Investigation of H_2O in 3D Nanoporous Spaces

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for US DOE's NNSA under contract DE-AC04-94AL85000.

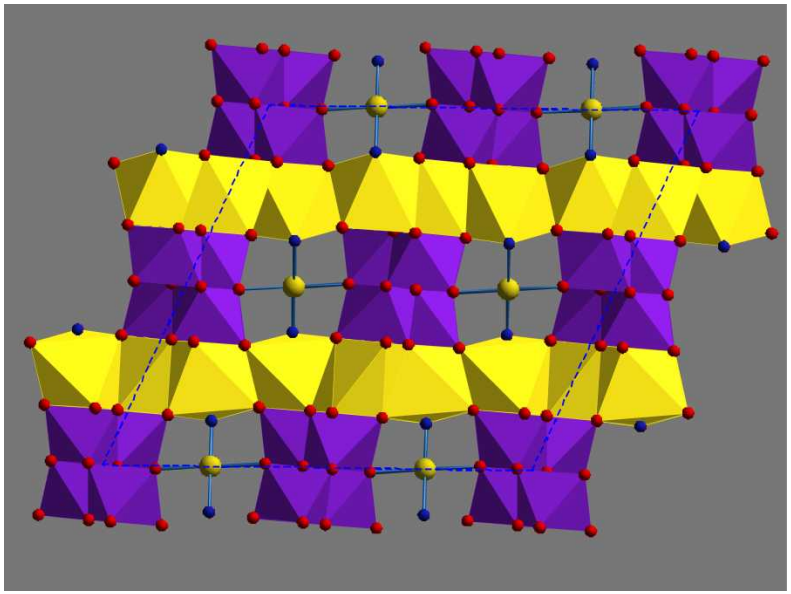
Introduction:

Zeolites: Metastable crystalline inorganic porous materials for bulk or membrane separations & Catalysis; pores 4-15Å; separations based upon size selectivity

What is the role of water with respect to ion exchange, adsorption, selectivity??

SOMS

$Na_2Nb_{2-x}M^{IV}_xO_{6-x}(OH)_x \cdot H_2O$

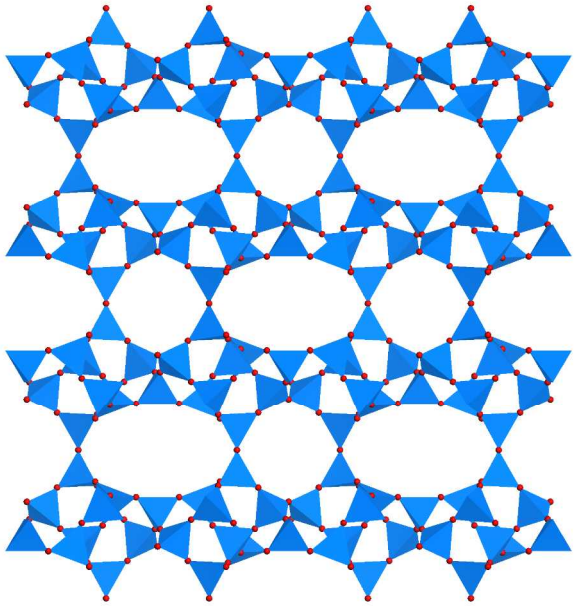


Monoclinic Unit Cell

a = 16.87(2), *b*=5.35(1), *c*=16.45(4)Å; β=113.9(6)°

Clinoptilolite / Heulandite

$[X]_{4-6}[Al_6(Al,Si)_4Si_{26}O_{72}] \cdot x\ H_2O$



Orthogonal Unit Cell

a = 15.916(4), *b* = 17.950(2), *c* = 7.435(1) Å

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Synthesis & Characterization Methods

Use of hydrothermal synthesis methods for novel phase formation

Synthesis

aqueous based chemistry
mild temperatures (RT-200° C)
organic templating reagents
mild pressures (<100 psi)
Oxide/alkoxide reagents

Parr reactor vessels, Teflon pouches

Characterization Methods

Inelastic Neutron Scattering (LANSCE)
X-ray and neutron diffraction
MAS NMR
TGA/DTA, calorimetry (UCD)
electron microscopy (SEM, TEM)
ICP/MS, AA, SEM/EDS
FTIR, Raman
BET, TPD

Modeling/Simulation

DFT to classical dynamics for structure and permeation studies

All methods combined for *Structure/Property* Relationship studies

What is the role of H_2O in the pores??

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SOMS: Sandia Octahedral Molecular Sieves

$Na_2Nb_{2-x}Ti_xO_{6-x}(OH)_x \cdot H_2O$ $(0 \leq x \leq 0.4)$
Synthesis and Ion Exchange Preparations

Hydrothermal Method:

Synthesis:

Temperature - 170 ºC

pH ~13.8

$Na:(Nb+M^{IV}):L:H_2O$ - 10:1:1.4:133

Alkoxide reactants:

- Niobium Ethoxide
- M^{IV} Alkoxide
- NaOH
- t-BuOOH
- H_2O
- Time - 4 h (Ti - 68 h)

SOMS Ion-Exchange:

SOMS
add 2 equivalents of M^{x+} per Na^+
stir, filter, wash
add 2 equivalents of M^{x+} per Na^+
stir, filter, wash

* Ion exchange successful for Co^{2+}, Ni^{2+} and Y^{3+}

** ION exchanged SOMS change color for transition metals

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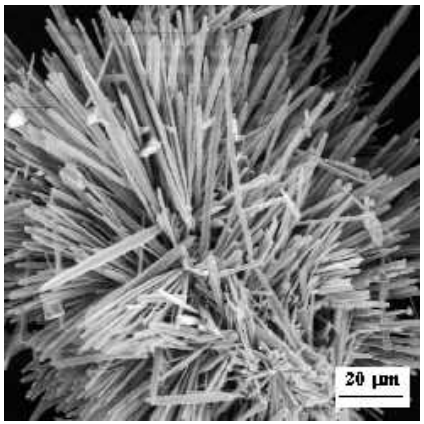
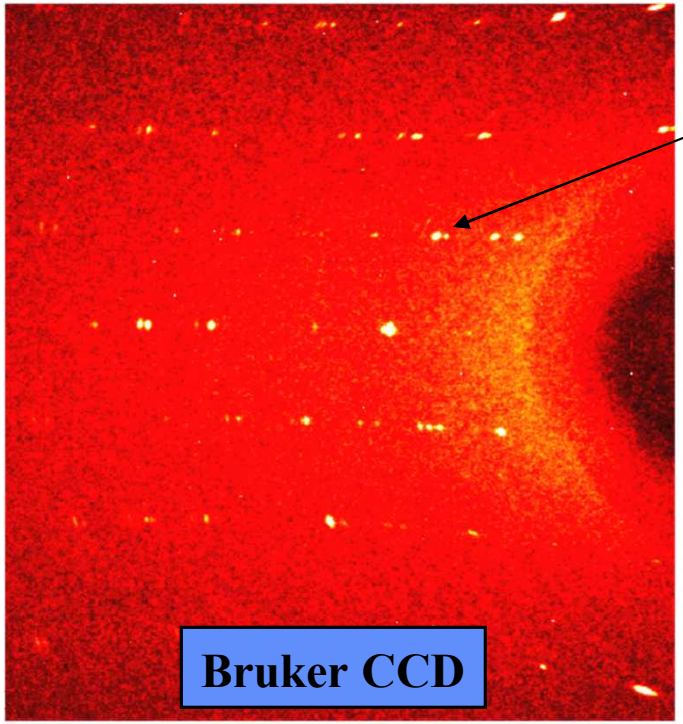
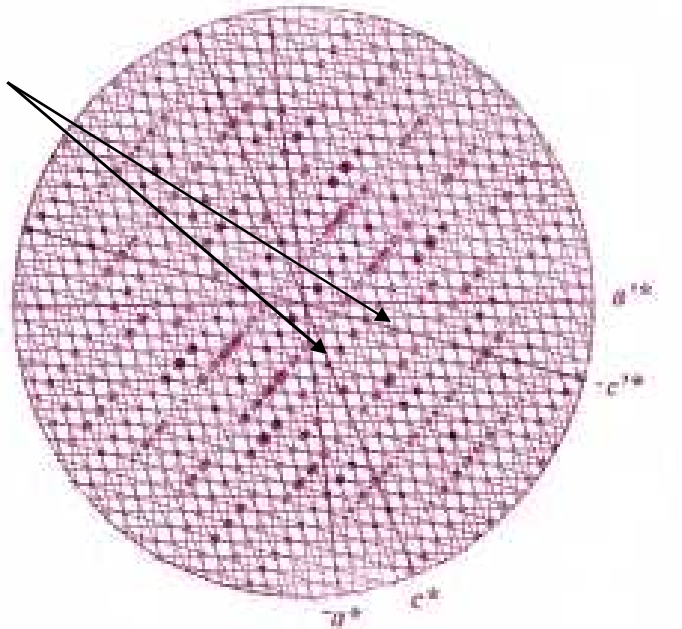
SOMS Structure Determined:
from 5x5x8 μm^3 Non-Merohedrally twinned crystal



Formula:	$Na_2Nb_{1.6}Ti_{0.4}O_{5.6}(OH)_{0.4}\bullet H_2O$
Space Group:	C2/c Monoclinic
Cell Dimensions	a = 16.87(2), b=5.35(1), c=16.45(4)Å; β=113.9(6)°
Data Collection:	SMART CCD, X3A1 NSLS, BNL
Data Index. & Partition:	GEMINI, Twin HKL
Synchrotron radiation:	λ = 0.643Å
Refinement on F^2:	R = 0.054, Rw = 0.144, GOF = 1.049
Reflections/Parameters:	2400/54
Largest diff. peak, hole:	1.393, -1.228 eÅ^{-3}



Non-merohedral twinning observed



2 Superimposed Reciprocal Lattices

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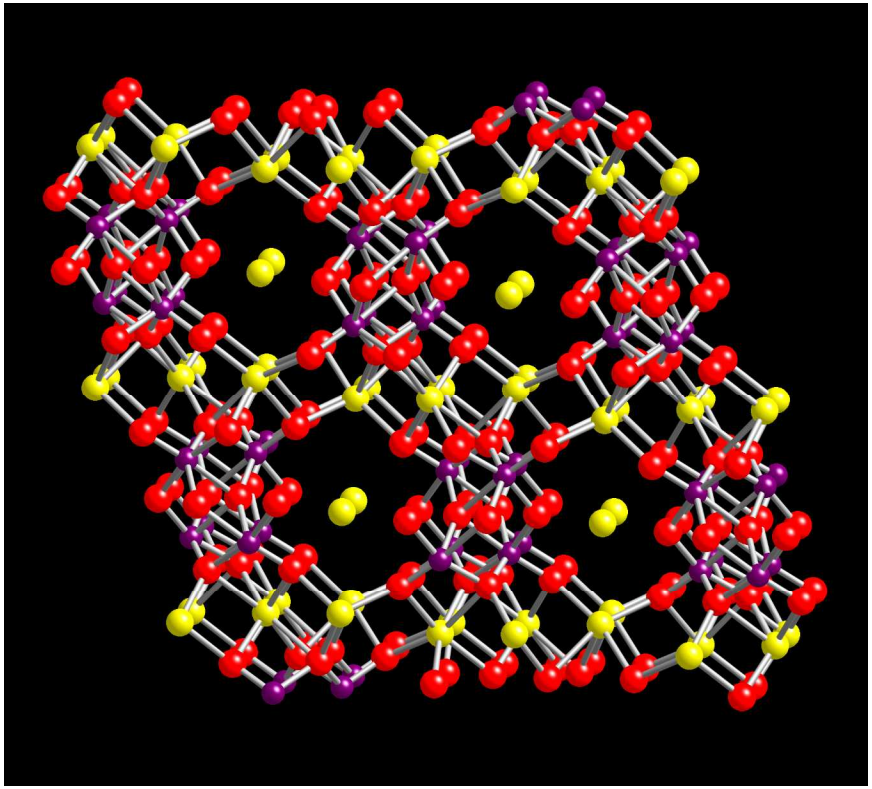
SOMS Zeolites and Selectivity



SOMS-1:

$Na_{16}Nb_{12.8}Ti_{3.2}O_{44.8}(OH)_{3.2}\bullet 8H_2O$

US Patent # 6,596,254; 7/03.
JACS, 2002, 124(8),1704; *Chem. Mater.*, 2004, *16*, 2034;
Chem. Mater. 2005, *17*, 950; *J. Mater. Res*., 2005, 20(3), 618

$K_d = [M]_{ie} / [M]_{sol}$

metal ion	6-coordinate radius (pm)	Ti-niobate phase Nb:Ti = 1:4
Ba^{2+}	149	> 99,800 *
Sr^{2+}	132	> 99,800 *
Ca^{2+}	114	2,300
Mg^{2+}	86	226
Pb^{2+}	133	66,467
Cr^{3+}	94	> 99,800*
Co^{2+}	89	> 99,800 *
Ni^{2+}	83	> 99,800 *
Zn^{2+}	88	> 99,800 *
Cd^{2+}	109	> 99,800 *
Cs^{+}	181	150
K^{+}	152	95
Li^{+}	90	8

**** 0.1 ppm detection limit***

K_d obtained from 50 ppm metal ion solutions (no competing ions)

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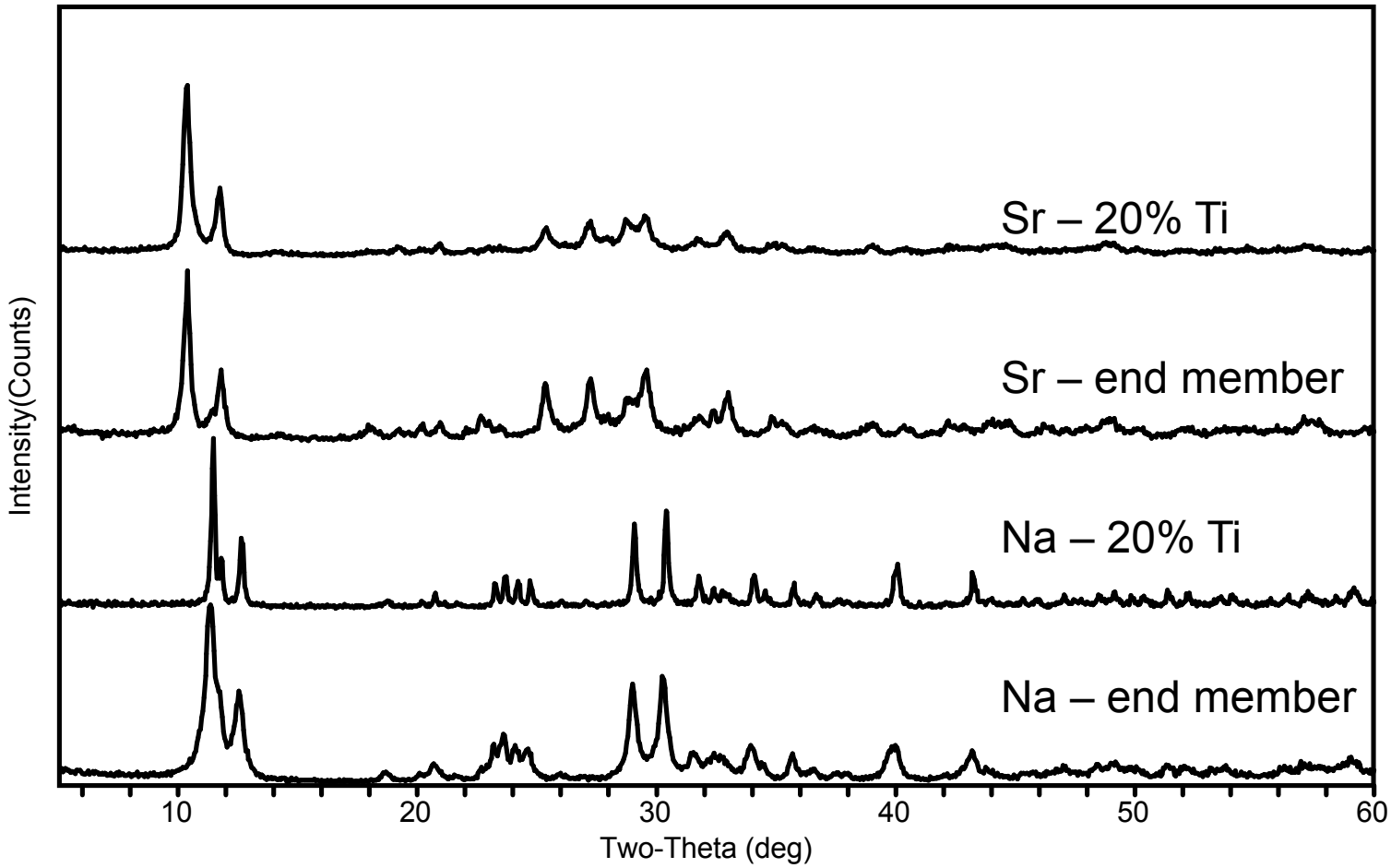
SOMS: Stability of Framework

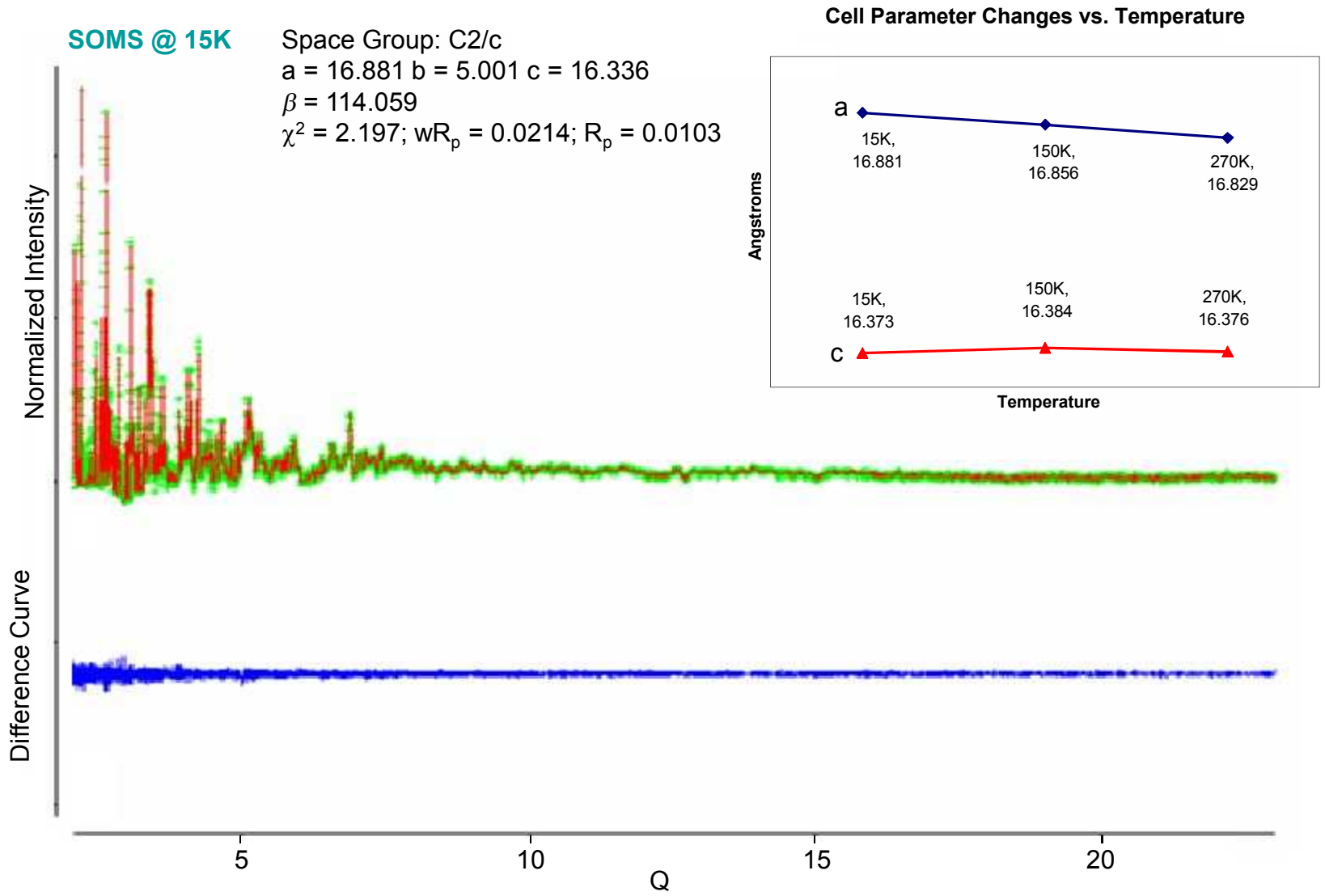
Substitution and Ion Exchange:

End Member: $Na_2Nb_2O_6 \cdot H_2O$

20% Ti-SOMS: $Na_{16}Nb_{12.8}Ti_{3.2}O_{44.8}(OH)_{3.2} \cdot 8H_2O$



Neutron Diffraction Structure Refinement



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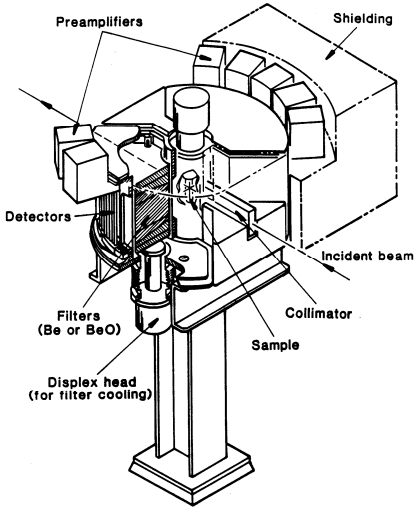
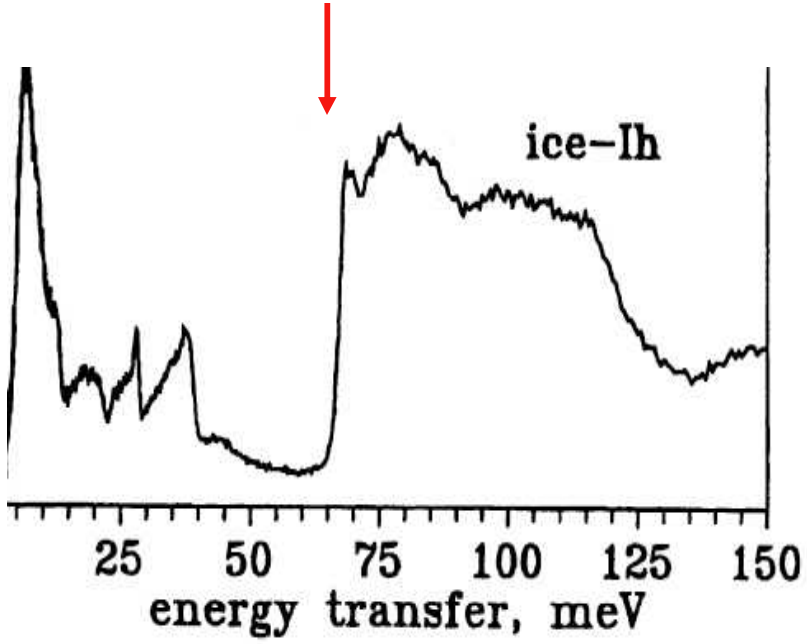
Inelastic Neutron Scattering (INS) / LANSCE

FDS Specifications	
Energy transfer range	6-620 meV (50-5000 cm^{-1})
Momentum transfer range	1.5-17 A^{-1}
Energy transfer resolution	2% to 5% (depending on data treatment)
Beam size at sample	2.5 cm x 10 cm (W x H)
Detectors	60 ^{3}He tubes
Filter analyzers	5 Be and 5 BeO wedges subtending a scattering angle of 18°; cooled to 20 K
Moderator	Chilled water at 10 °C
Sample environment	10-325 K closed-cycle refrigerators; in situ gas absorption cell; Be-Cu pressure cell to 20 kbar; 20-800 K hot-stage, closed-cycle refrigerator
Sample size	0.5-100 g
Typical experiment duration	2 hours to 2 days





INS data of Ice; J. Molecular Liquids 100/1 (2002) 1-39.

Neutron Vibrational Spectra:
(1) strength of bonds formed with neighboring atoms/molecules, (2) the proximity of cations, and (3) the environment (charge density,dipole moment density, etc) all influence:
librational (rotational oscillations) and translational motion of H_2O molecules.

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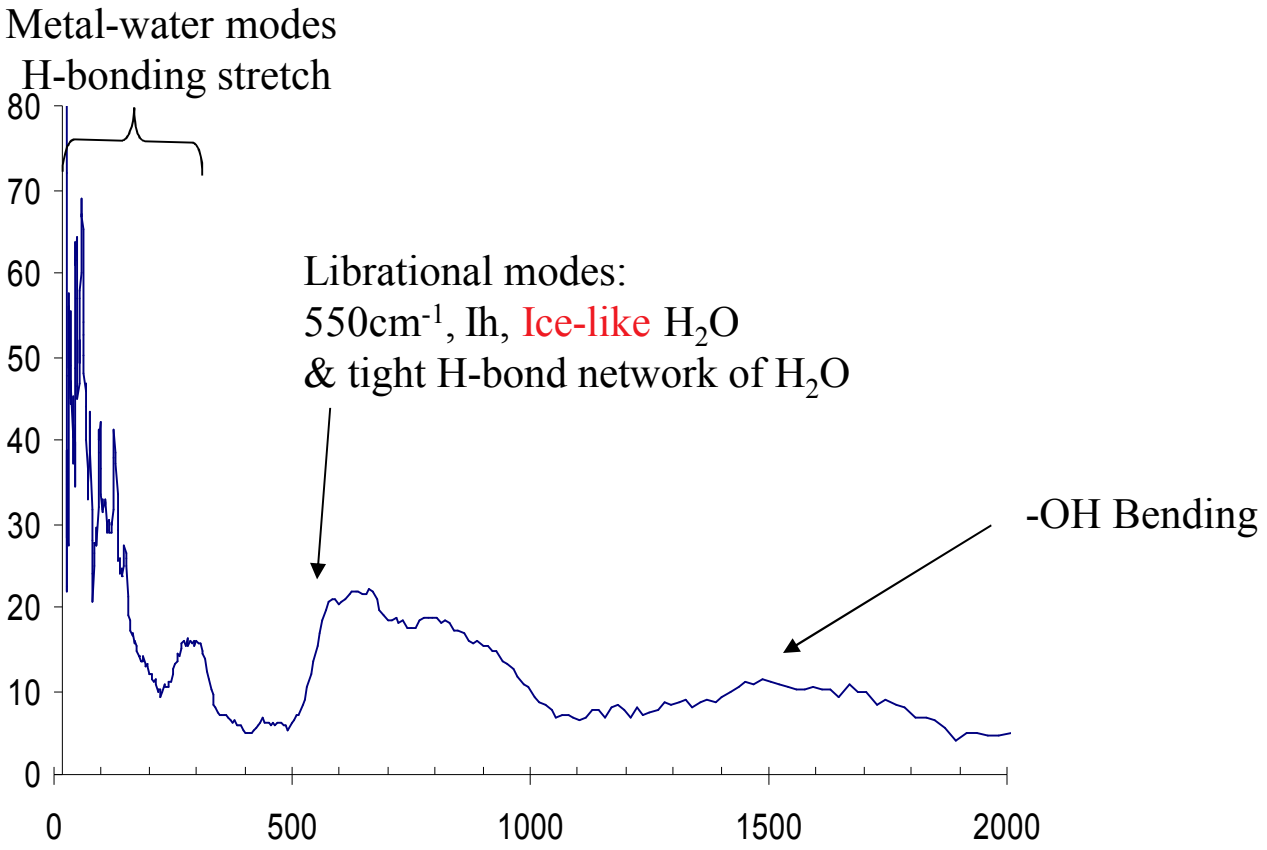
LANSCE
Los Alamos Neutron Science Center

INS data for "end member"

Inelastic Neutron Scattering, SOMS End Member $Na_2Nb_2O_6 \cdot H_2O$
Low selectivity, $K_d \approx 3800$



Aquo complexes: H_2O is bound to metal by partial covalent bonding (100-350 cm^{-1})
Lattice water: H_2O oxygen is bound to metal in almost ionic bond, water molecule may be considered a crystal (300-600 cm^{-1})

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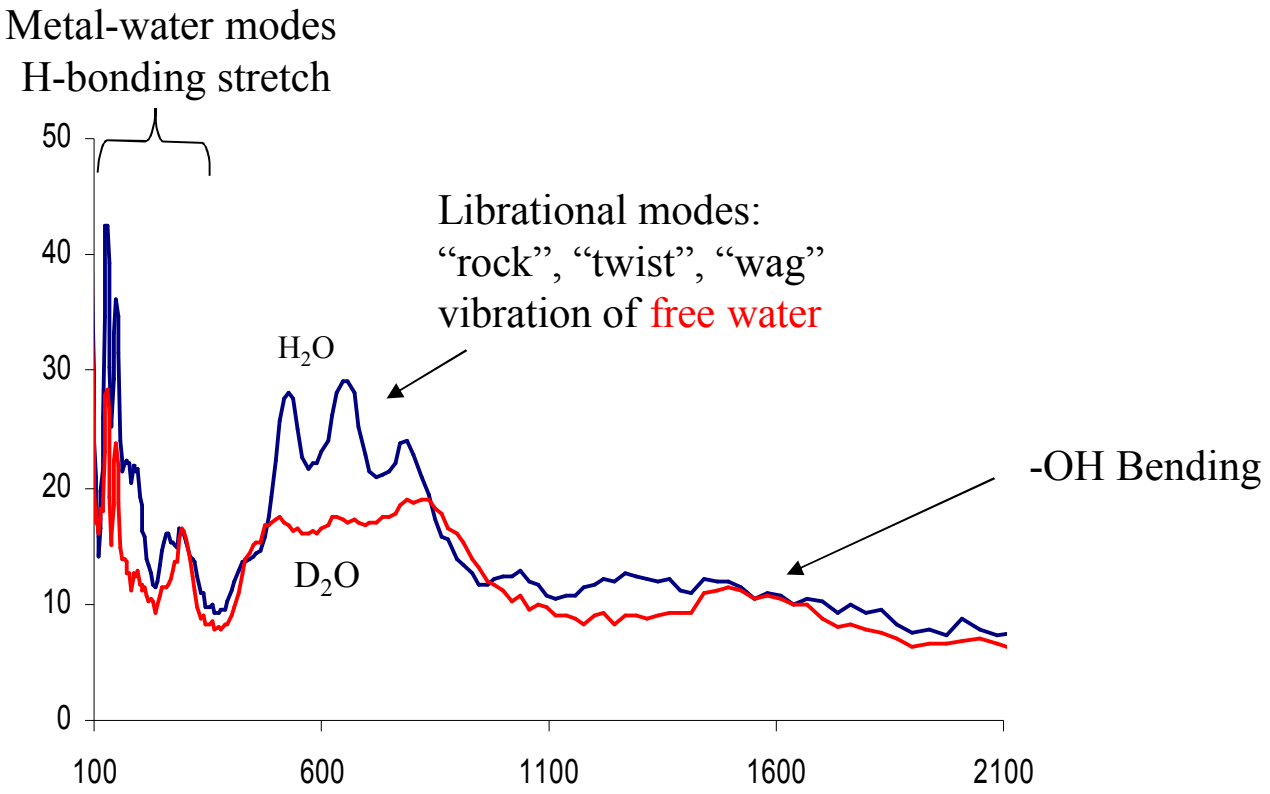
INS data for 20% Ti-SOMS

Inelastic Neutron Scattering; SOMS, $Na_2Nb_{1.8}Ti_{0.2}(OH)_{0.2}O_{5.6}\bullet H_2O$
High selectivity, $K_d \approx 26000$



Aquo complexes: H_2O is bound to metal by partial covalent bonding (100-350 cm^{-1})
Lattice water: H_2O oxygen is bound to metal in almost ionic bond, water molecule may be considered a crystal (300-600 cm^{-1})

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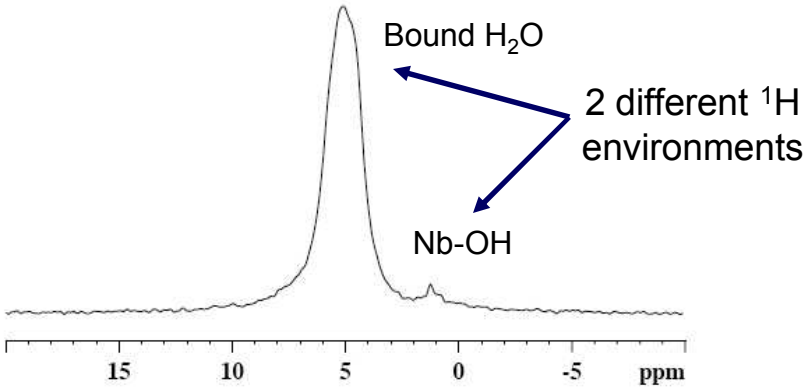
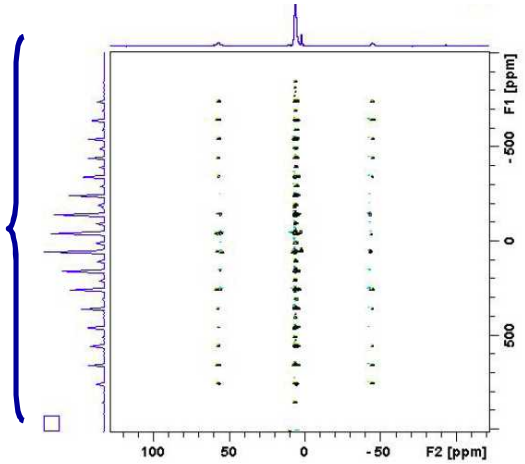
MAS NMR for "end member" SOMS ($Na_2Nb_2O_6 \cdot H_2O$)

^{1}H MAS NMR; Bruker 600; 2.5 mm MAS probe, ν_R = 30 kHz



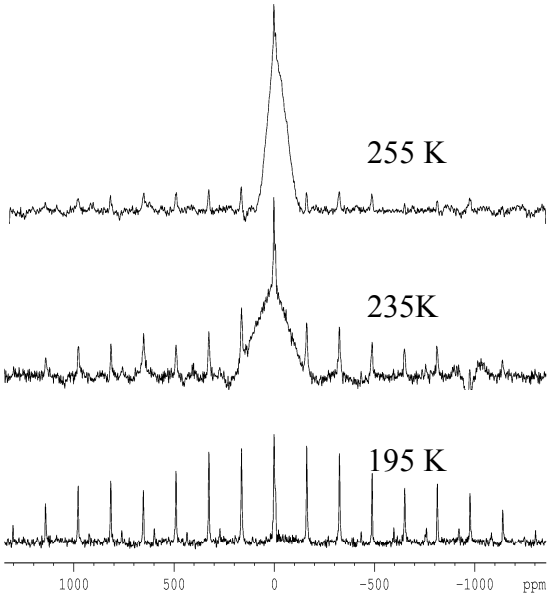
Double Quantum (DQ) ^{1}H MAS Sideband Analysis

Width of DQ SSB provide sensitive to dipolar coupling



Dipole coupling 28KHz = rigid H_2O species
Immobile water 32.8 kHz

Variable temperature ^{2}H MAS NMR



Possible: multiple water sites that "freeze out" at different temperatures

^{2}H NMR; Bruker 400, 4mm MAS probe,
9 μs π/2 ^{2}H pulse; 298 K, ν_R = 10 kHz

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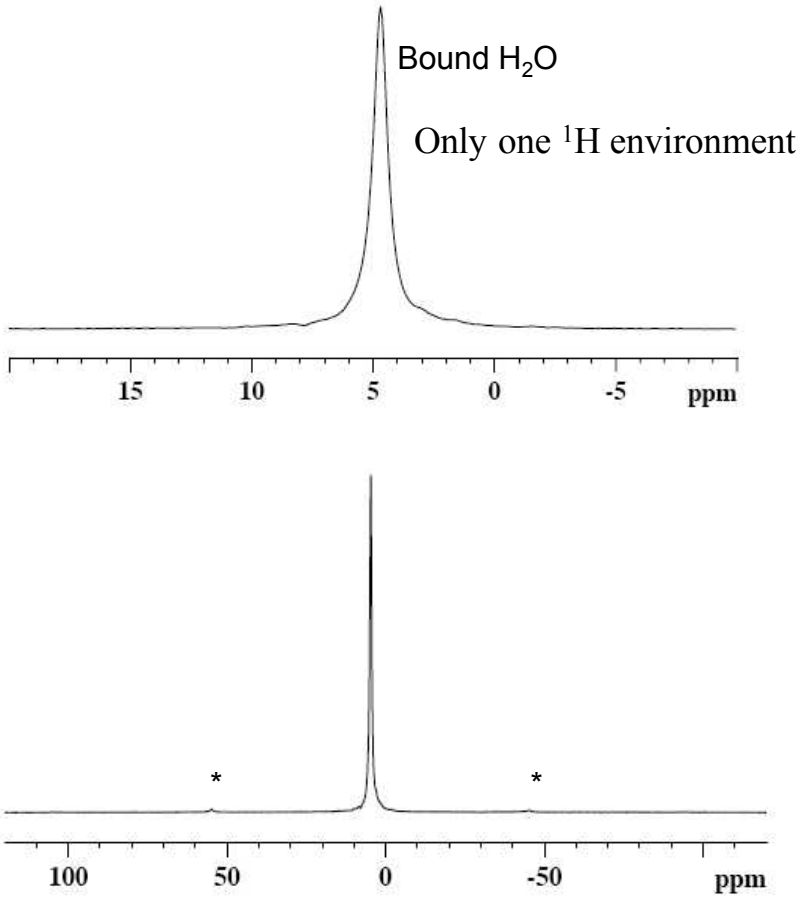
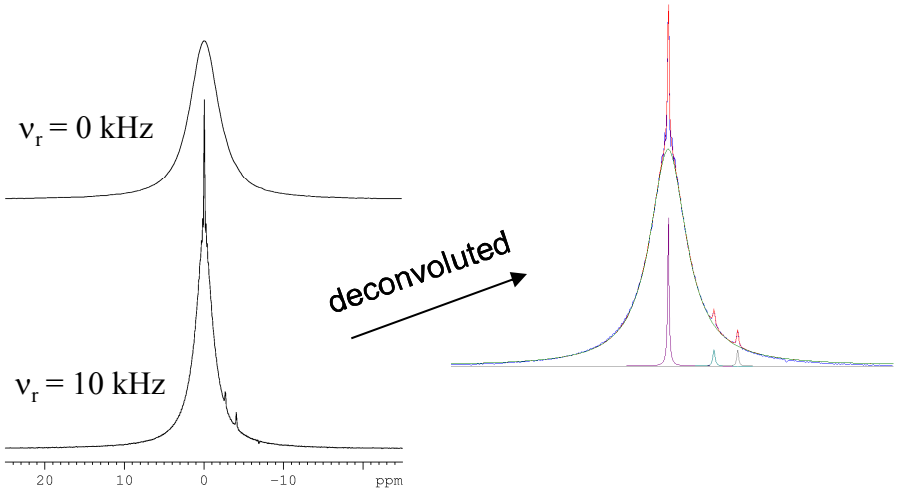
MAS NMR for 20%Ti-SOMS ($Na_2Nb_{1.8}Ti_{0.2}(OH)_{0.2}O_{5.6}\bullet H_2O$)

^{1}H NMR; Bruker 600; 2.5 mm MAS probe



Narrow line width & small SSB (*) suggests mobile water
NO DQ MAS NMR – small dipolar coupling!

^{2}H NMR; Bruker 400, 4mm MAS probe,
9 μs π/2 ^{2}H pulse; 298 K



Very narrow deconvoluted water peaks.
Most of the water is mobile,
some very mobile (7 Hz-wide line)
Most likely surface water.

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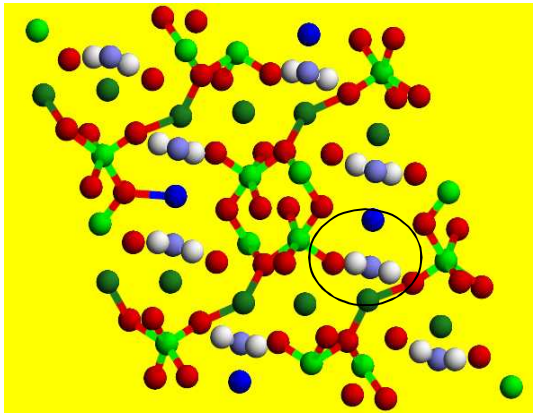
DFT Modeling: Water Configuration

- Optimized SOMS network atoms using DFT/PBE
- Run MD at 900 K for 2 ps, then apply geometry optimization

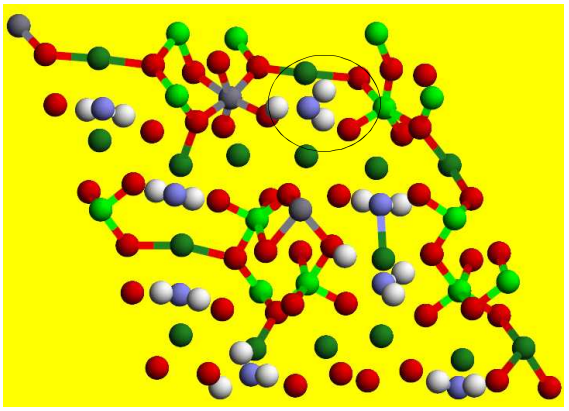
$Na_2Nb_2O_6 \cdot H_2O$



O
Nb
Na
H_2O

DFT Results :
- H_2O configuration extremely robust
- each water proton H-bonds to a framework O^{2-}; water O coordinates to a framework and a pore Na^+ ; O-Na distance agree with exp.
- water locks into ice-like configuration near framework

$Nb_{13}Ti_3Na_{16}O_{45}(OH)_3 \cdot (H_2O)_{16}$



H
O
O
Nb
Ti
Na

DFT Results :
- H_2O is easily trapped in metastable states
- H_2O can coordinate to framework and pore Na^+, framework -OH and O^{2-}
- Multiple energy minima mean more mobile H_2O!

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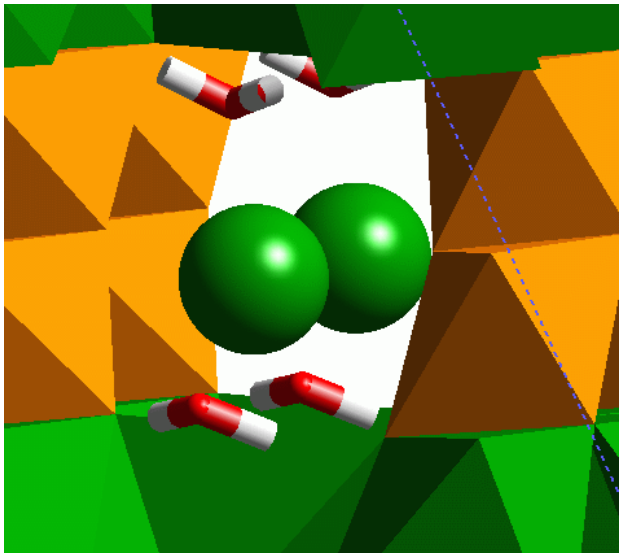
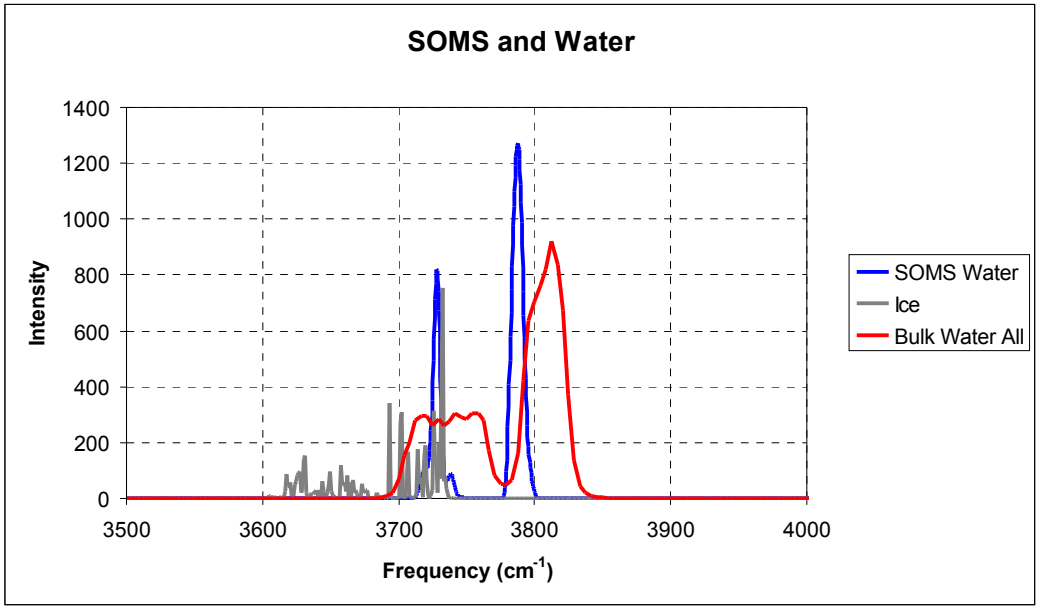
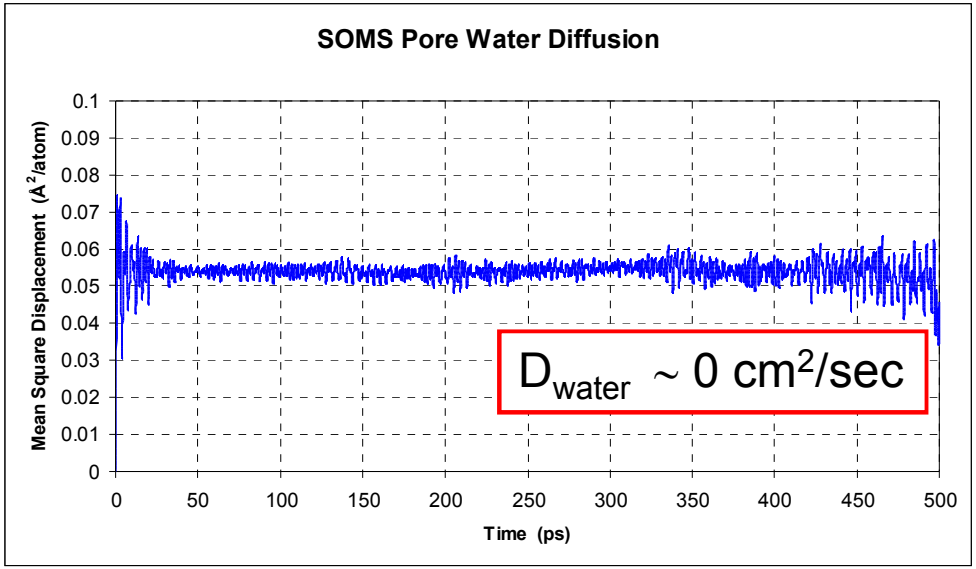
Classical Dynamics Simulations: End Member SOMS

Force field approximated; OFF







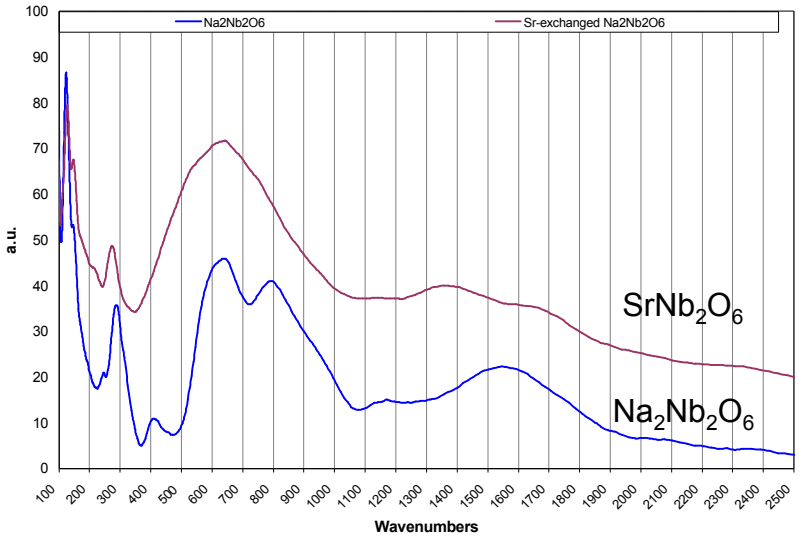
Highly static water in pores of end member SOMS

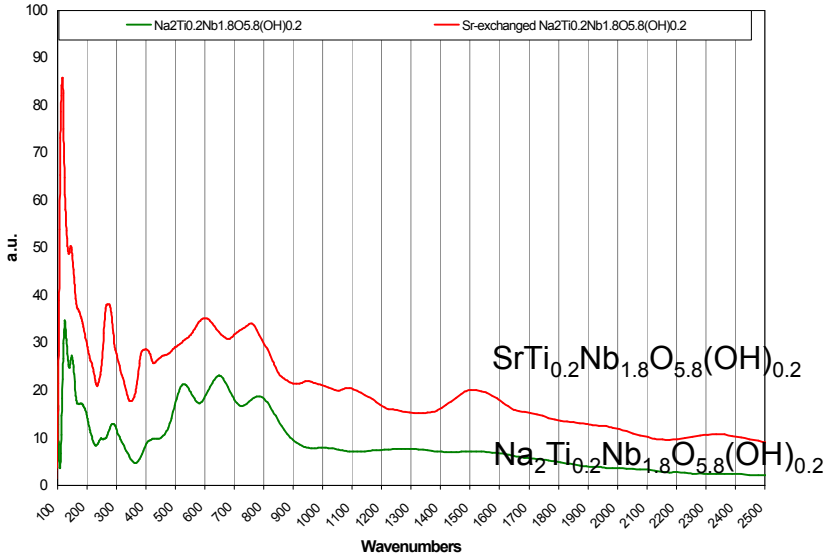
Strong H-bonding to framework,
Strong O-bonding to Na^+ cation.
"Ice-like" behavior.

Agreement between DFT & classical MD

INS data (On-going): Sr exchanged End Member & 20 %Ti-SOMS

Loss of ice-like characteristics when monovalent Na^+ was ion exchanged for divalent Sr^{2+} ions, resulting in half the # of cations present in the framework.





Sr exchanged end member: loss of ice-like peak

Broad librational modes, overlapping.
Two possible explanations:
- 2 distinct networks of water molecules (H-bonding, but not to each other)
- loss of long-range order in the network(s) of H-bonded water molecules

Sr exchanged 20% Ti:

Librational modes for H_2O observed.
No ice-like water behavior.

*Slight shift to lower frequencies may be due to larger size of Sr^{2+} cations & presence of -O_fH inhibiting H-bonding in pores.**

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* J. Phys.: Condens. Matter 17 (2005) 7925

Conclusions

The cation solvation environment and the ion exchange capability of the SOMS molecular sieves are related

End Member (non-doped) $Na_2Nb_2O_6 \cdot H_2O$, has both a low K_d value and ice-like occluded water molecules.

20% Ti-doped SOMS: $Na_{16}Nb_{12.8}Ti_{3.2}O_{44.8}(OH)_{3.2} \cdot 8H_2O$, has both high K_d values and mobile occluded water molecules

The ice-like waters of the Na-end member are different in nature and "freeze out" at different temperatures.

Sr^{2+} exchange disrupts longer range H-bonds & ordering of waters in end member; no ice-like fingerprint in INS data

* Varying time scales of characterization reveal subtle changes in water molecule behavior.

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- Synthesis: Jason Pless, Nate Ockwig
- Modeling: Kevin Leung, Randy Cygan
- INS: Luc Daemon, Monica Hartl
- NMR: Jacalyn Clawson, Todd Alam
- May Nyman (SNL); Akhilesh Tripathi & John Parise (SUNY-SB)

- "Study of Interfacial H_2O", Sandia LDRD FY06-09
- Co-PIs: Jeff Brinker, Bruce Bunker, Randy Cygan, Peter Feibelman, Tina Nenoff