence (decrease with T):

$$I(T) \propto \frac{1}{1 + \sum_i e^{-E_i/k_B T}}$$

Peak at 11 meV is due to a vibrational type excitation.
Peak at 0.27 meV is unaccounted for. (No current explanation)

Temperature dependence of remaining peaks is consistent with quantum tunneling but inconsistent with Bose statistics (Vibration).

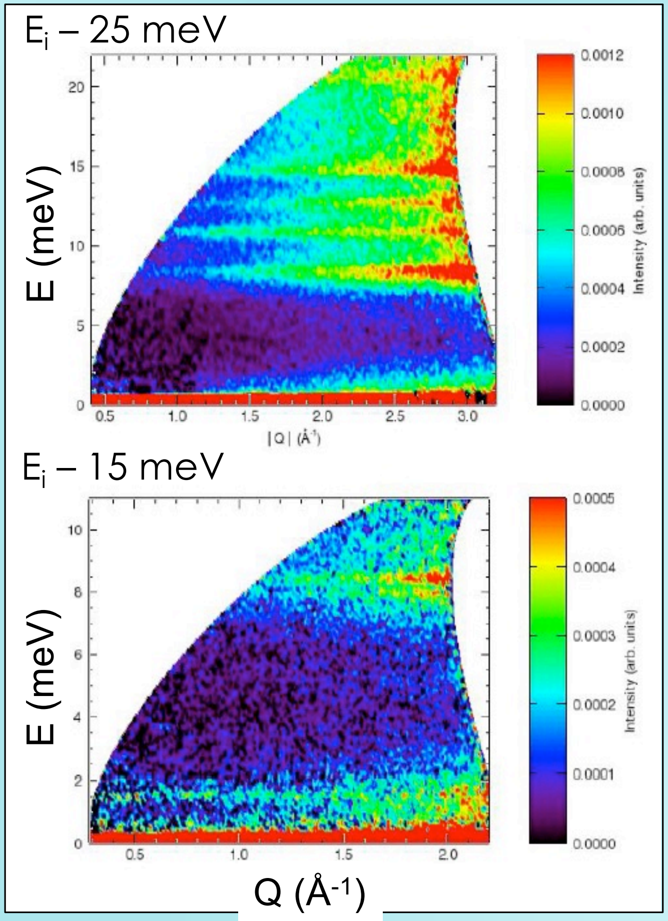
Hydrated vs Dry Beryl Spectra

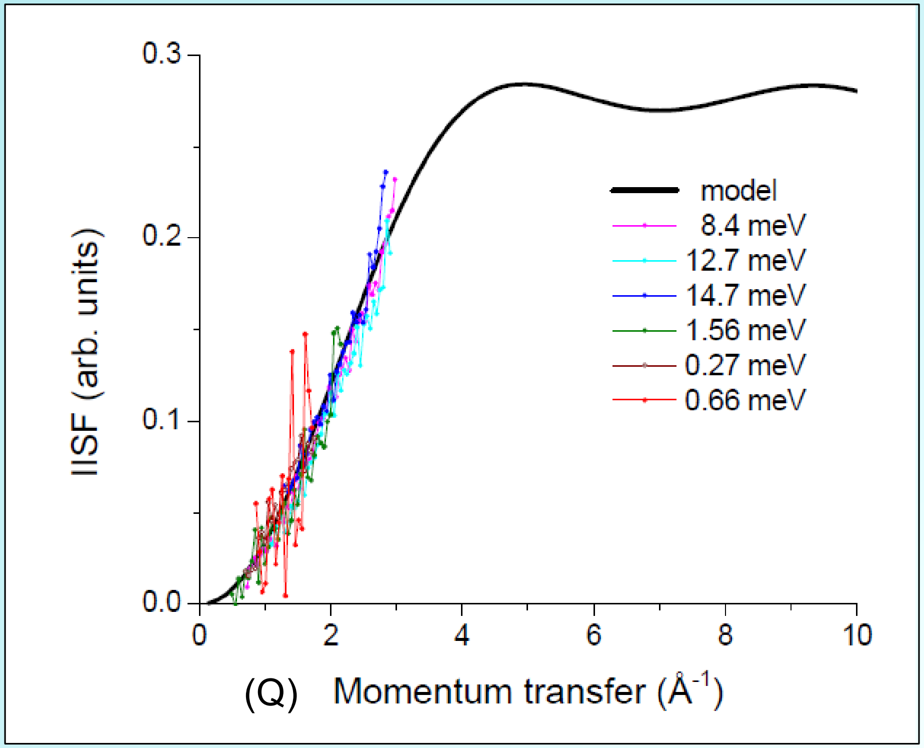


T=1.5 K with **Q**⊥*c*, CNCS spectrometer, E_i=28 and 3 meV

Therefore: The observed peaks are due to water

Q-dependence

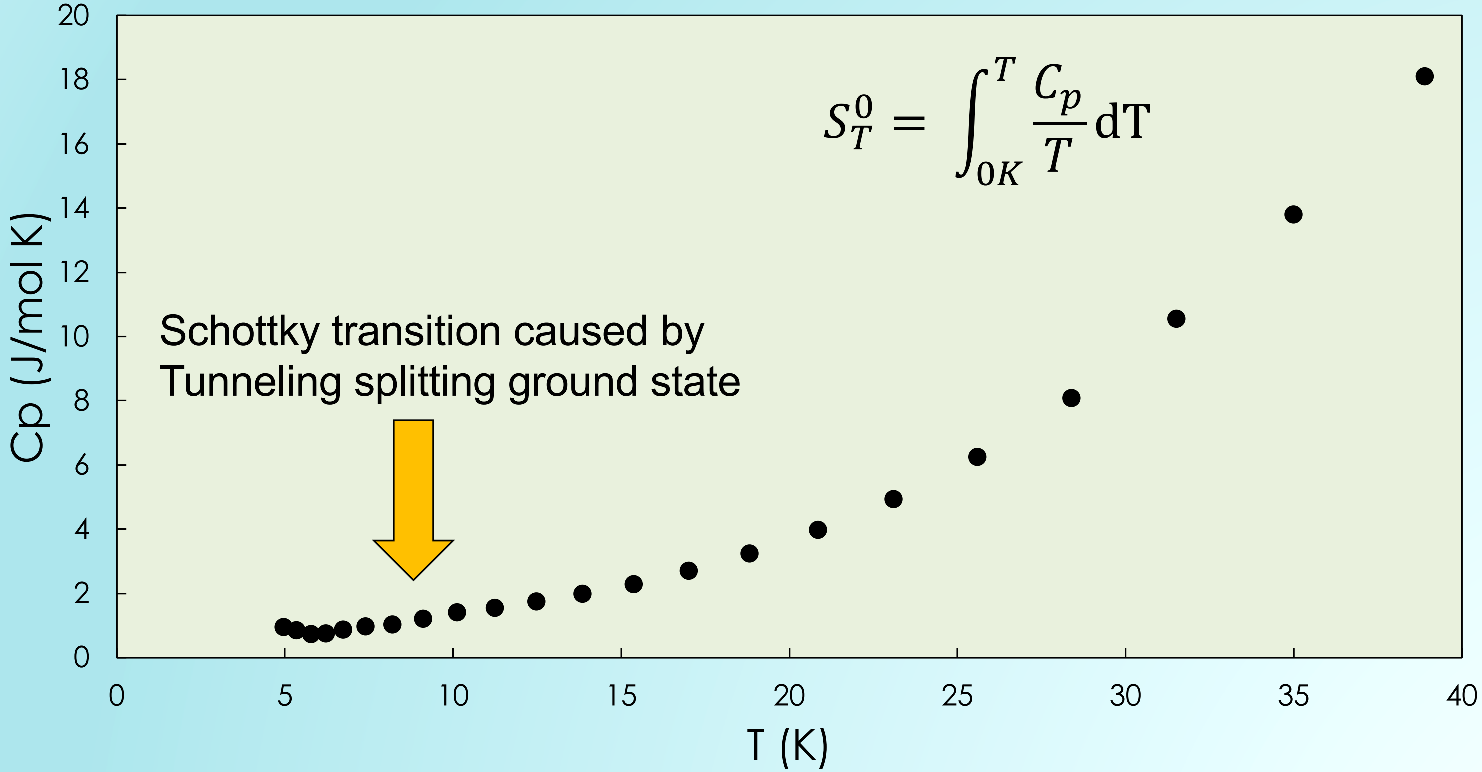




$$I(Q) \propto \sum_{l=1}^{5}\sum_{k=1}^{6} j_0\left(2Qd\sin\frac{\pi k}{6}\right)\cos\frac{2\pi l k}{6}$$

The form factor is consistent with tunneling and inconsistent with magnetism.

Heat Capacity of Beryl



$$S_T^0 = \int_{0K}^{T} \frac{C_p}{T} \mathrm{dT}$$

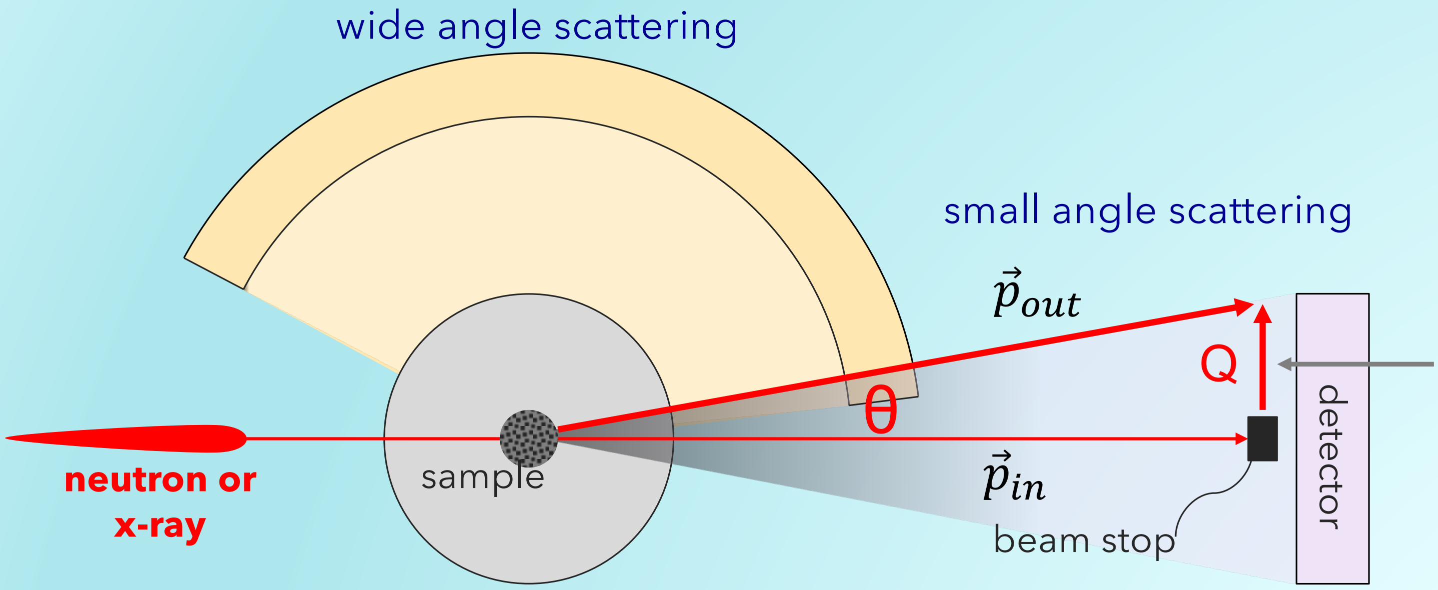
Schottky transition caused by
Tunneling splitting ground state

"The heat capacity of beryl is unexpectedly high at low temperatures (less than 30 K) for a compound with such a low mean atomic weight. …
We have no explanation for the deviation of our measured heat capacities from our theoretical estimates." (Hemingway et al., 1986)

Further Experimental Proof?

First, a Theoretical Aside

About Q



Q as a Scattering Vector

Momentum of Incoming particle: $\vec{p}_{in} = \frac{2\pi}{\lambda}$

Scattering Vector: $\vec{p}_{in} + q = \vec{p}_{out}$

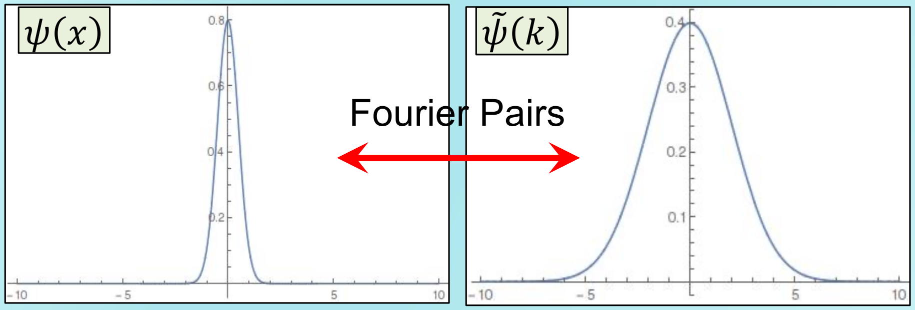
Elastic, so: $|\vec{p}_{in}| = |\vec{p}_{out}|$

Therefore: $q = 2\vec{p}_{in} sin\theta = \frac{4\pi}{\lambda} sin\Theta$

Q is not just a scattering vector, It is a transfer of momentum

A Little Quantum Mechanics

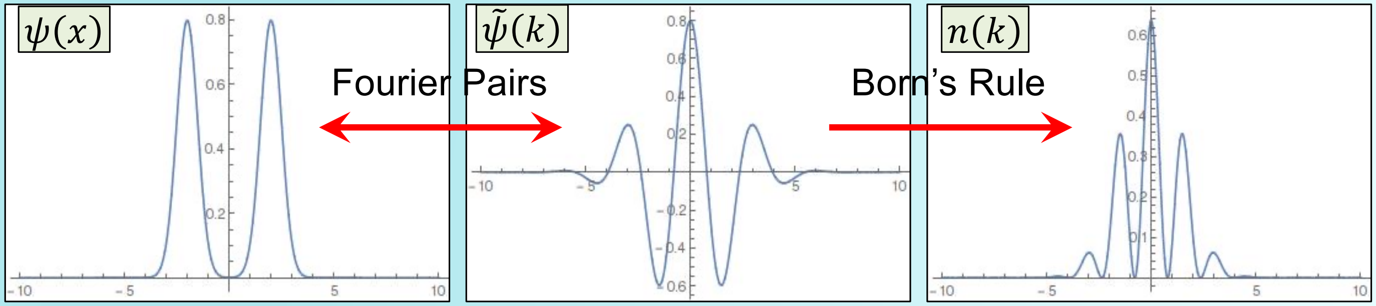
Particle localized about one position:



Position

Momentum

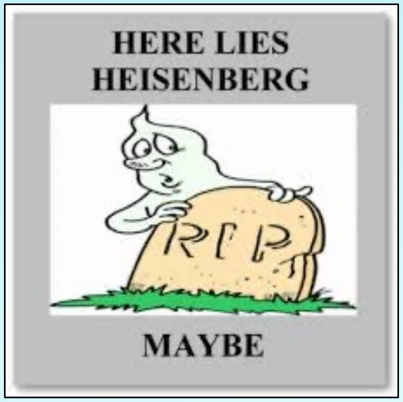
Particle delocalized over two positions:



Position

Momentum

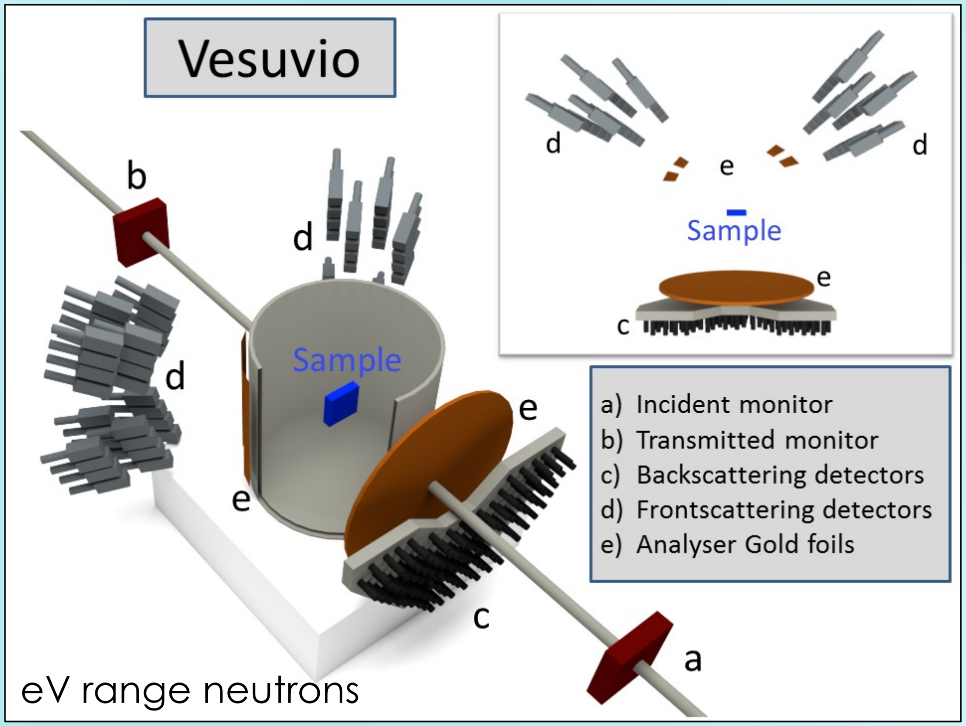
Momentum Probability



Born's Rule
the probability density of finding a system in a given state, when measured, is proportional to the square of the amplitude of the system's wavefunction at that state

Oscillations in the Momentum Distribution n(k) are a signature of quantum tunneling
Need to go to high Q

Measurements at Large Q and E
(Impulse Approximation for Individual Atoms)



- a) Incident monitor
- b) Transmitted monitor
- c) Backscattering detectors
- d) Frontscattering detectors
- e) Analyser Gold foils

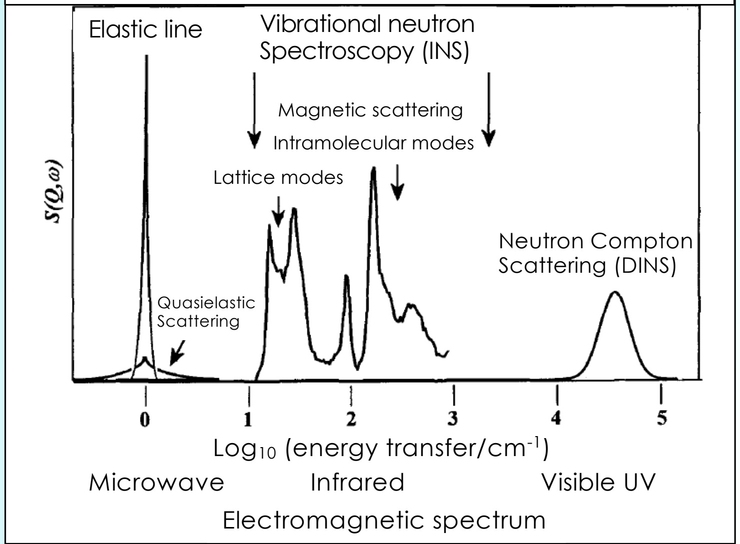
eV range neutrons

VESIVIO
Neutron Compton Scattering
(Deep Inelastic Neutron Scattering, DINS)
ISIS (Oxford)

High E (1-100 eV) implies short time (Fourier pairs)
Impulse Approx. - Atoms look like free
Particles with some momentum distribution

High Q ~ 30 – 200 Å^{-1}
Small distances (0.03 – 0.2 Å)
So, data on individual atoms

Inelastic Neutron Scattering Spectrum



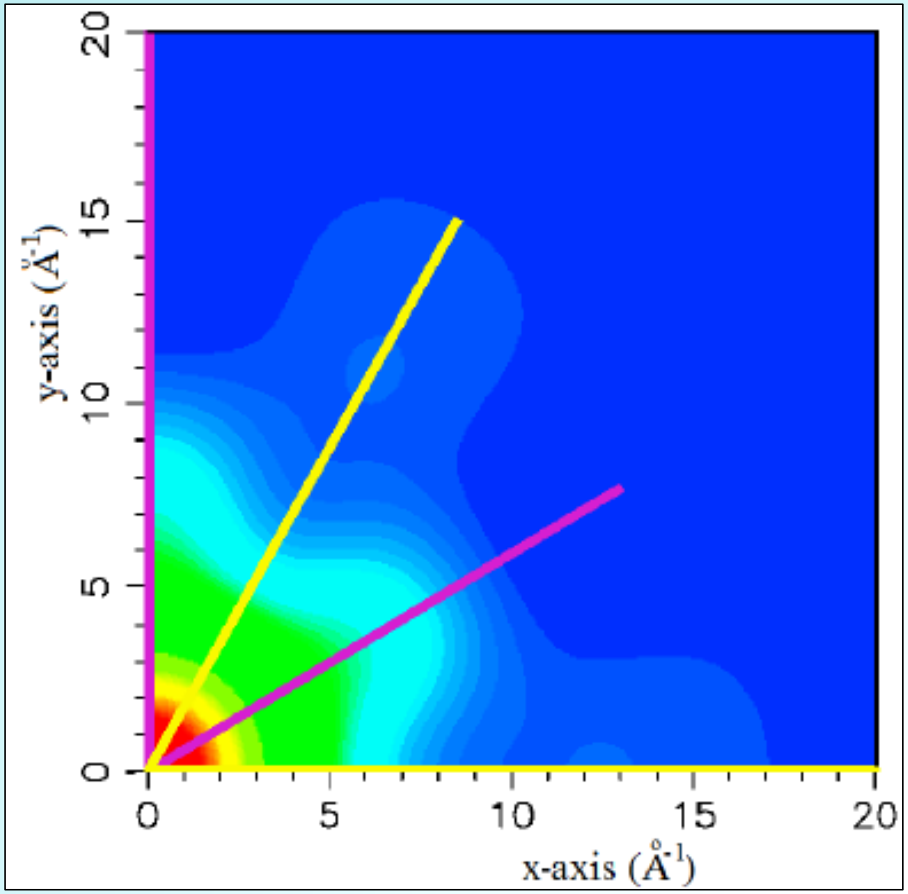
Deep Inelastic Neutron Scattering

Oriented Single crystals yield 2D Momentum Map

Projection of n(p) onto the xy plane shows the 6-fold symmetry.

Expected oscillations present every 60°

The additional maxima are due to proton tunneling.



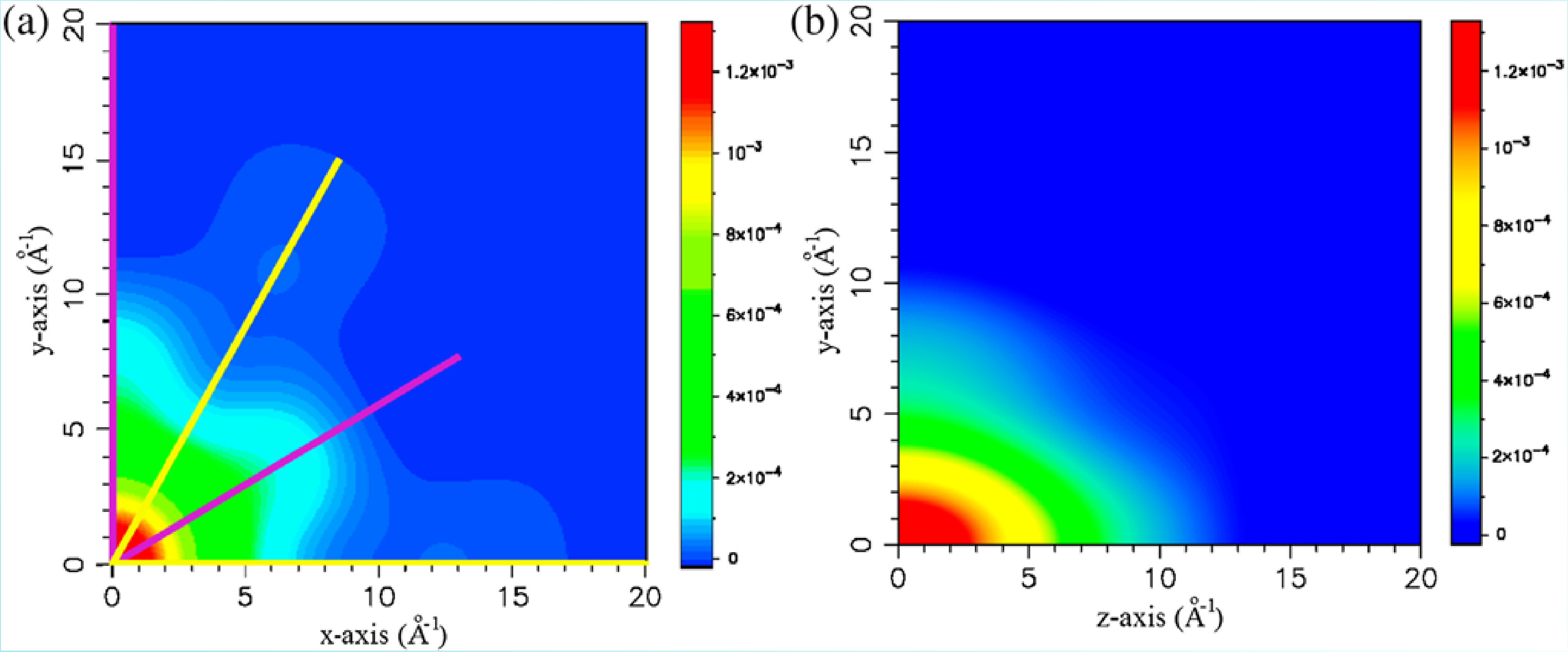
The statistical variances of $n(\mathbf{p})$, $\sigma_x = 3.66$ Å^{-1}, $\sigma_y = 3.61$ Å^{-1}, and $\sigma_z = 4.98$ Å^{-1}, yield average kinetic energy E_k as:

$$E_k = \frac{\hbar^2}{2M}\left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right),$$

Yields 106 meV for water protons,

Much smaller than in bulk water (~150 meV)

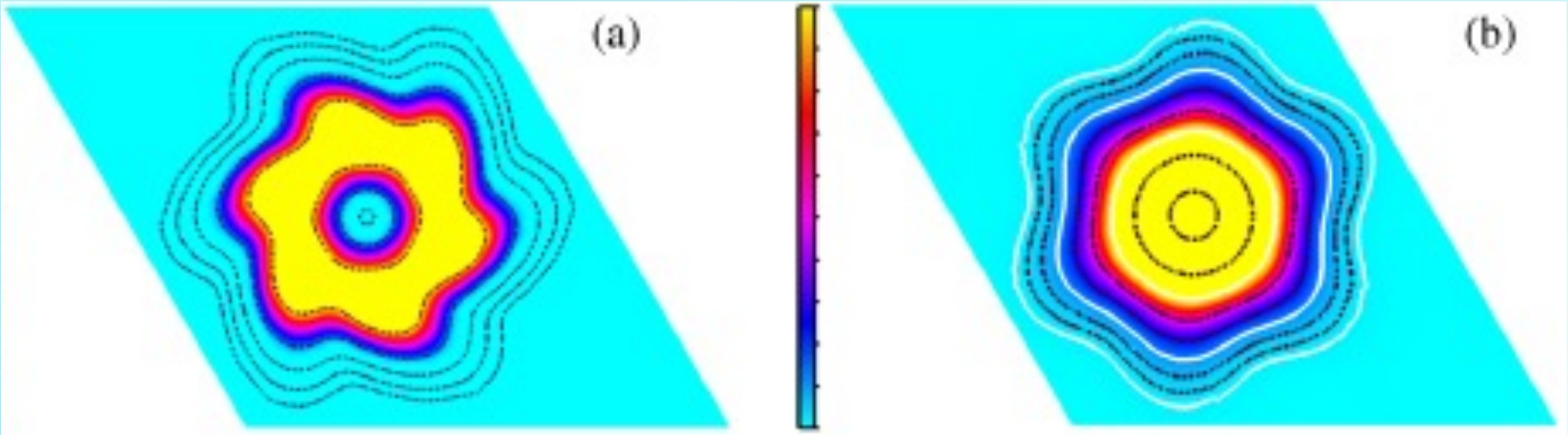
Parallel vs Perpendicular to C



The oscillations or interference fringes present in the momentum distribution imply that the hydrogen atoms are coherently delocalized over six equivalent positions

Around the channel, not Parallel to it

Calculated Charge Densities



DFT/PIMD in the ab plane: (a) protons, (b) oxygen

<u>Tunneling in beryl is unusual compared to other examples of molecular rotational tunneling</u>

Others (methyl and ammonia groups): tunneling and non-tunneling molecules look identical.

Beryl: Tunneling water protons occupy different positions from non-tunneling molecule

- Molecule “looks” like a double-ended top
- Center of gravity and dipole moment are modified by tunneling

We've satisfied
Mr. Holmes' criterion

Water in Beryl tunnels
A new form of water

But what happens if
we start to change things?

Specifications and Limitations

but

It's Astounding
Time is fleeting

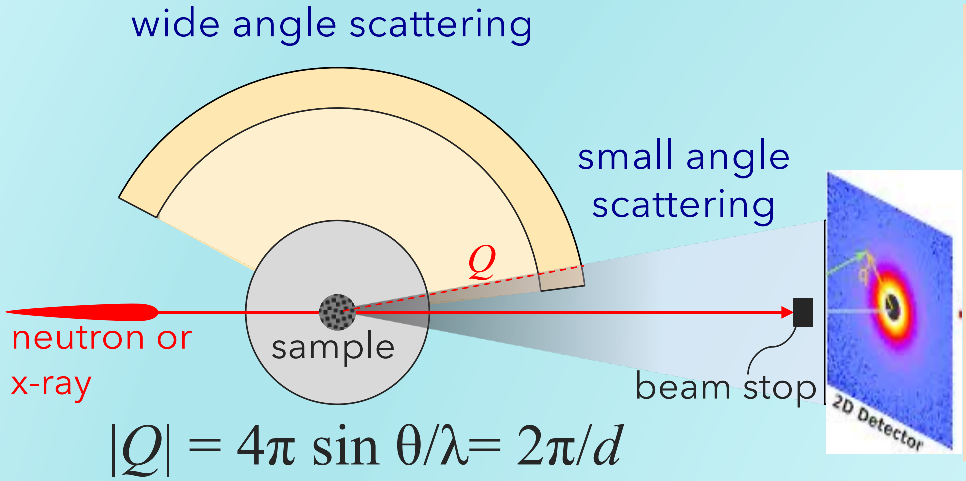
And that question will have to wait for

Another Day

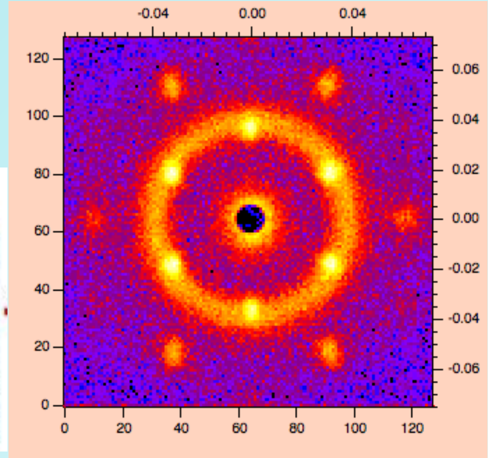
Thank You

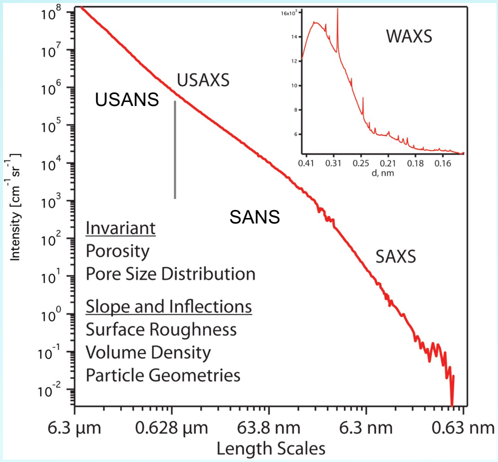
Additional Slides

Small Angle Neutron/X-ray scattering (and Imaging?): Multiscale Pore Distributions

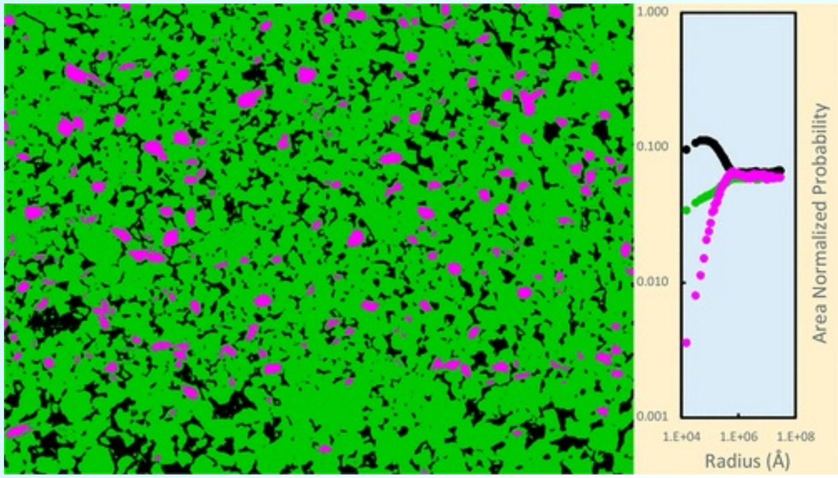


$$|Q| = 4\pi \sin\theta/\lambda = 2\pi/d$$





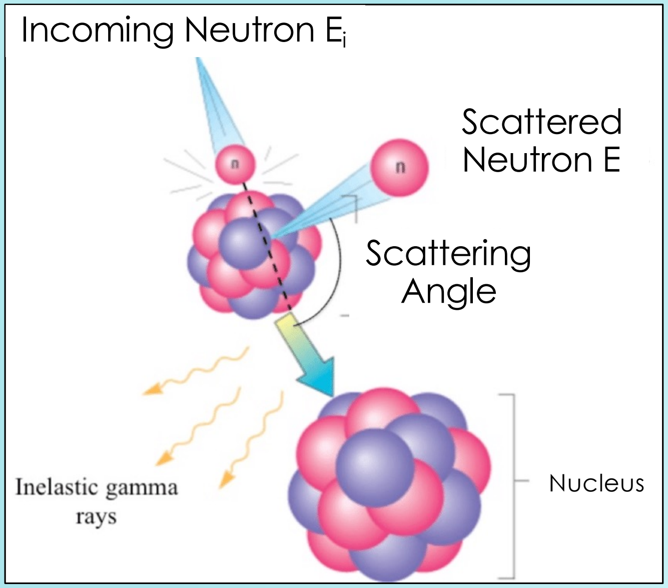
- Momentum transfer (*Q*) related to reciprocal of distance
- Can be done on standard thin sections or powders
- Combine scattering with imaging techniques to obtain distributions of pore size ~1nm – 1 cm (7 orders of magnitude!).



Anovitz and Cole (2015) ***Rev. Mineral Geochem. 80,*** **61-164**

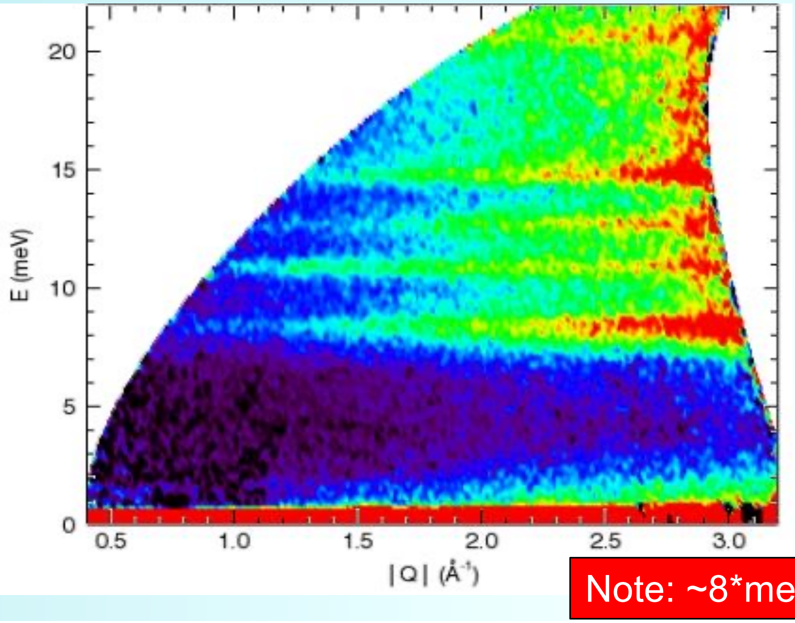
Inelastic Neutron Spectroscopy

Measures Energy and Scattering Vector (Q)
Similar energy range to FTIR, Raman
Mostly sees hydrogen
No selection rules



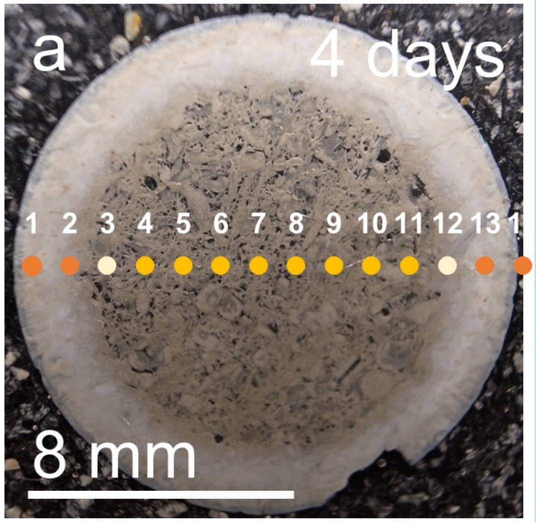
Measures:
Vibrations and Librations
Momentum distributions
Phonon Spectra
Magnetic properties

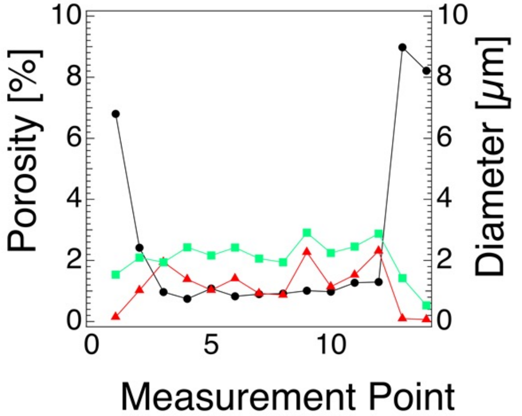
SEQUOIA Spectrometer, SNS, ORNL

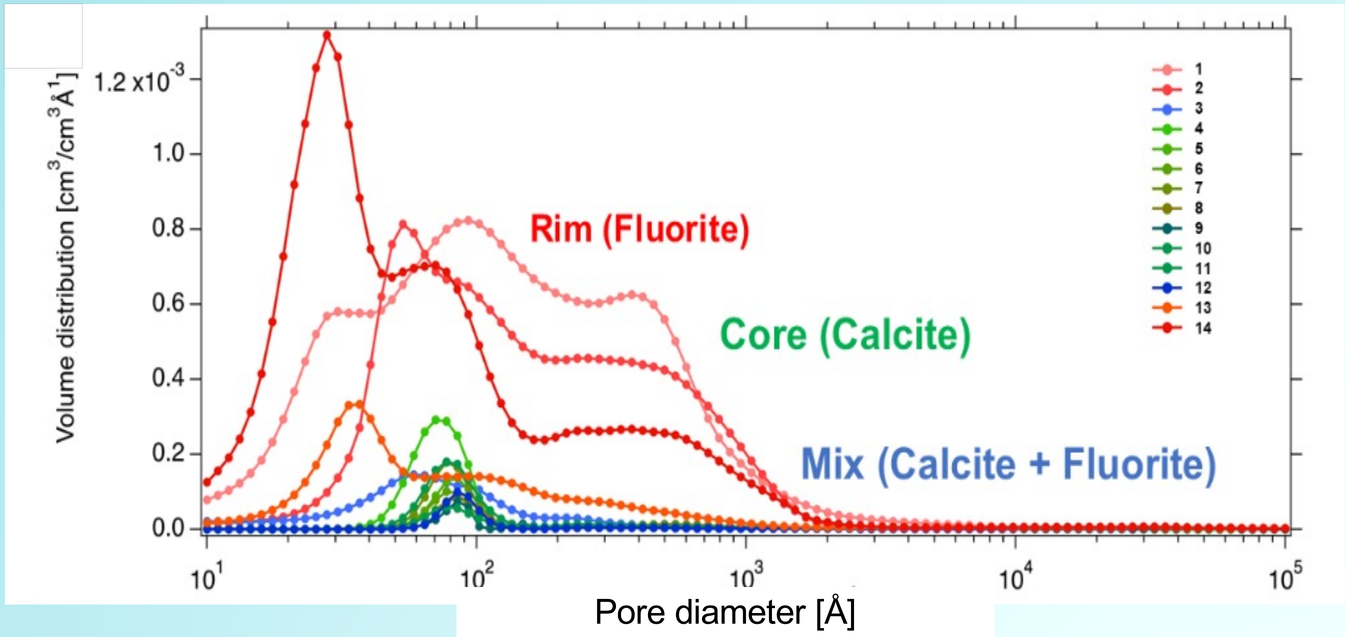


Note: ~8*meV = cm^{-1}

Porosity: Low Porosity Limestone (U)(W)SAXS: 4 Days







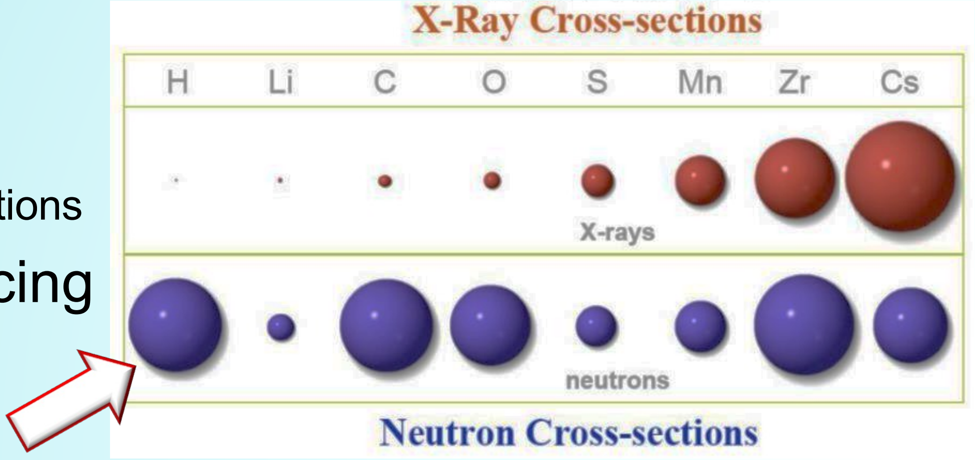
- ❖ Replacement rim forms
- ❖ Rim porosity is higher
- ❖ More nanopores and more macropores in rim

Replacement rate?

Weber et al., **2019**

Why Neutrons?

- No charge
  - Highly penetrating,
- Probe nucleii
  - Light atoms, isotopic substitution
- Have magnetic moment, spin
  - Study magnetic materials
- Coherent scattering – structure and collective motions
- Incoherent scattering – atomic motions
- Energies similar to elementary excitations
  - Molecular vibrations, phonons, molecular motions
- Wavelengths similar to atomic spacing
  - Structure
- Isotopic Contrast Matching



Why NOT Neutrons?

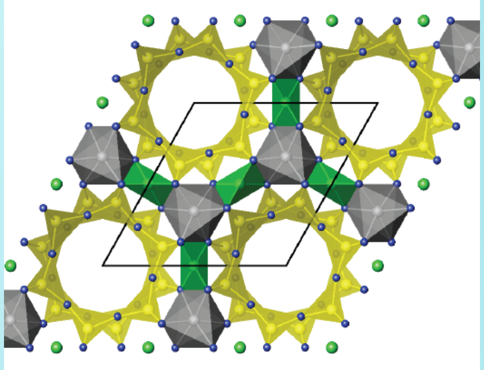
- Low Flux
  - Relatively slow, limited time
- Larger samples
- Wrong, different contrast
- Activation
- Large Beams
  - Good for integrating
  - Bad for mapping, small samples

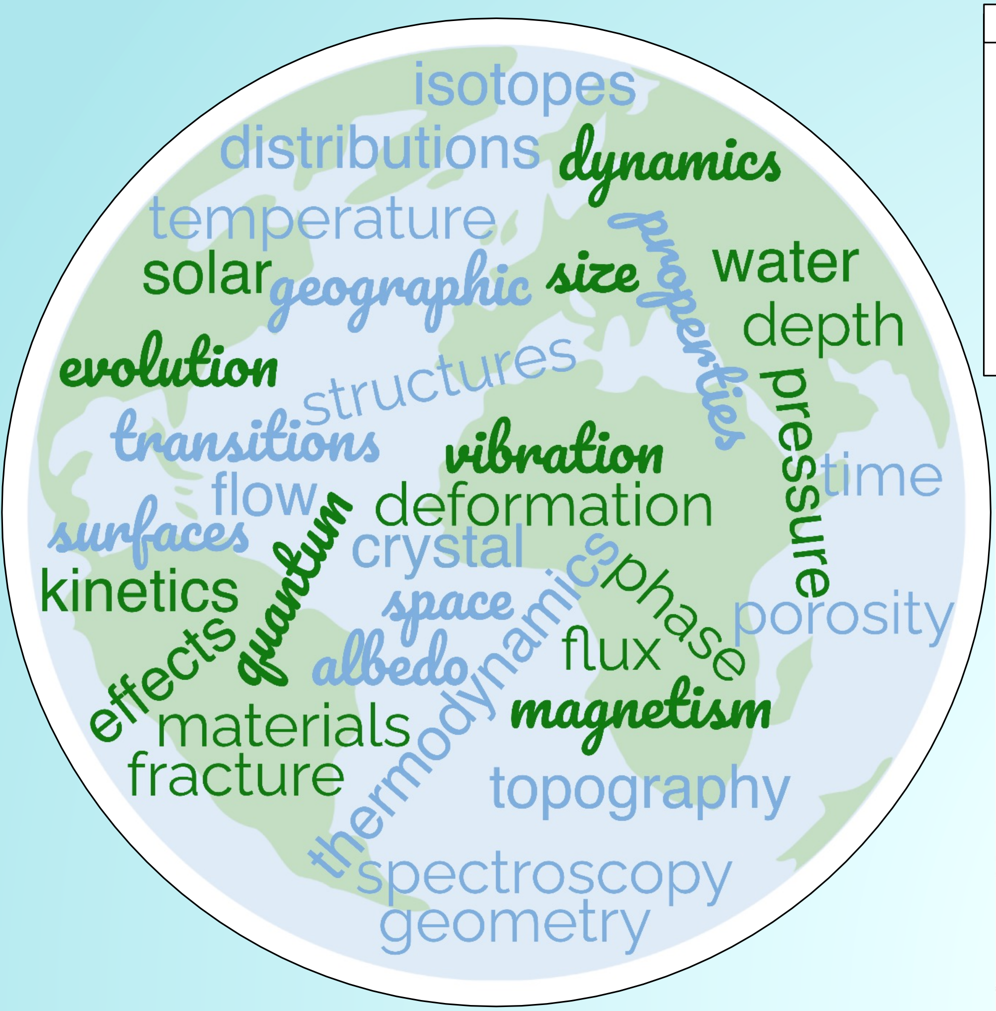
- Incoherent H-background
  - Limits some studies
- X-rays see heavy atoms really well
- Bad proposals!
  - Data to tell a good story

Take Home Points:
1) If you can do it with X-rays, use X-rays!
but
2) Neutrons/X-rays/Imaging are Complementary!

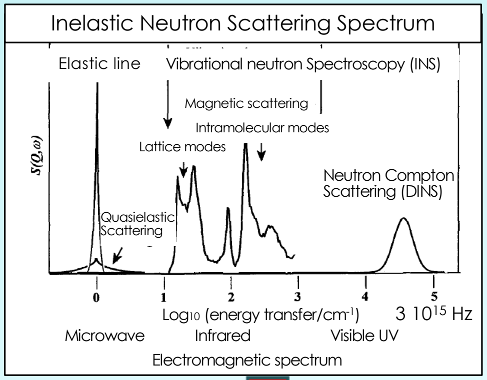
There he Goes Again
Getting Up on His High Horse

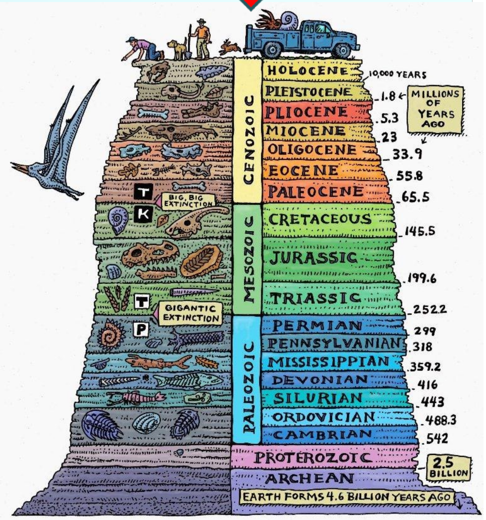
What Geoscientists Actually Measure



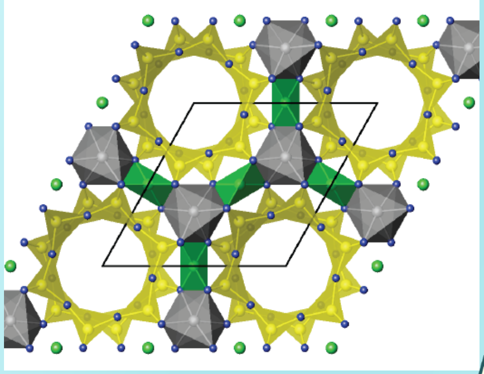


isotopes
distributions
dynamics
temperature
properties
solar
geographic
size
water
depth
evolution
structures
pressure
transitions
vibration
time
flow
surfaces
quantum
deformation
crystal
kinetics
space
phase
thermodynamics
porosity
effects
albedo
flux
magnetism
materials
fracture
topography
spectroscopy
geometry





What Geoscientists Actually Measure



Temperature

Quantum Isotopes

Fracture Materials

Thermodynamics Space

Deformation Pressure

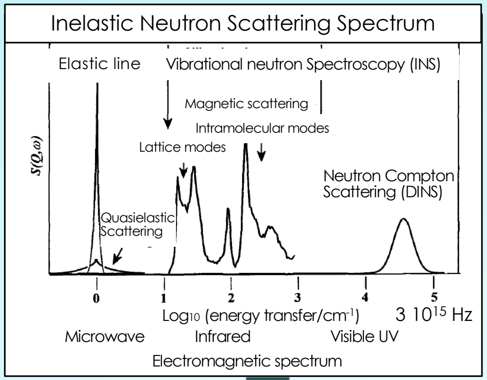
Magnetism Time Vibration

Astrophysics Kinetics

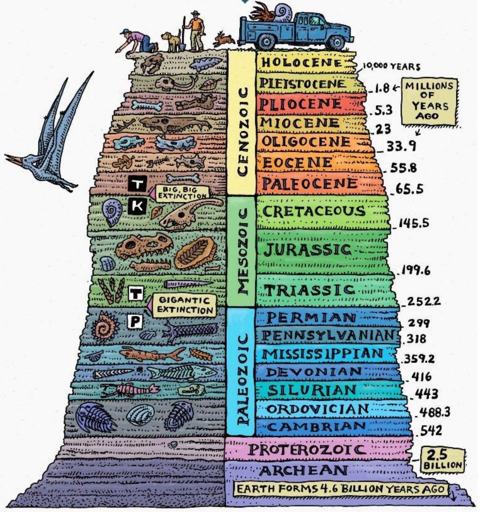
Surfaces Confinement

Crystallography

Evolution

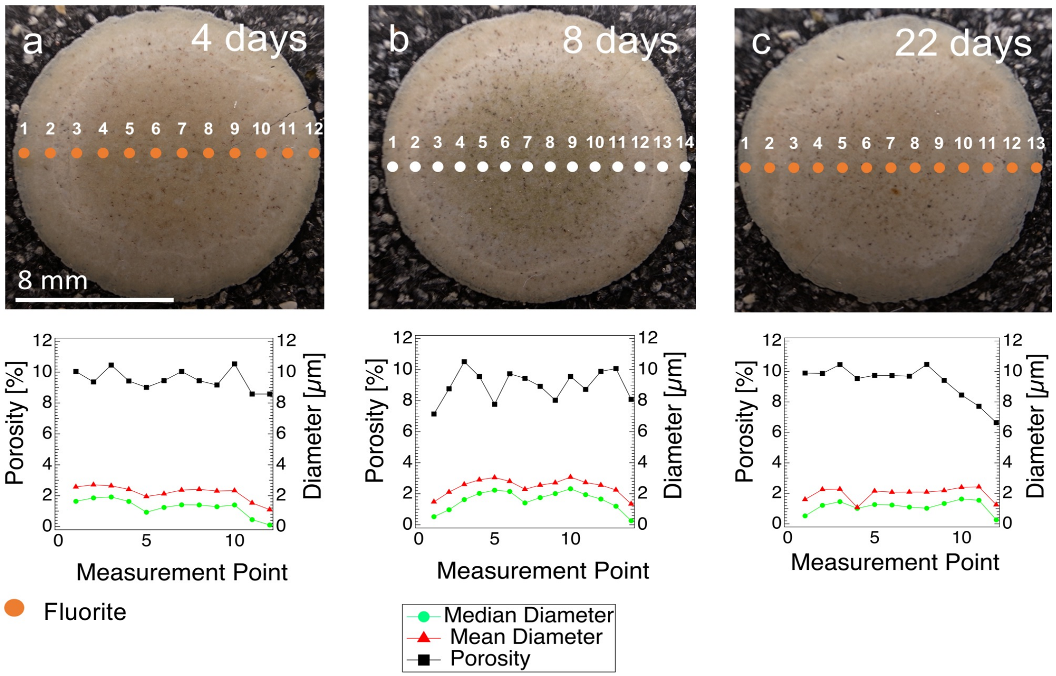


Inelastic Neutron Scattering Spectrum



Fast Replacement for High Porosity Limestone

High porosity limestone

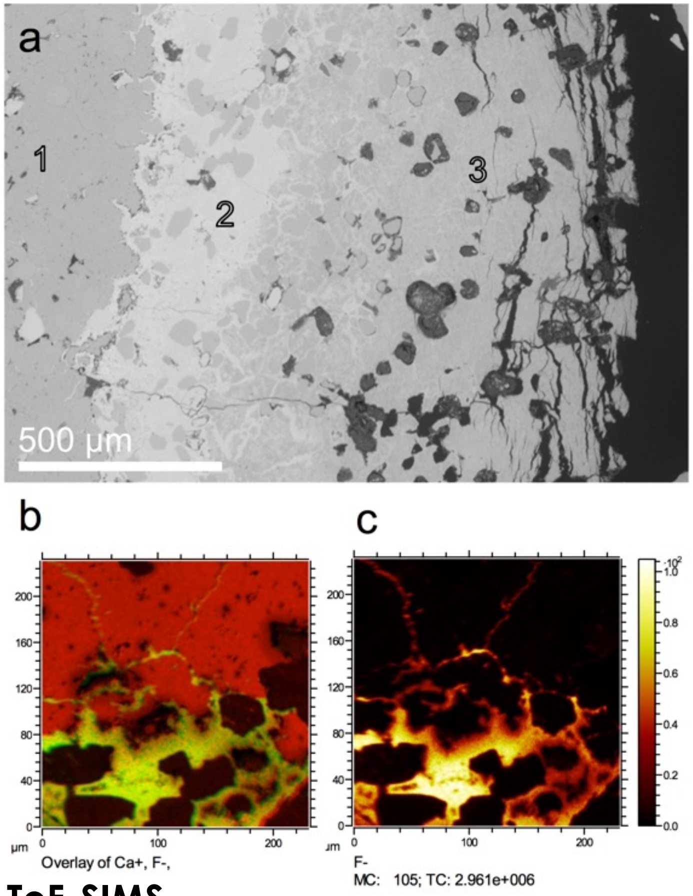


- ❖ Rim width does not correlate with porosity, complete replacement after 4 days
- ❖ Nearly no changes in the porosity once limestone is replaced

Replacement rate?

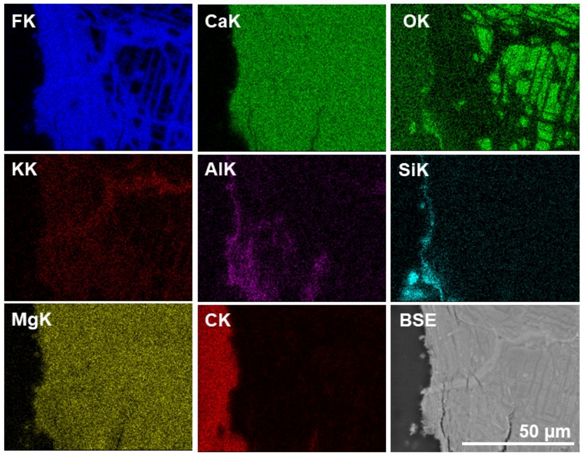
Weber et al., **2019**

Replacement of Dolostone



ToF-SIMS

- Reaction rim for dolomite replacement shows two different regions
- Replacement along grain boundaries and possibly twin boundaries

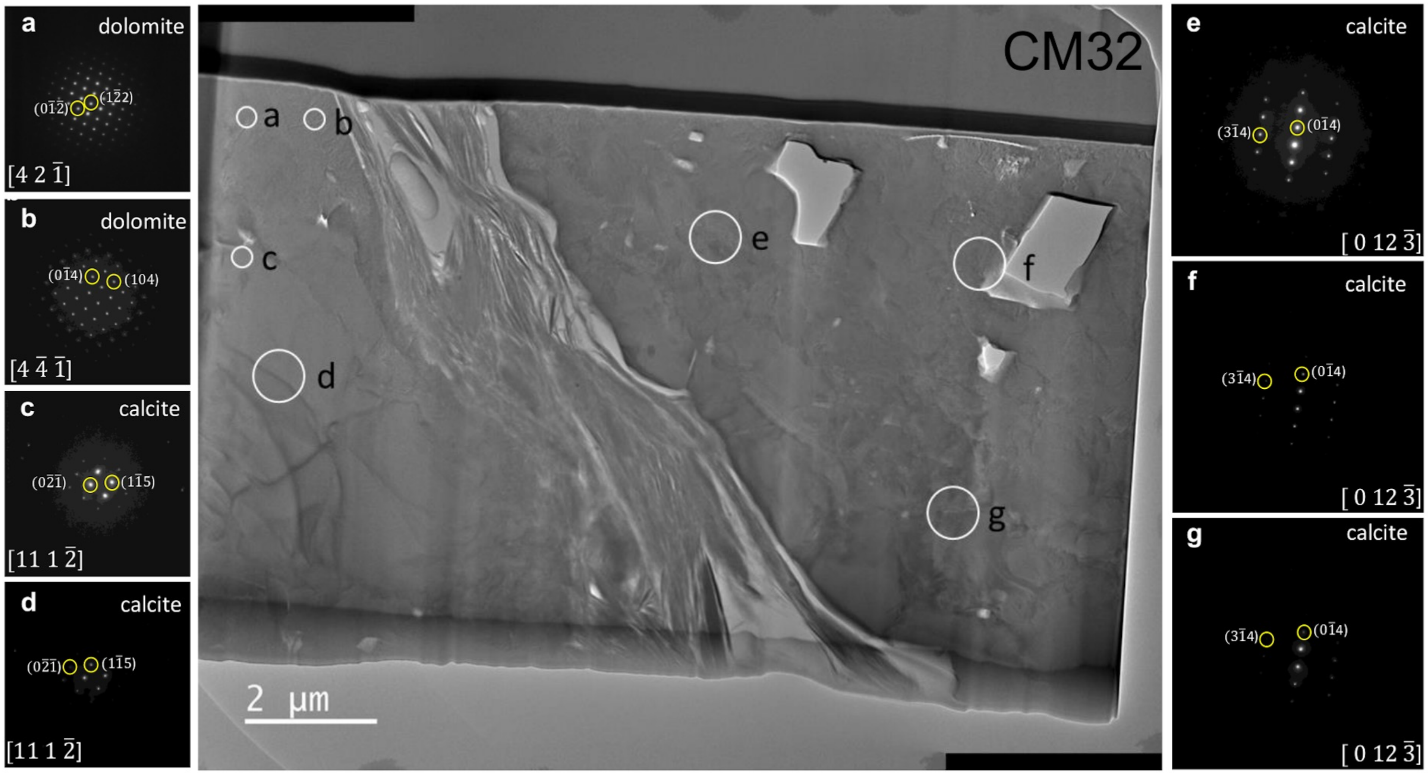


SEM-EDX

Weber et al., 2019 ACS Earth and Space Chemistry

Replacement speed?

Grain Boundary?

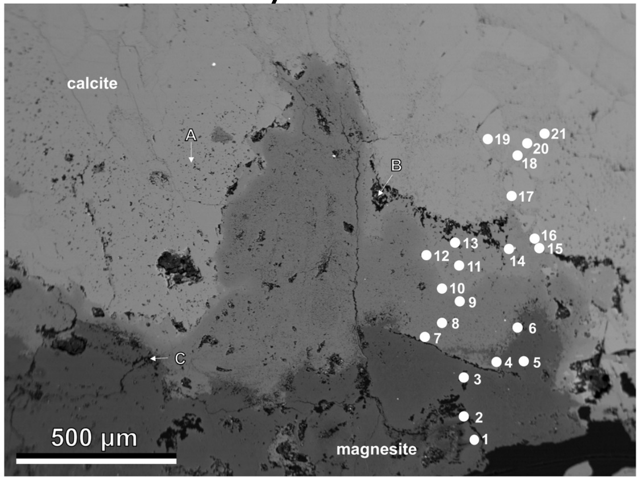


HF-5000 TEM, BF imaging + SAED

Weber et al., **2021**

Chemical Changes – Low/High Porosity Limestone

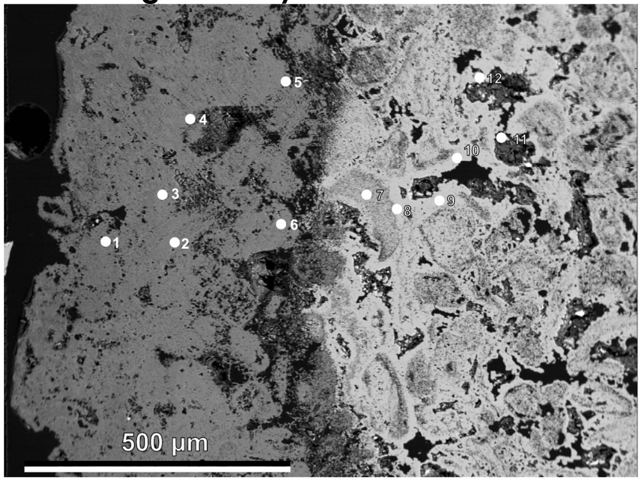
EPMA - Low Porosity Limestone



Four different phases:

- ❖ Magnesite (containing up to 5% Ca)
- ❖ Two intermediate phases:
  - ❖ $Ca_{0.623}Mg_{0.377}CO_3$ (darker gray)
  - ❖ $Ca_{0.781}Mg_{0.217}CO_3$ to $Ca_{0.772}Mg_{0.226}CO_3$ (lighter gray)
- ❖ Original limestone

EPMA - High Porosity Limestone



Two phases:

- ❖ Magnesite (containing up to 5% Ca)
- ❖ $Ca_{0.625}Mg_{0.374}CO_3$ to $Ca_{0.629}Mg_{0.369}CO_3$

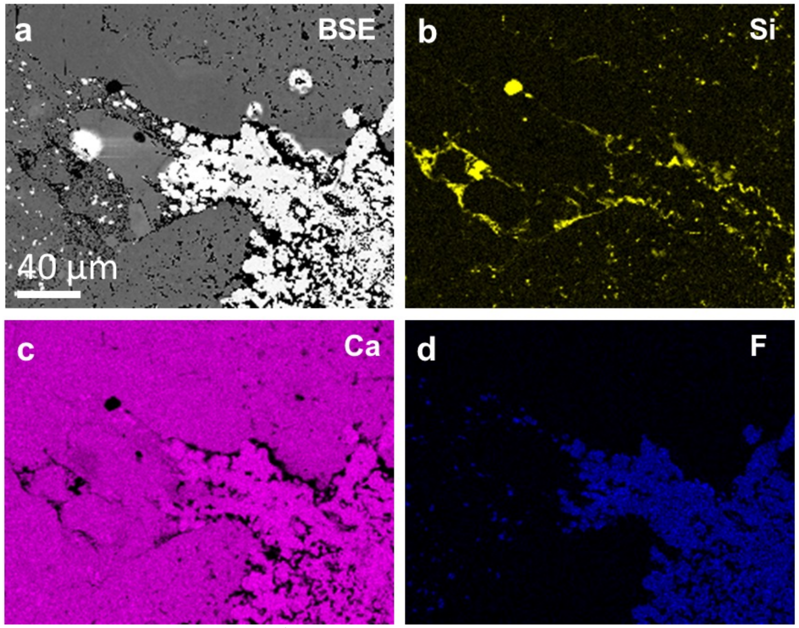
→ More pore space allows for equilibration leading to lower number of phases

Porosity Changes?

Weber et al., **2021**

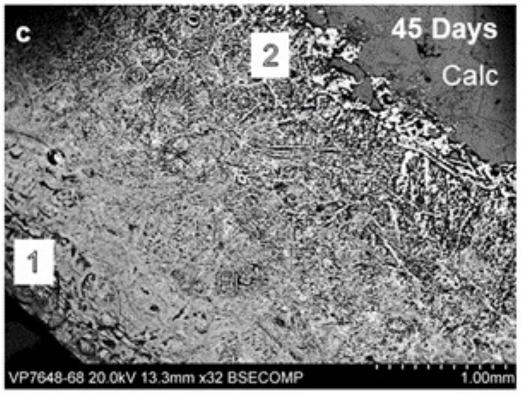
Replacement along Grain Boundaries

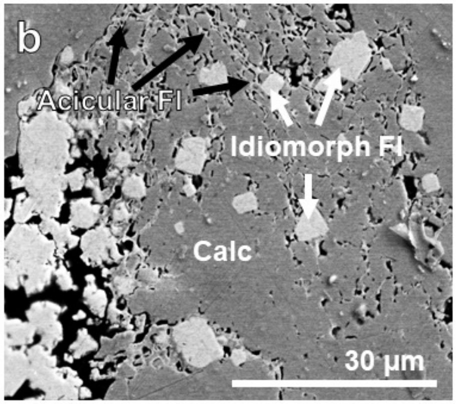
Low porosity limestone



SEM-EDS mappings

- Preferential replacement along grain boundaries
- Acicular fluorite growth due to confinement?

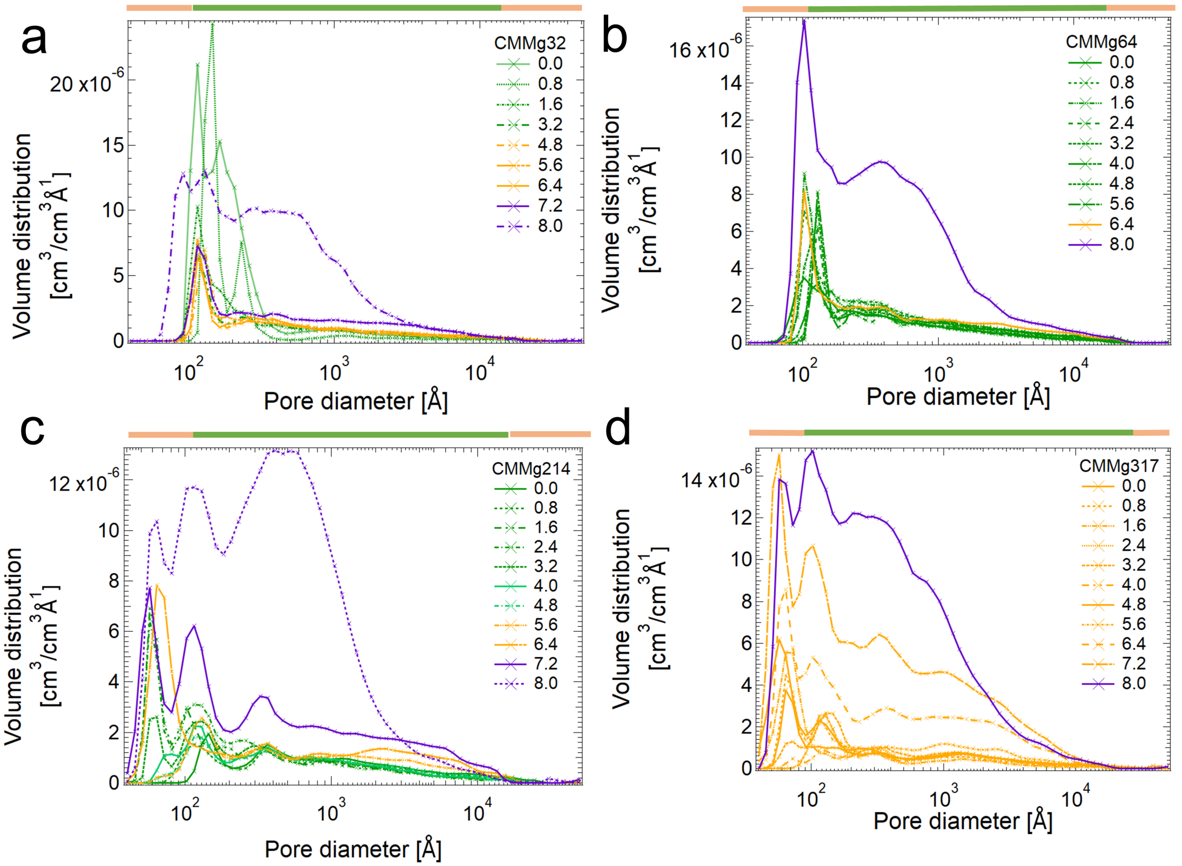




Weber et al., **2019**

Porosity Development with Replacement

(U)SAXS



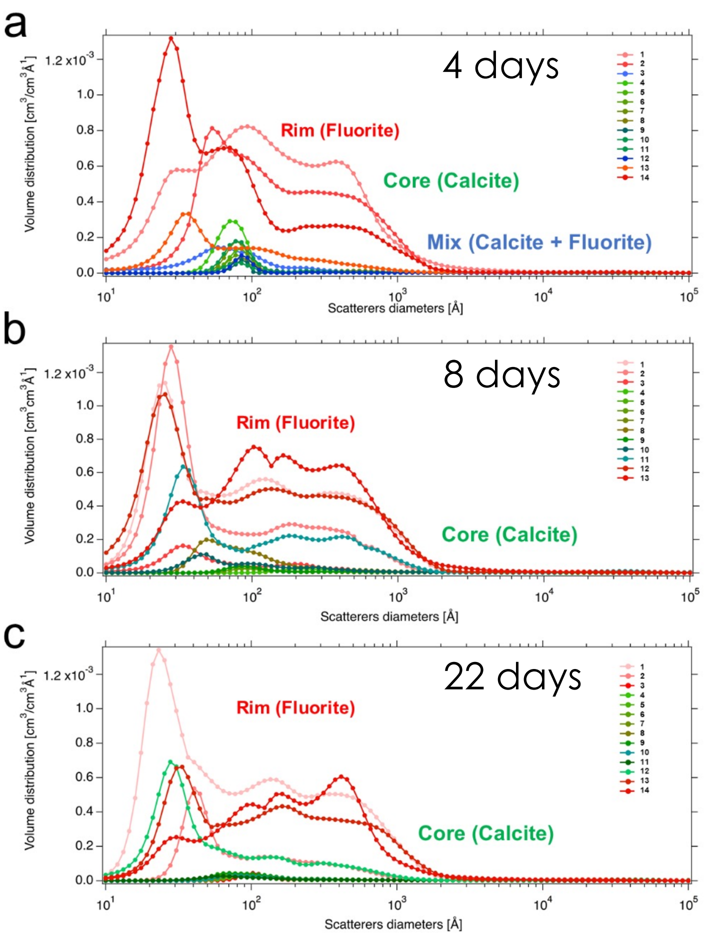
Original calcite

Dolomite/magnesite rim

Grain Boundary Diffusion?

Weber et al., **2021**

Nano-Porosity Development By Replacement



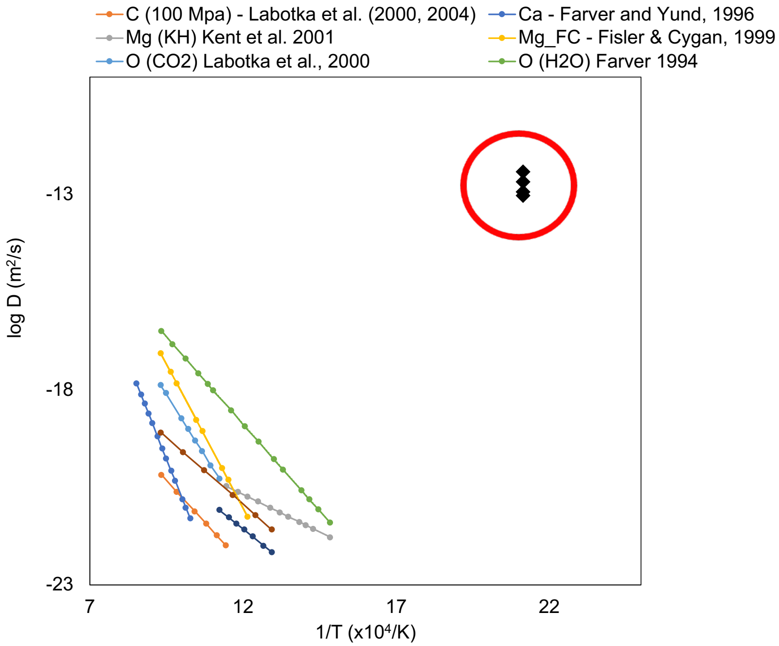
Low porosity CM limestone:

- →Shift to higher number of nano-pores in replaced material

Pathways?

Weber et al., **2019**

Comparison of GB Diffusion Rate w Bulk Diffusion



Charniak et al., 2010

- Grain boundary diffusion rates between ~ 10 orders of magnitude faster than solid diffusion and ~ 4 order of magnitude slower than self diffusion in aqueous solution (10^{-9} m^2/s, Zhong and Friedmann, 1988)

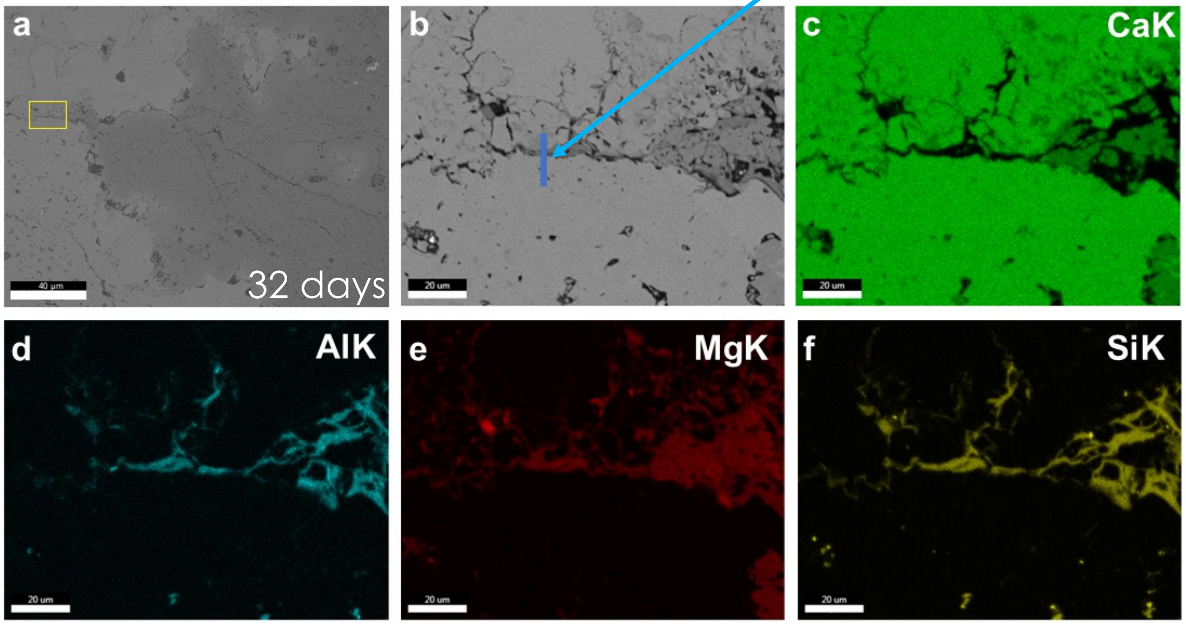
→ Grain boundaries are important for replacement reactions

Weber et al., **2021**

FIB Lift-Out of Grain Boundary

Low Porosity Limestone

top view



FIB lift out location

SEM-EDS mappings

- ❖ Targeted a potential grain boundary for TEM analyses

Replacement along Grain Boundaries?

Weber et al., **2021**

Model Systems for Volume-Reducing Replacement

1) Calcite ($CaCO_3$) Replacement by Fluorite (CaF_2)

- $CaCO_3 + 2NH_4F = CaF_2 + 2NH_3 + H_2CO_3$

  $\Delta V_s = -33.51$ vol. %

2) Calcite ($CaCO_3$) Replacement by Dolomite ($CaMg(CO_3)_2$)

- $2CaCO_3 + MgCl_2 = CaMg(CO_3)_2 + CaCl_2$

  $\Delta V_s = -12.899$ vol. %

Calcite ($CaCO_3$) Replacement by Dolomite ($CaMg(CO_3)_2$)

- $CaMg(CO_3)_2 + MgCl_2 = 2\ MgCO_3 + CaCl_2$

  $\Delta V_s = -12.906$ vol. %

Characterization of Microstructure

Static, saturated replacement experiments → Dried & Thin section preparation → **Chemical Imaging** → (Ultra)-Small Angle Scattering Techniques for Porosity analyses

Scanning Electron Microscopy with EDS

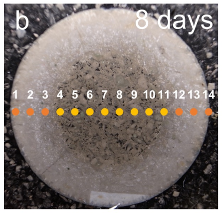
FIB preparation → TEM +STEM

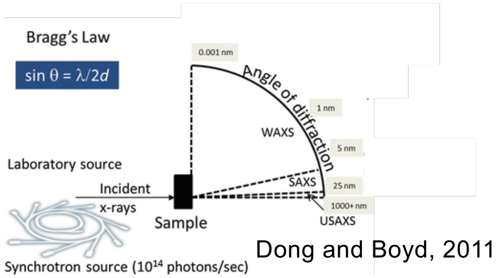
ToF-SIMS

Electron Probe Microanalysis (EPMA)

Small Angle Scattering for Porosity Analyses

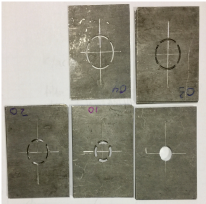
(U)SAXS + WAXS (detection limit: 20 nm – 2 µm pores)

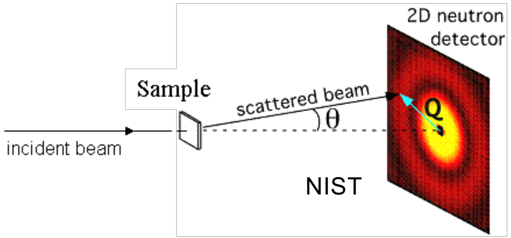




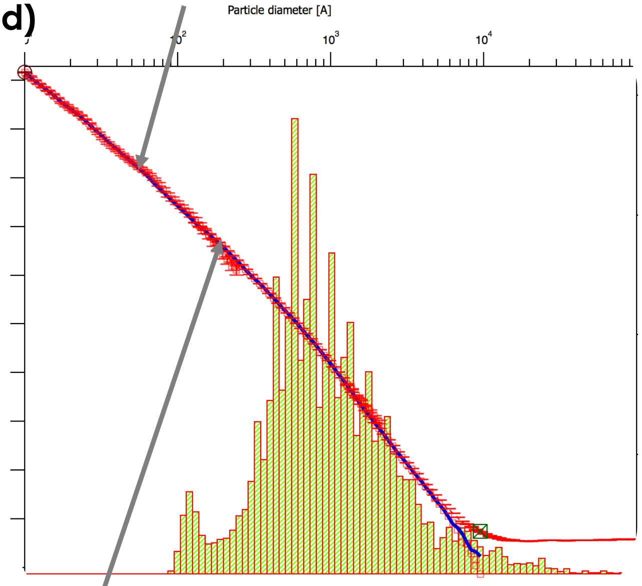
Dong and Boyd, 2011

(U)SANS (detection limit: 20 nm – 20 µm pores)





(U)SANS/(U)SAXS curve (red)



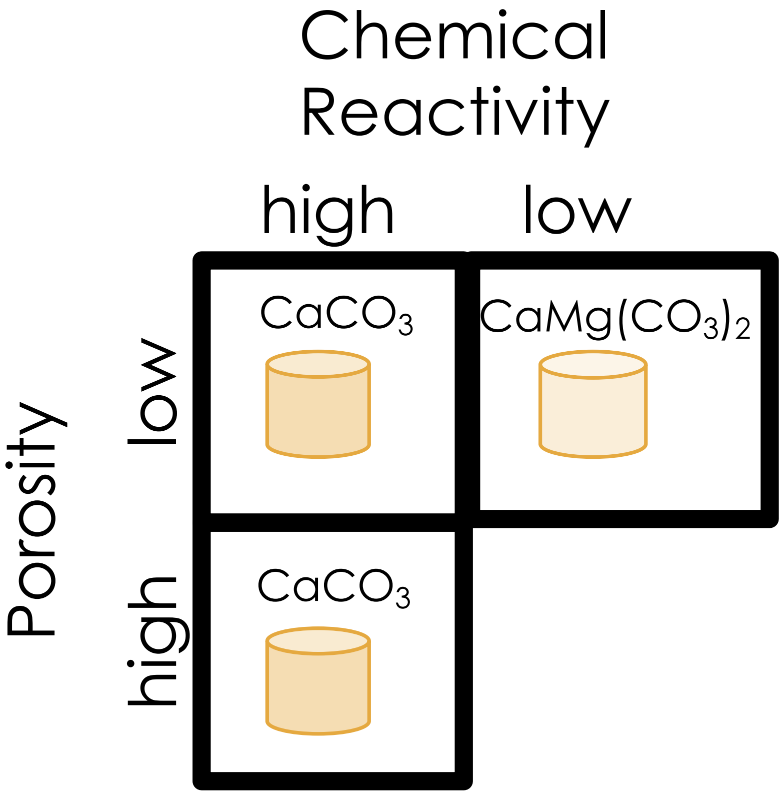
Fit Function (blue)

- ❖ Fit of (U)SAXS/ (U)SANS curves to power law for porosity determination based on two phase system assumption (Radlinski et al., 2006)

APS Beamline 9-ID

Model system 1 – $CaCO_3$-CaF_2

Varying Microstructure and Chemical Reactivity



Chemical Reactivity

high low

Porosity

low high

$CaCO_3$

$CaMg(CO_3)_2$

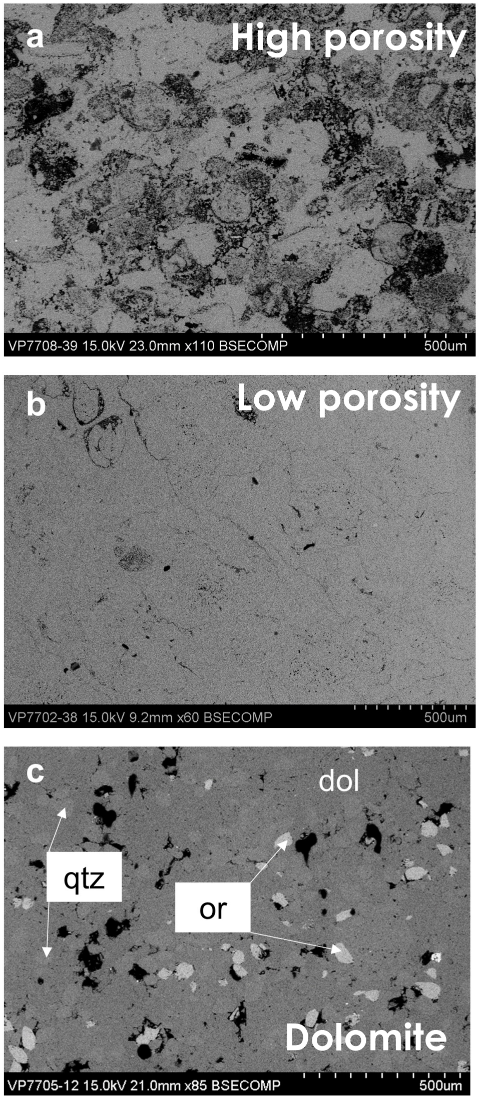
$CaCO_3$

Solubility products:

$$logK_{CaCO_3} = -8.48$$
$$logK_{CaMg(CO_3)_2} = -17.09$$

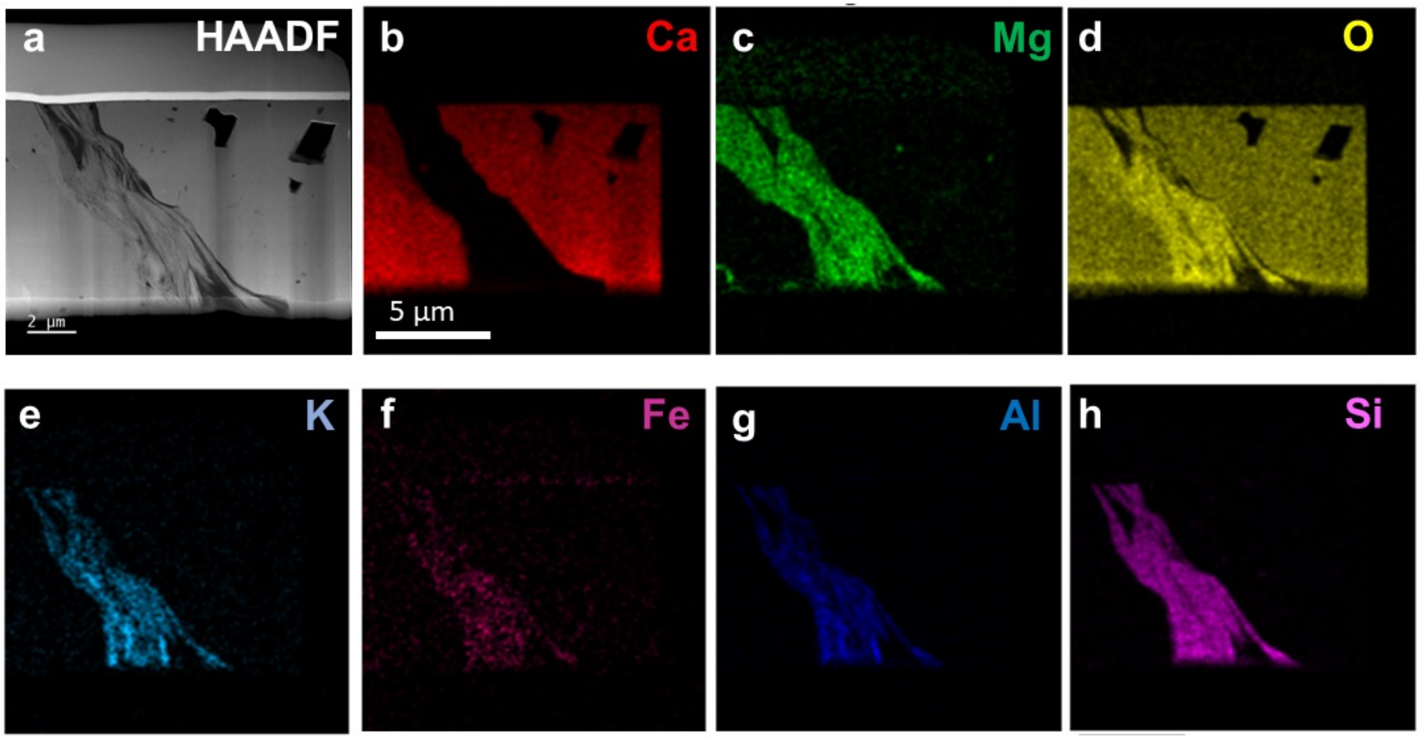
(Ball & Nordstrom, 1991)

SEM Backscattered Contrast



Transport Along Grain Boundary

Low Porosity Limestone



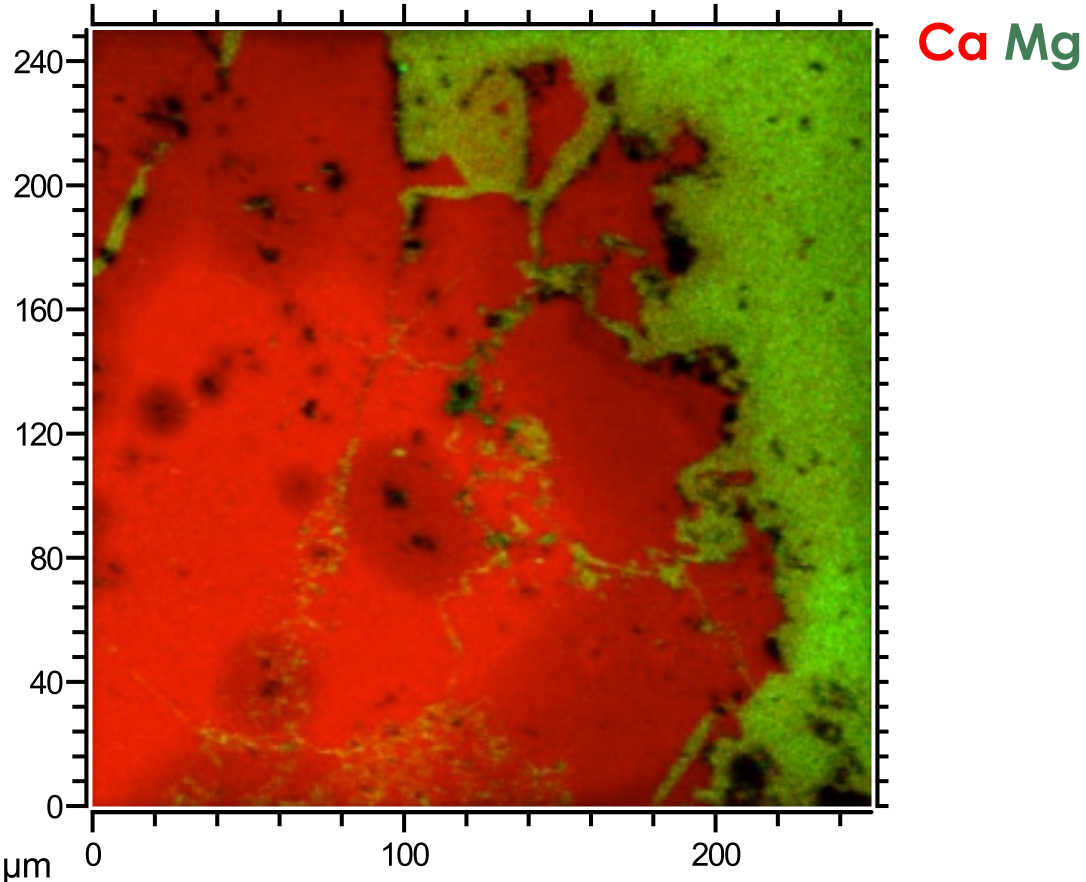
HF-5000 TEM, STEM-EDS mapping

- ❖ Electron diffraction shows this is a grain boundary
- ❖ STEM-EDS shows high Mg content at grain boundary region

Weber et al., **2021**

Dolomitization of Limestone – Grain Boundaries?

Low Porosity Limestone



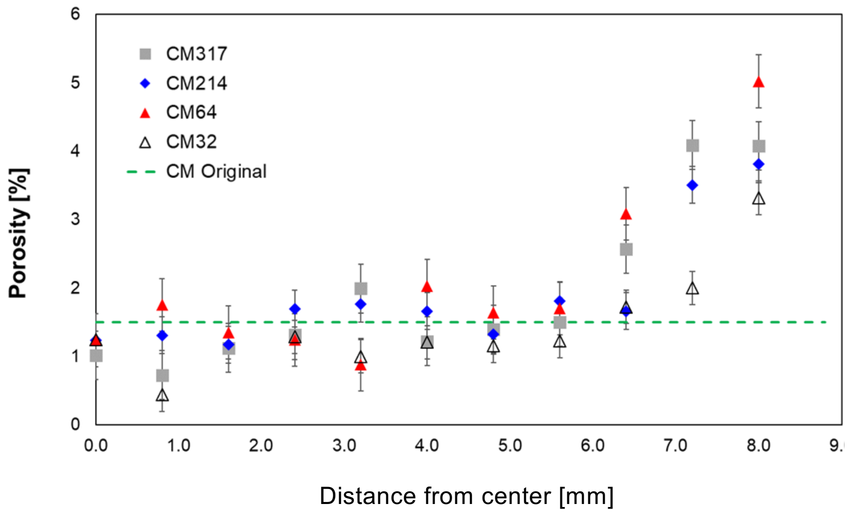
ToF-SIMS

Analyses of Grain Boundary Region?

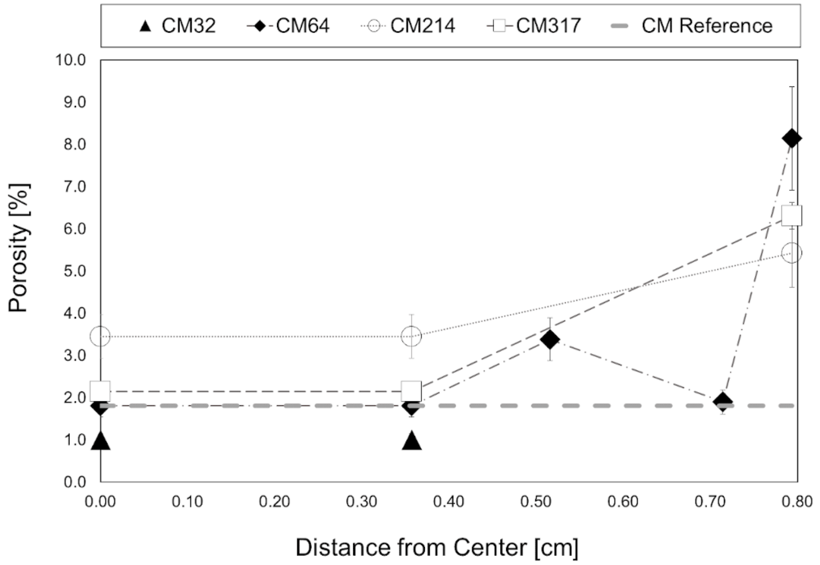
Weber et al., **2021**

Porosity Development with Replacement

Low Porosity Limestone



(U)SAXS



(U)SANS

- ❖ Porosity elevated in rim as expected based on molar volume change
- ❖ But no progression of rim with time as would be expected

Reaction and porosity formation proceeds along grain boundaries → transport rate?

Weber et al., **2021**

Grain Boundary Diffusion Rate

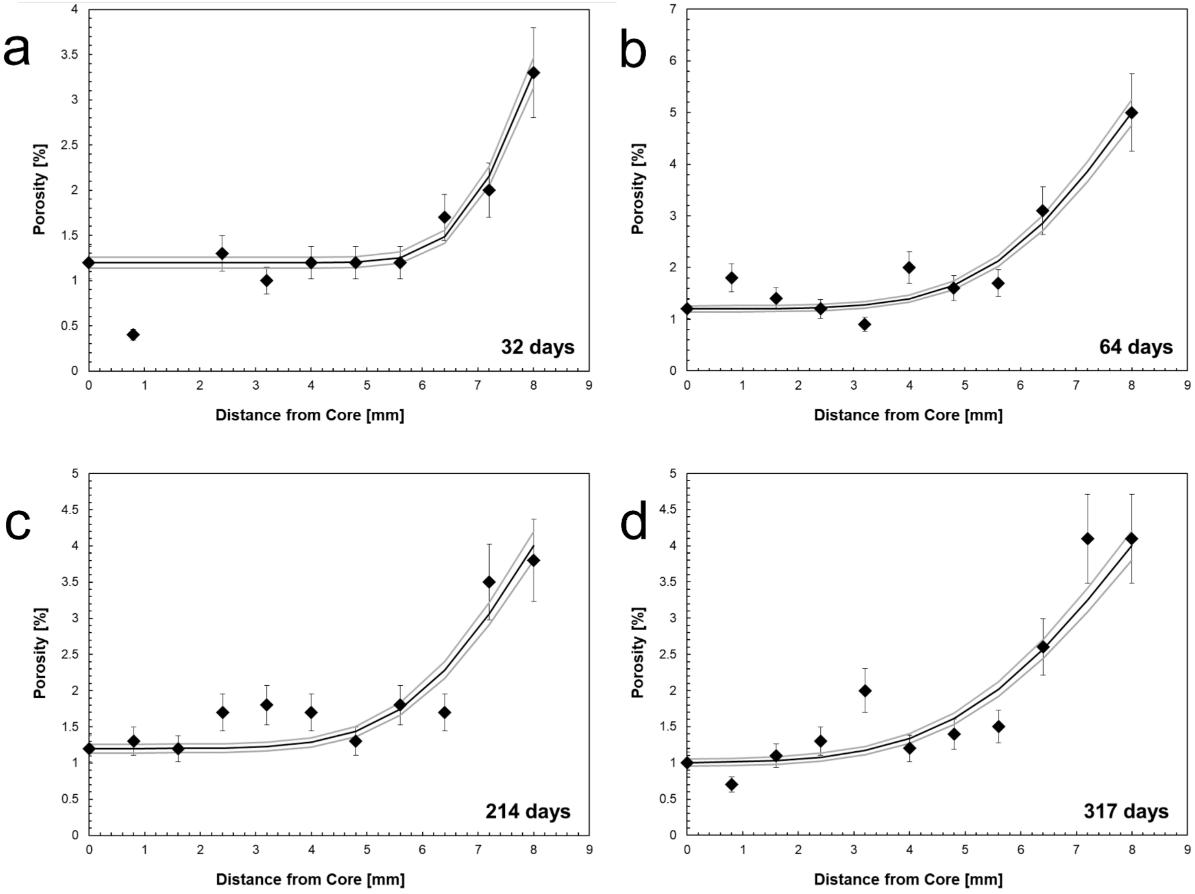
- Fit of porosity as a function of reaction depth to diffusion equation

Fitted diffusion coefficients for the CM experiments.

Sample	D mm^2/day	D m^2/sec
CM32	0.018	2.08E-13
CM64	0.033	3.82E-13
CM214	0.008	9.26E-14
CM317	0.010	1.16E-13

$$C_t = erf\left(\frac{d}{2sqrt(Dt)}\right)(C_c - C_r) + C_r.$$

(Crank, 1979), rearranged



Comparison to bulk diffusion?

Weber et al., **2021**

Model System 2 - Dolomitization of Limestone

Experiments:

- Reaction of two limestones (high/low porosity) with saturated $MgCl_2$ solution
  - What are the reaction paths for dolomitization in a low porosity limestone?
- Reaction conditions: 200 °C

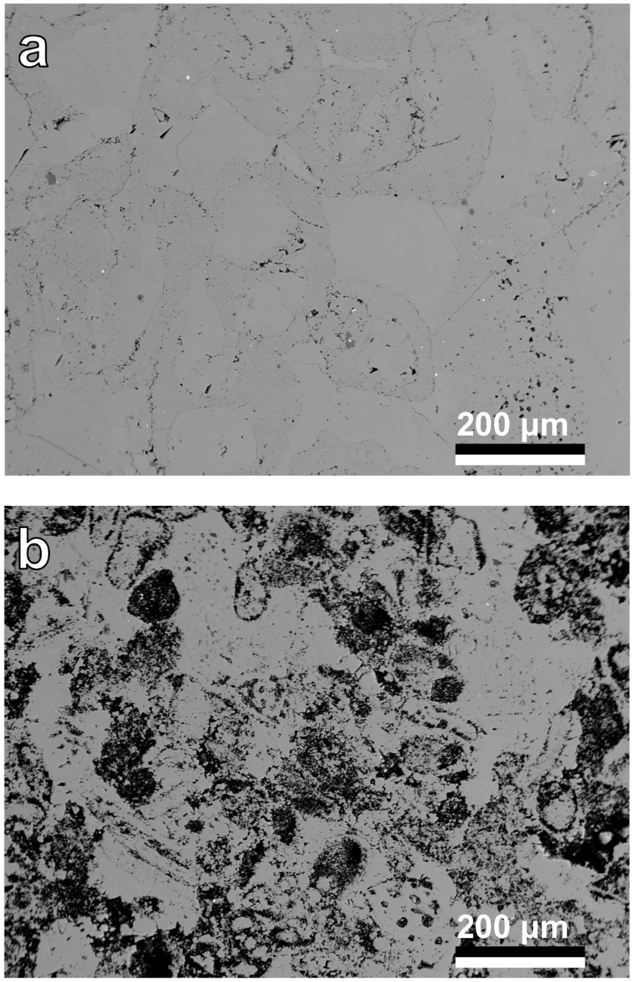
Starting Materials:

- **Low porosity limestone (a):**

  -100 wt% calcite with trace amounts of quartz
  -1.5% porosity by fluid saturation measurements, 1.8% by (U)SANS

- **High porosity limestone (b):**

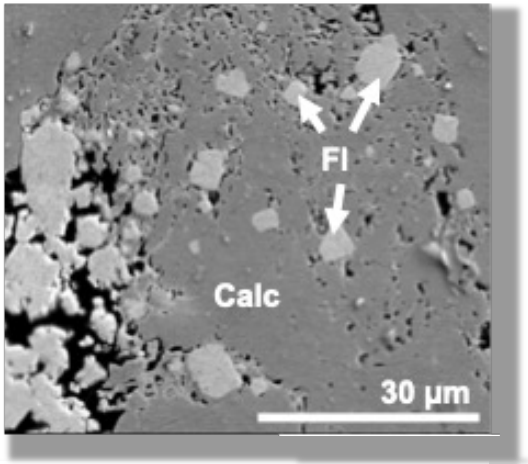
  -99 wt% calcite, 0.5 wt% sylvite and 0.5 wt% quartz
  - 25% porosity by fluid saturation measurements, 8% by (U)SANS

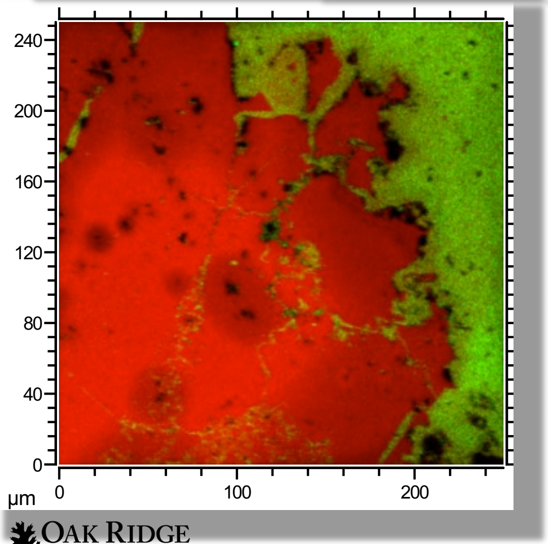


SEM Backscattered Contrast

Open slide master to edit

Summary and Conclusions



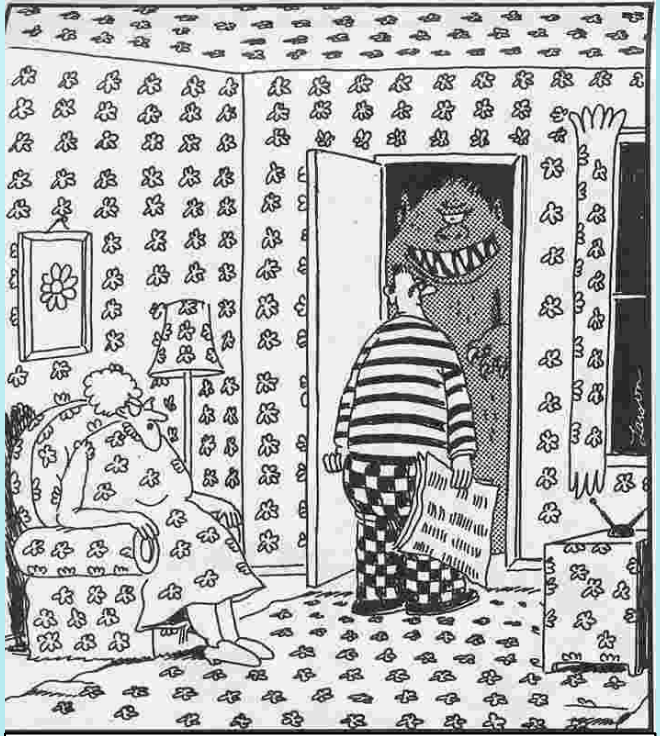


Porosity Changes during Replacement

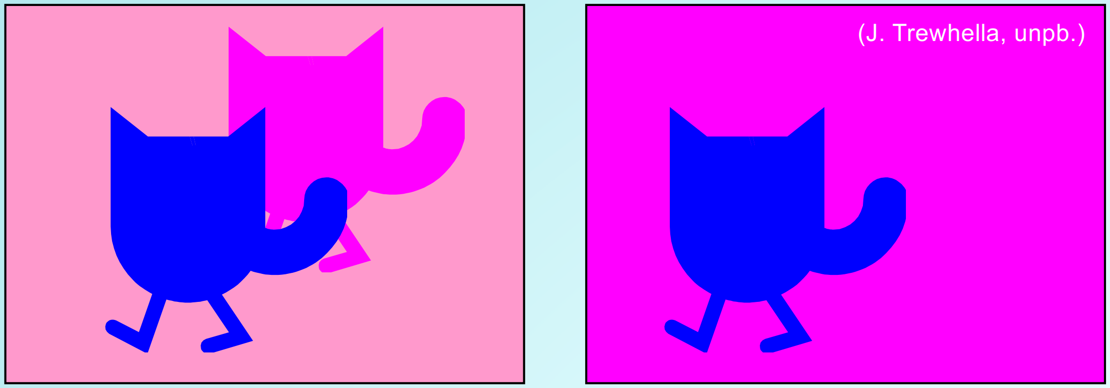
- ❖ Microstructure can have a bigger effect on replacement speed than chemical reactivity
- ❖ Grain boundary diffusion is faster than bulk diffusion and speeds up replacement rate in low porosity materials

Isotopic Contrast Matching

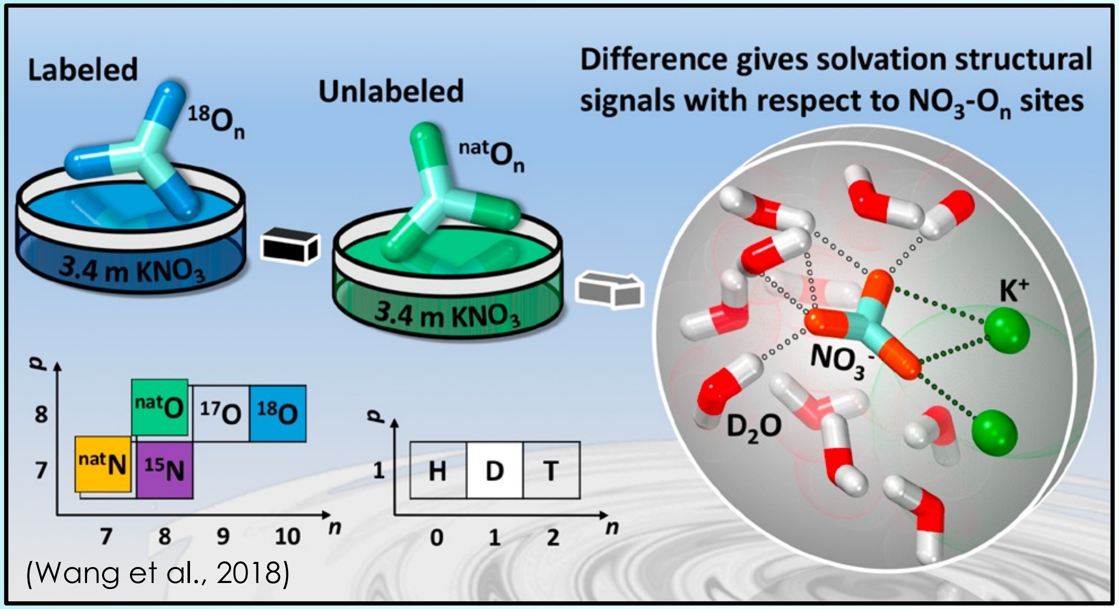
Facilitates study of one component by rendering another “invisible.”



When the monster came, Lola
Like the peppered moth and
The arctic hare, remained
motionless and undetected.
Harold, or course, was
Immediately devoured



(J. Trewhella, unpb.)



Difference gives solvation structural signals with respect to NO_3-O_n sites

(Wang et al., 2018)

Research Questions –
How Does Microstructure Affect Replacement?

Microstructure

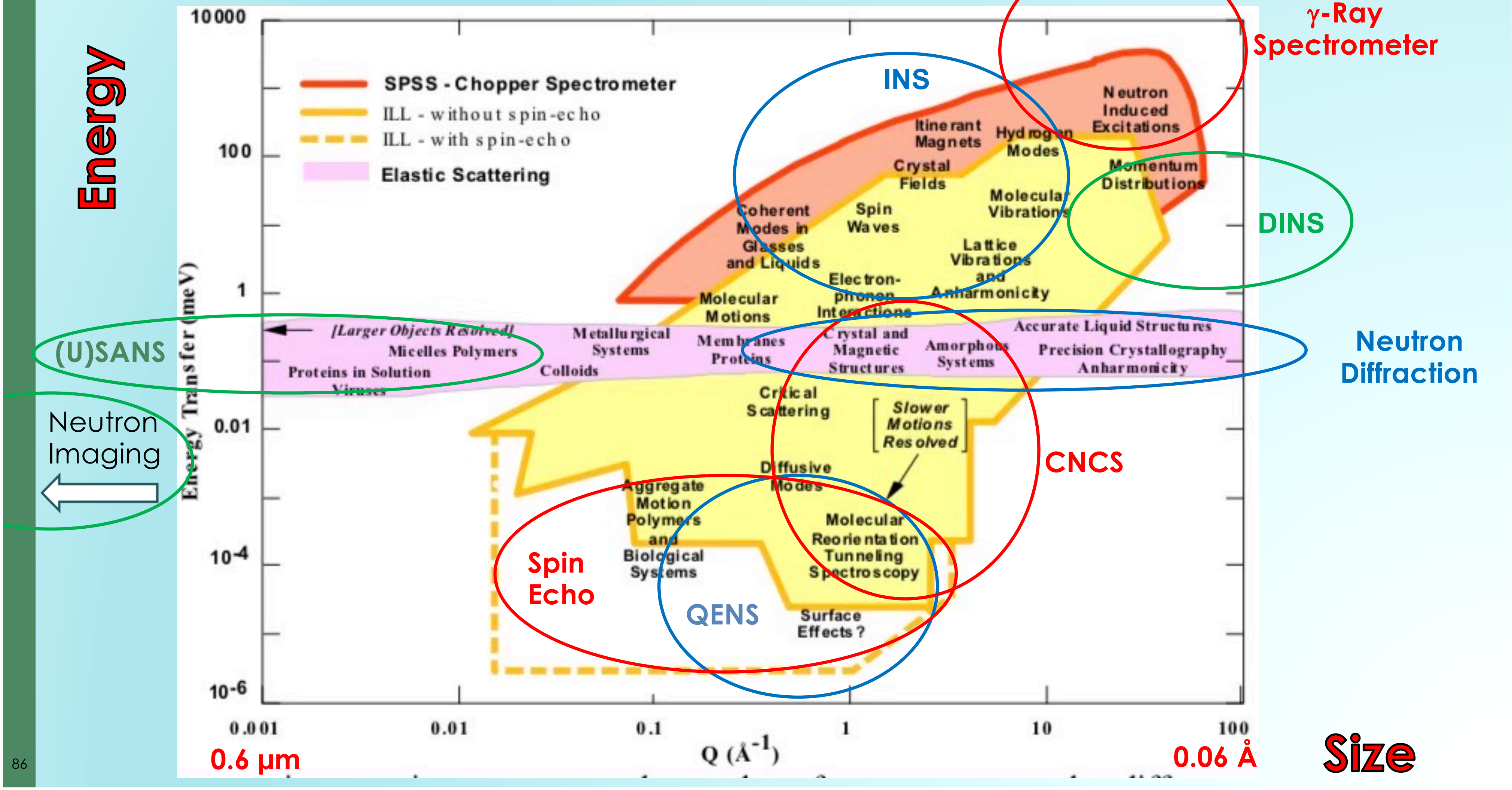
vs.

reaction rate?

How do microstructural features (e.g., grain boundaries) influence replacement rate?

Neutrons or a COMBINATION of neutron studies with other techniques, provide a way to approach many of these problems

Neutrons in Condensed Matter Research



Conclusions

Weathering (and other geo-processes) are not just chemical

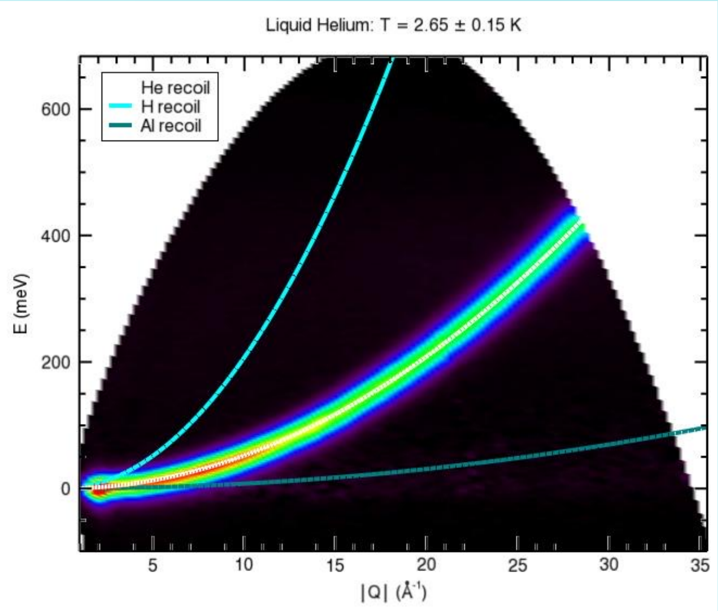
Scale and Mechanics Matter

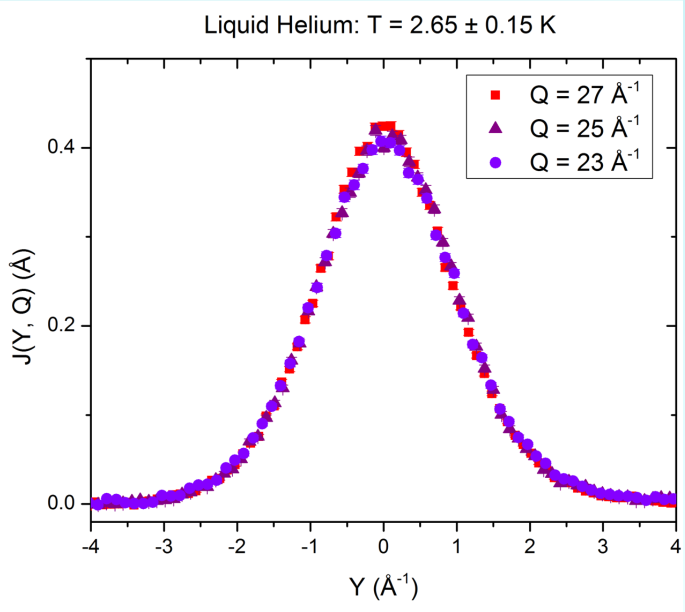
1) Stylolites - aren't present at plug scale
    1) increase permeability
    2) Provide a failure plane
2) Micron scale detachment is eclipsed by larger-scale mechanical detachment around the stylolites.
3) This may lead to large changes in total surface area – sub µm pores count!

Process Matters Too

1) Freeze/Thaw
2) Surface rocks not continuously exposed to fluids. There is always drying. Effects are unknown.

Neutron Compton Scattering (DINS)





The lineshape of the atomic recoil peak yields the momentum distribution.

$$J(Y,\hat{q}) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{\frac{-Y^2}{2\sigma^2}} \sum_{n,l,m} a_{n,l,m} H_{2n+l}(Y) Y_{lm}(\hat{q})$$

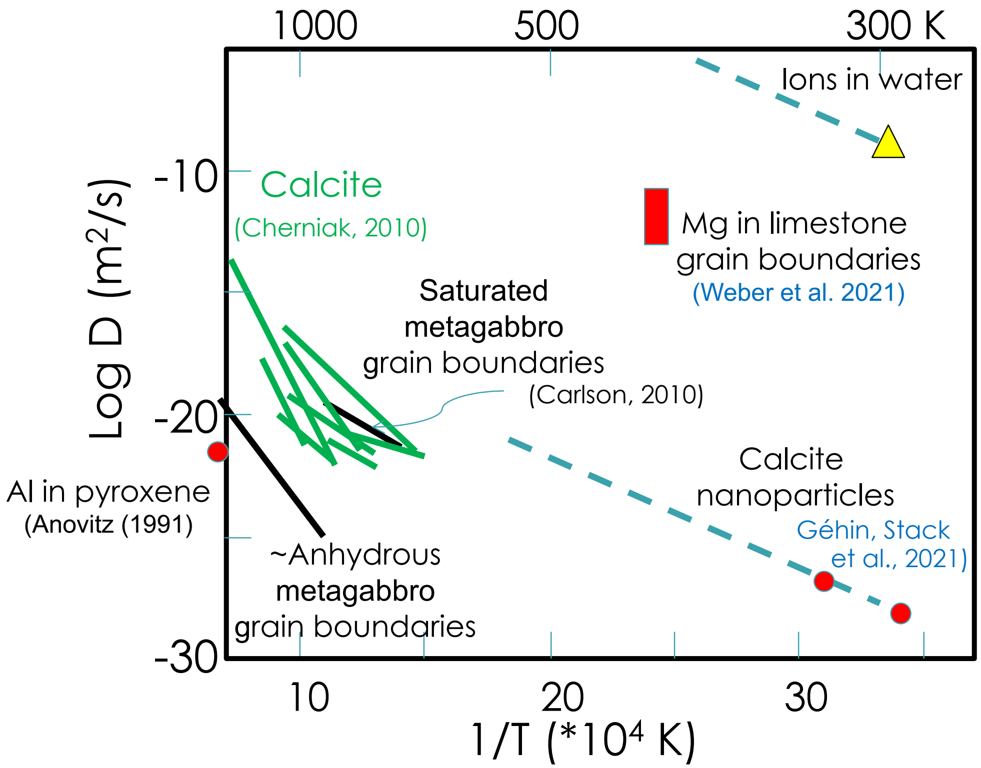
$$n(\mathbf{k}) = \frac{1}{(2\pi\sigma^2)^{3/2}} e^{\frac{-k^2}{2\sigma^2}} \sum_{n,l,m} 2^{2n+l} n!\,(-1)^n a_{n,l,m} k^l L_n^{l+1/2} Y_{lm}(\hat{k})$$

Y = momentum component parallel to Q.
J = projection of the momentum distribution (Radon transform)

T.R. Prisk *et al J. Low Temp. Phys.* ***189***, 158-184 (2017).

Analysis by the late George Reiter

Comparison of Grain Boundary Diffusion Rate w Bulk Diffusion



- ❖ Grain boundary diffusion rates between ~ 10 orders of magnitude faster than solid diffusion and ~ 4 order of magnitude slower than self diffusion in aqueous solution (10^{-9} m²/s, Zhong and Friedmann, 1988)

→ Grain boundaries are important for replacement reactions