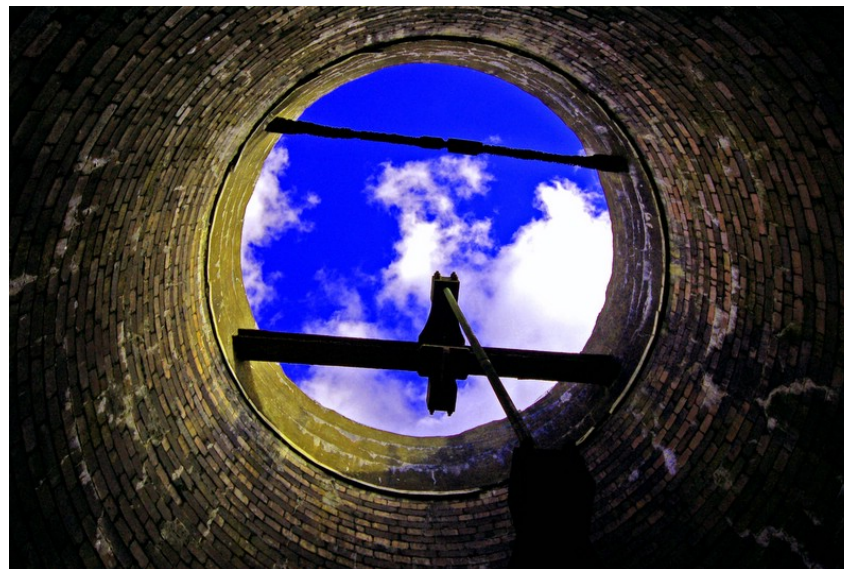


Computational Material Science for Desal Membrane Design

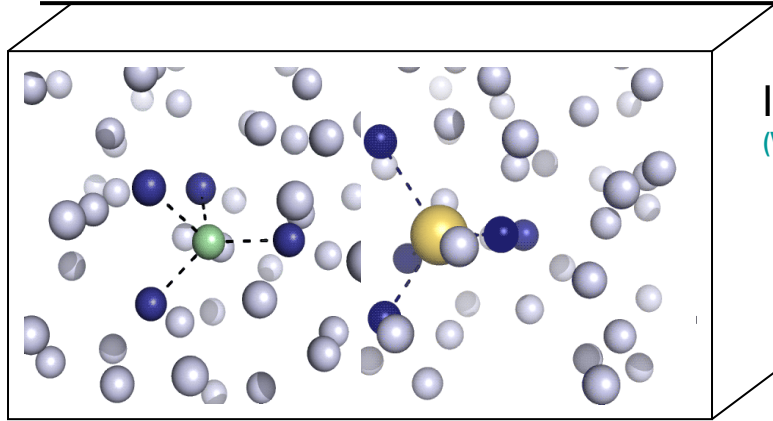


Water well: www.pbase.com/mescalroman/images/57217408

Susan Rempe

Sandia National Labs, Albuquerque, NM

Natural protein channels: Not just simple holes!



Ions in water
(Varma & Rempe, 2007)

- Water 'happy' in channel, not ions!

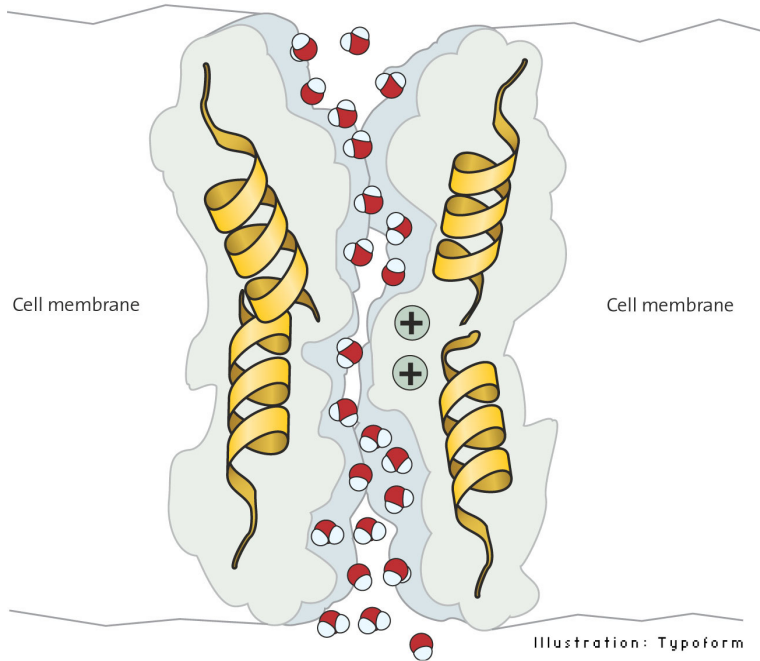
Unresolved Questions:

- How do channels work?

Smaller Na^+ ions **rejected**

K^+ ions **rejected**

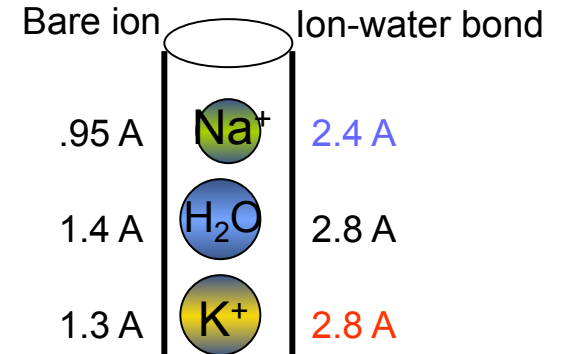
Water channel



4 nm x
2.8 radius

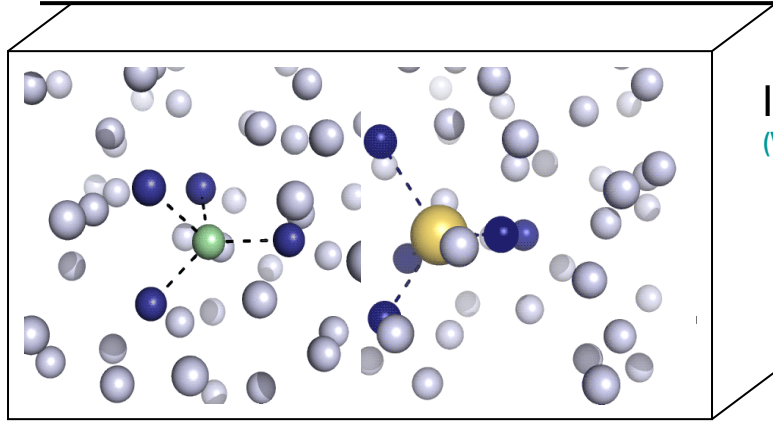
Illustration: Typoform

Aquaporin molecule
(www.nobelprize.org)



- Water transported fast!
- ions & water similar in size

Natural protein channels: Not just simple holes!

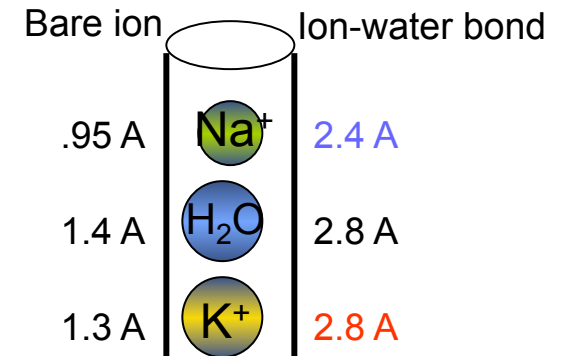
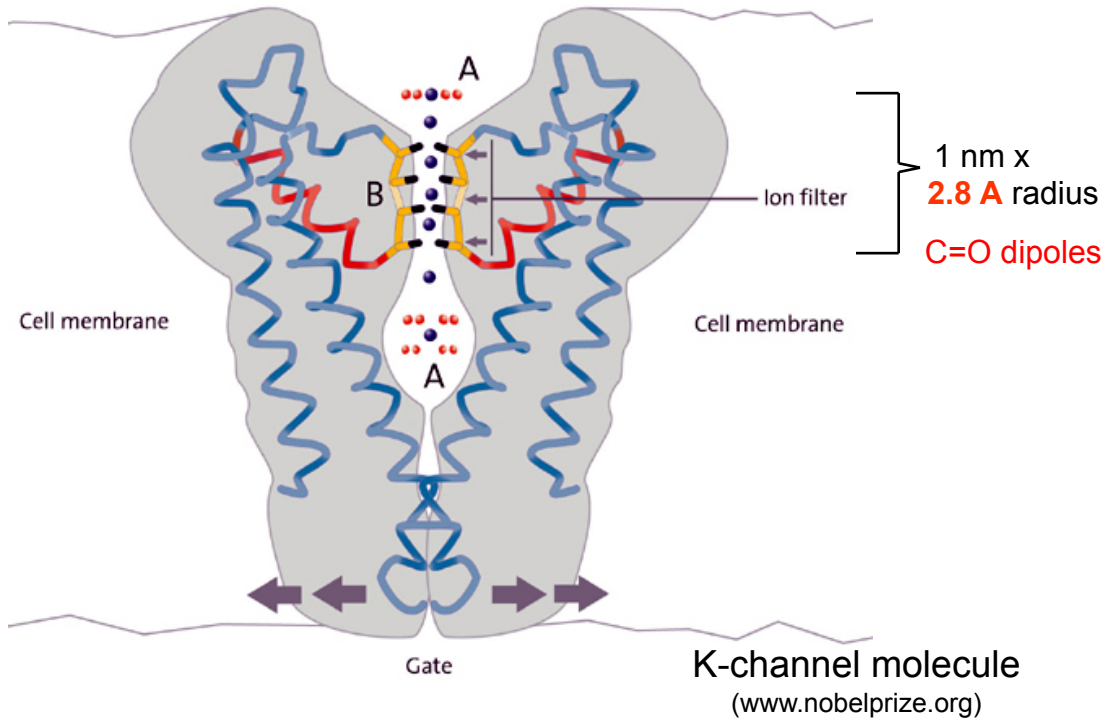


Ions in water
(Varma & Rempe, 2007)

- Ions 'happy' in aqueous solutions
- Unresolved Questions:**
- How do channels work?

Smaller Na^+ ions rejected

K^+ ions permeate **fast**

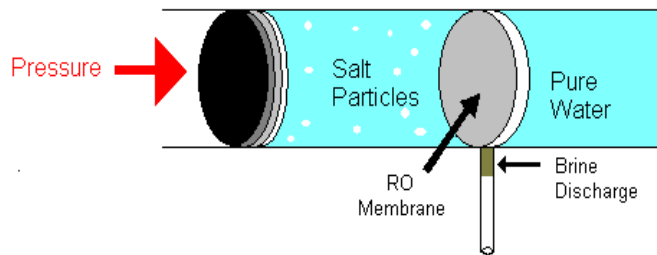


- K^+/Na^+ exquisite discrimination:
 - same charge
 - larger ion transported, fast!

Desalination: A Global Crisis

Half the world lacks clean water

- reverse osmosis technology is expensive
- produces unhealthy water

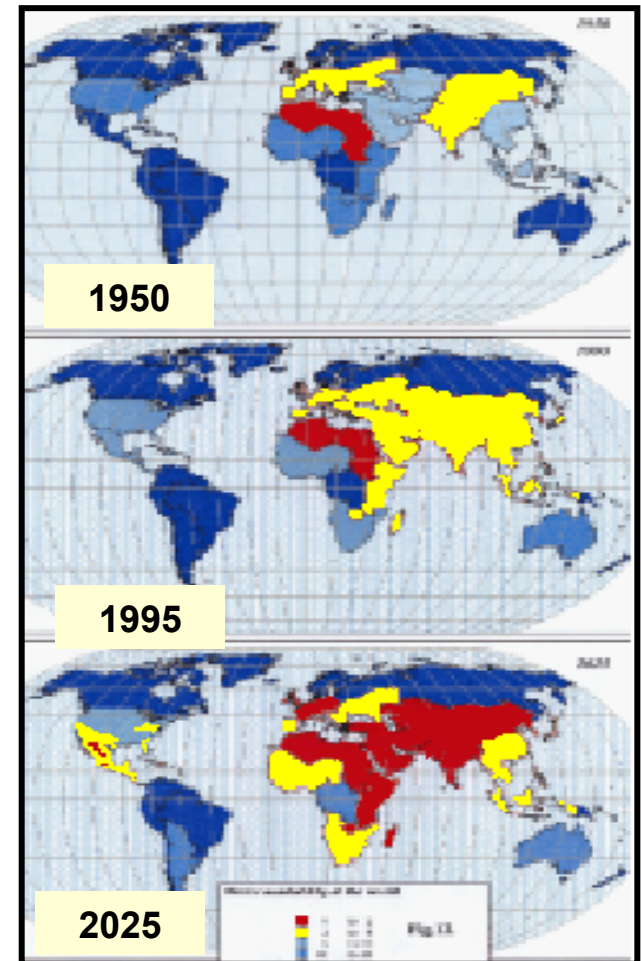


Breakthrough needed in membrane design

- current non-porous design since 1970's
- need faster water + select ion exclusion

“Water promises to be to the 21st century what oil was to the 20th century: the precious commodity that determines the wealth of nations.”

Fortune Magazine, May 15, 2000

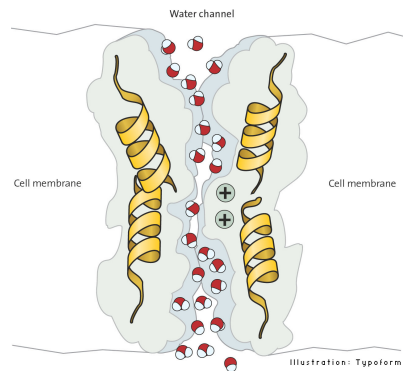


shortage

Efficient Membranes: Porous

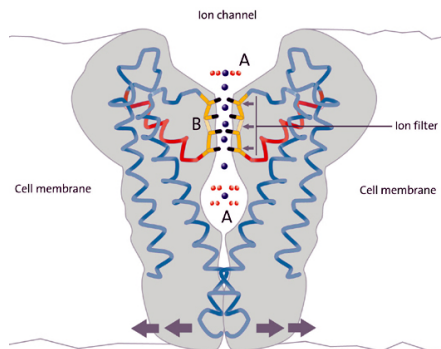
Understand, design, engineer nano-channels for desalination

Water channels

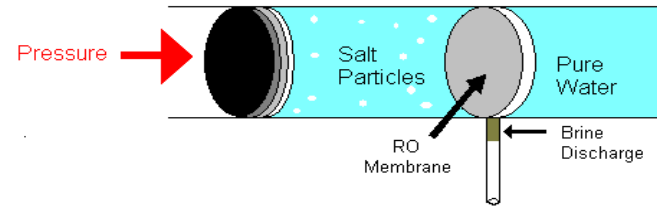


- transport H₂O fast

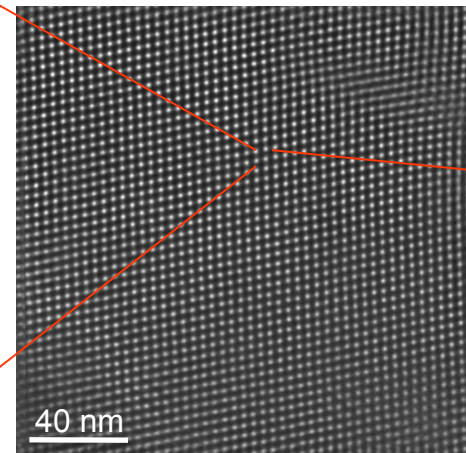
Ion channels



- select minerals fast



- Bio-inspired design



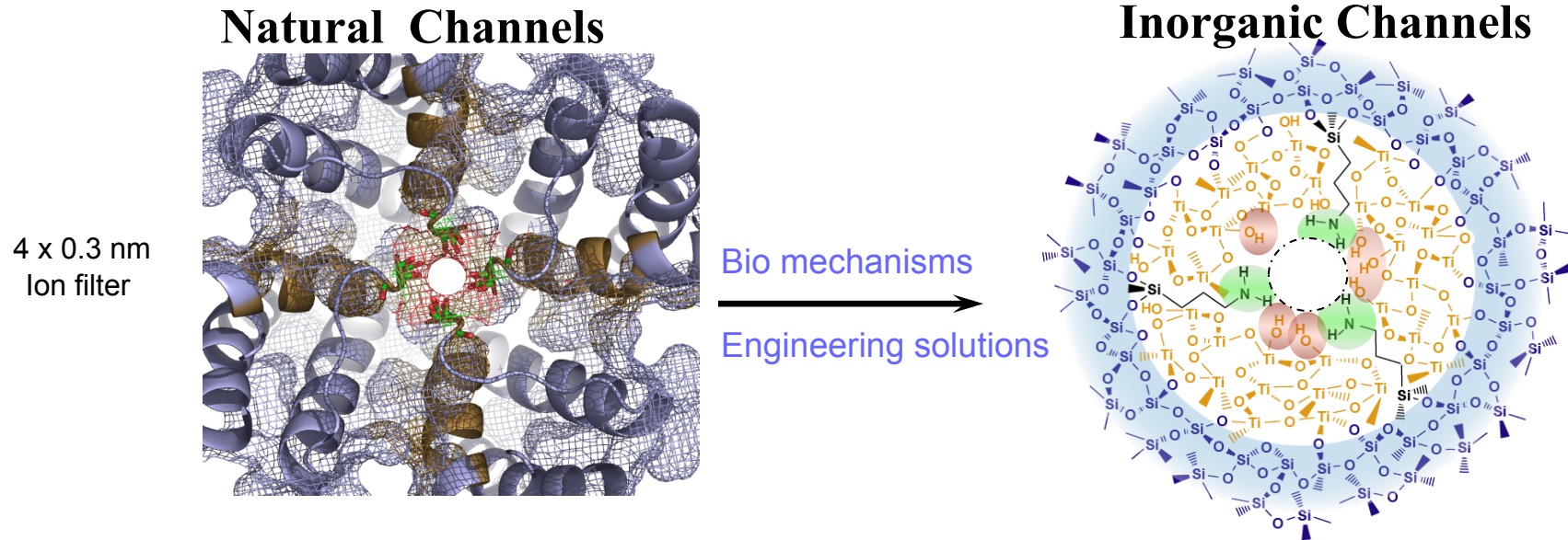
- Theory to reveal mechanism

- Membrane synthesis & function evaluation



Solution: Harness molecular biomechanisms.
Gain 10x in water flux + minerals.

What determines fast selective transport for single pores?



Critical Channel Design Issues:

- What's significant about
- (1) Mouth?
 - (2) Narrow, thin filter?
 - (3) Chemistry & Architecture?

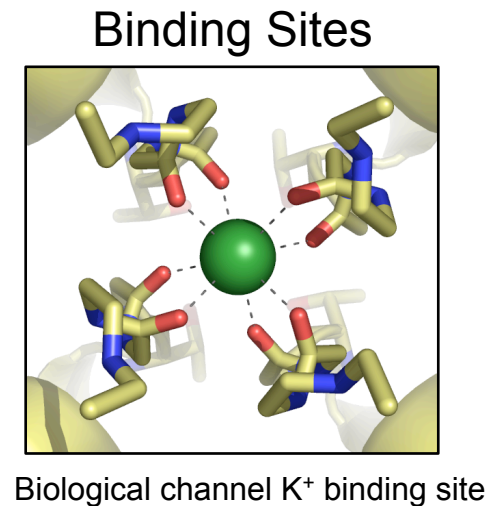
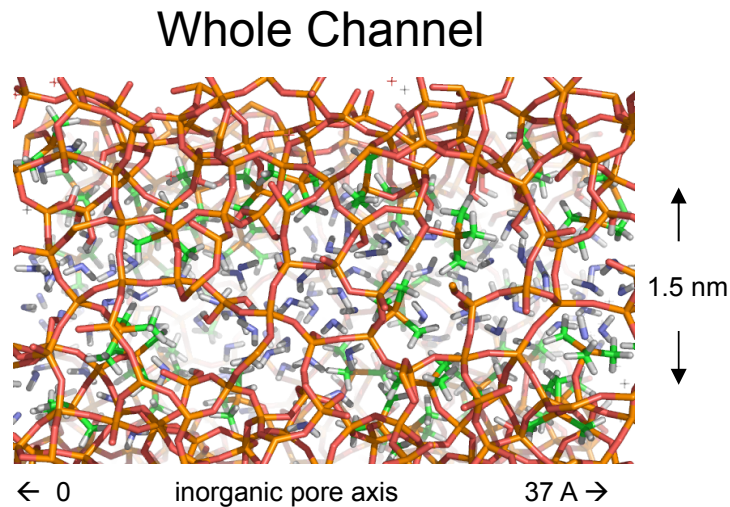
Subtle, challenging questions demand accurate studies:

—————> **Molecular Modeling + Molecular Synthesis**

Modeling Approach

- **Multi-scale modeling is essential**

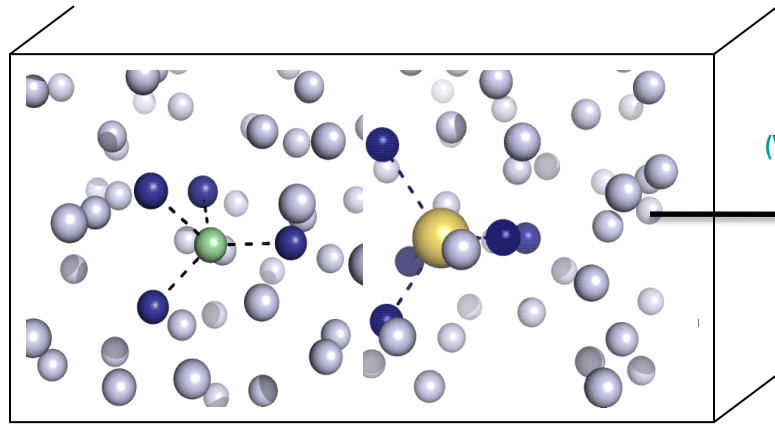
- vary structure, calculate transport & selective ion binding
- predict key structural features for desalination



- **Quantum (QM) approaches preferred**

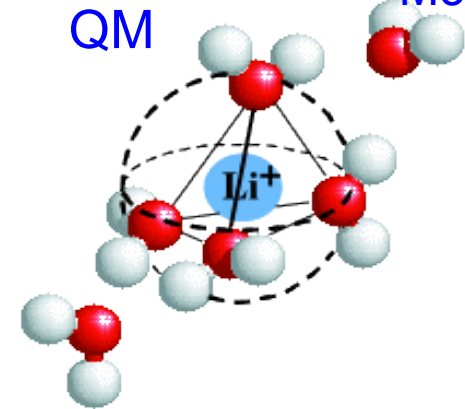
- need efficient route to thermo predictions
- need structural insights for pore design
- develop new theoretical framework

Structure vs Function Predictions:



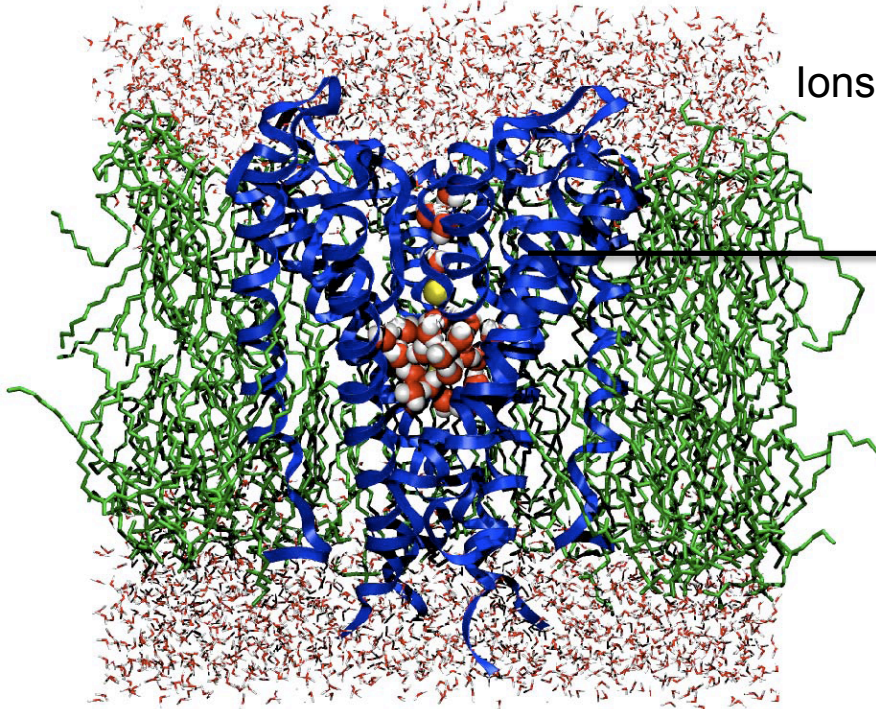
Whole System

Ions (aq)
(Varma & Rempe, 2007)

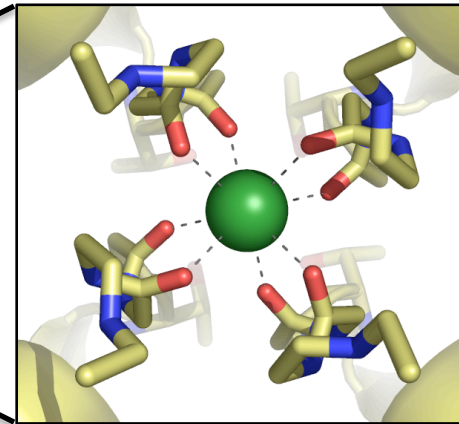


'Binding Site'

Coarser
Models



Ions in K⁺ channel

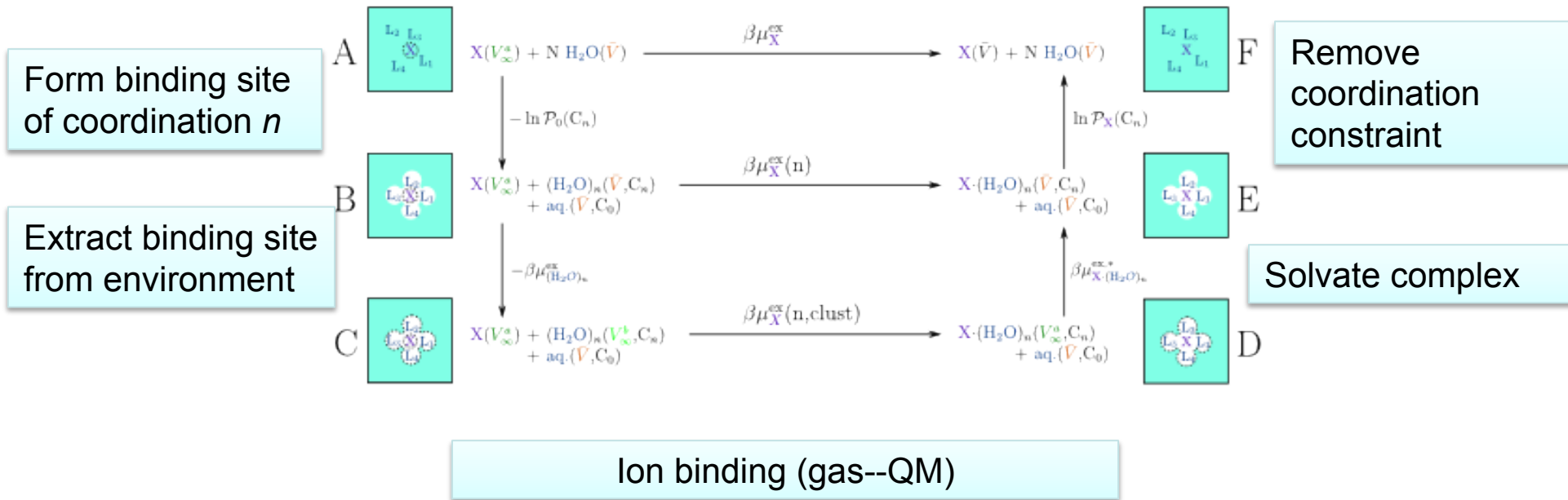


$$\beta\mu_A^{\text{ex}} = -\ln \left[\sum_{n \geq 0} K_{n,\Gamma}^{(0)} \left[\frac{\langle \langle e^{-\beta\Delta U_{AB_n}} \rangle \rangle_{0,\Gamma}}{\{ \langle \langle e^{-\beta\Delta U_B} \rangle \rangle_0 \}^n} \right] C_B^n \right]$$

Structure vs Function Predictions: Efficient QM + structural insights in inhomogeneous environments

Leung, Rempe et al. *JCTC* (2009)

Ion solvation

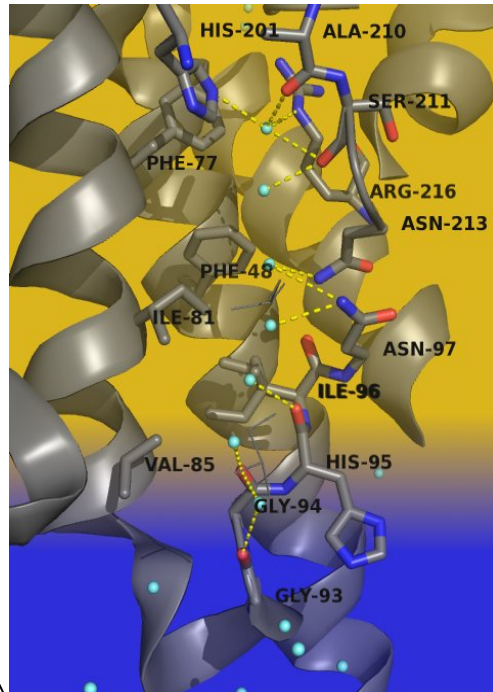
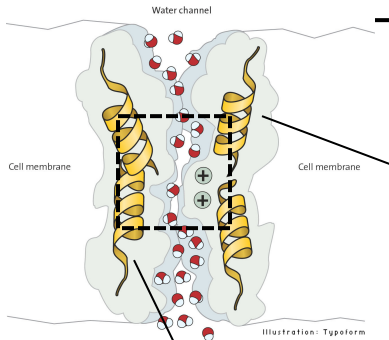


Varma & Rempe
Biophys J 2007
JACS 2008

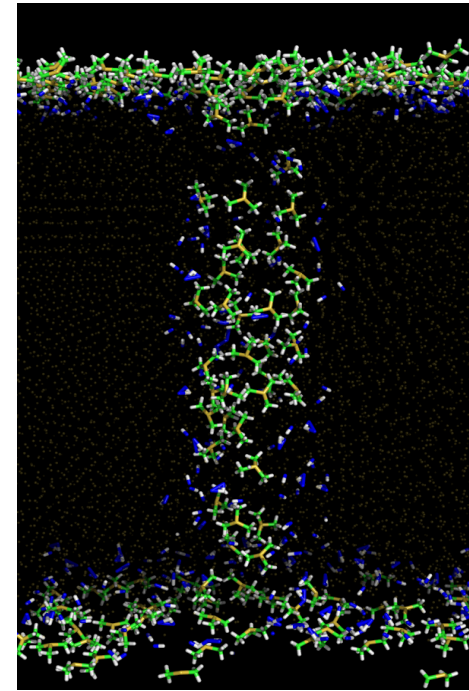
AsthaGiri, Rempe, Varma, et al.
Chem Phys Lett (cover) 2010

Rogers & Rempe *JACS* 2011
(submitted)

Key structural features for Fast water transport & ion rejection



**Bio water channel
(crystal structure)**
(www.nobelprize.org)

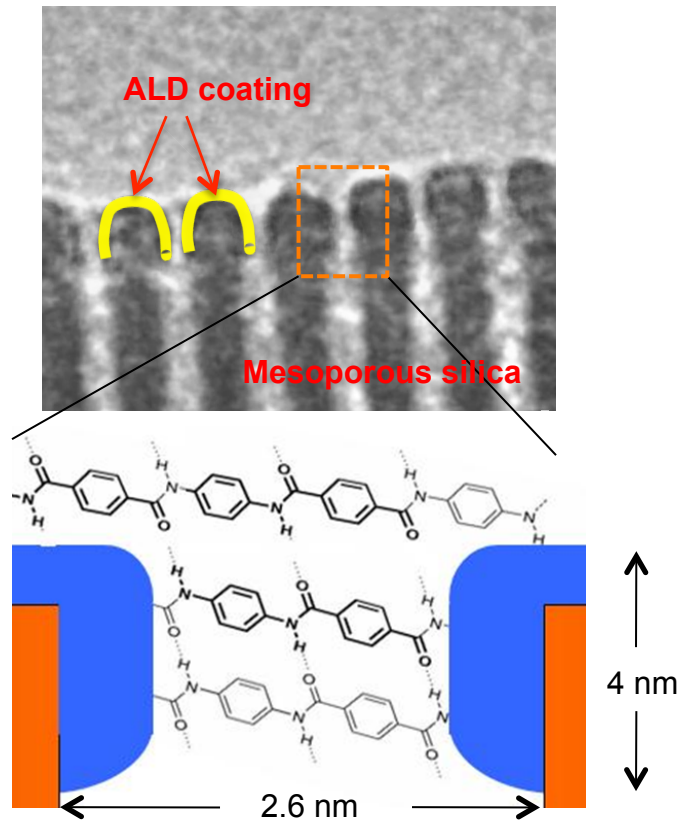


**Model inorganic pore
(simulation results)**
([Leung, Rempe et al Phys Rev. Lett 2006](#))

- narrow passageway
- repulsive hydrophobic walls (**rings**)
- staircase of stabilizing dipoles
(**C=O**, **N-H**)
- no symmetric dipole clusters

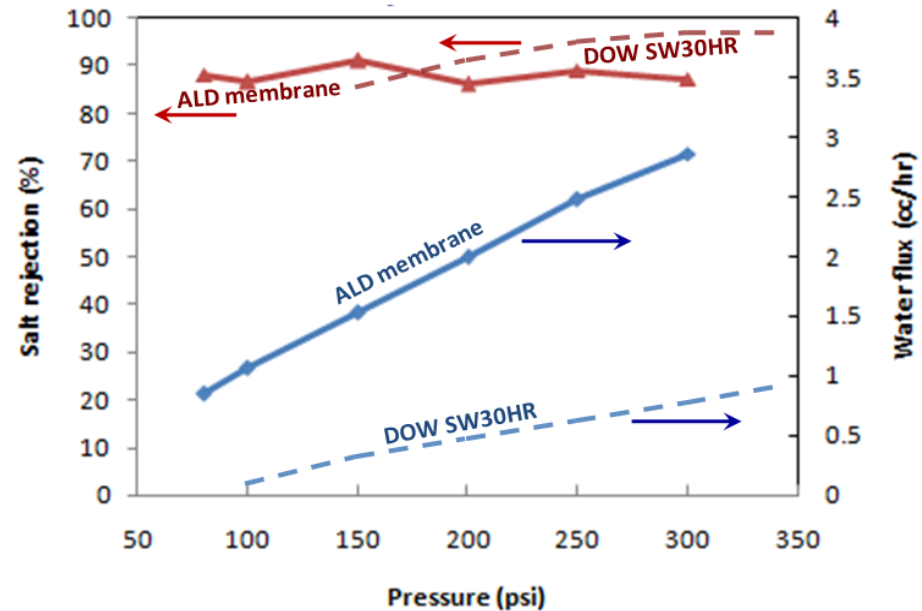
- >1 nm stabilizes ions
- hydrophobic walls destabilize ions, but immobilize waters
- symmetric dense dipoles bind cations **or** anions

Atomic-layer deposition of polypeptides: Translates key designs & realizes higher desal efficiency



- C=O, N-H dipoles stabilize water
- **hydrophobic** rings prevent sticking
- **no** symmetric dipole clusters for ions
- **narrow** passageway excludes hydrated ions

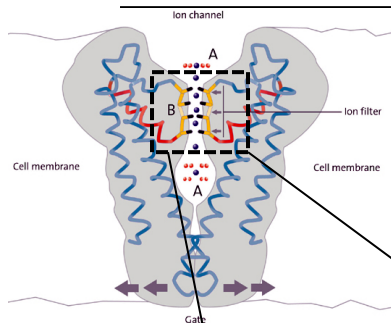
Biomimetic (ALD) vs DOW



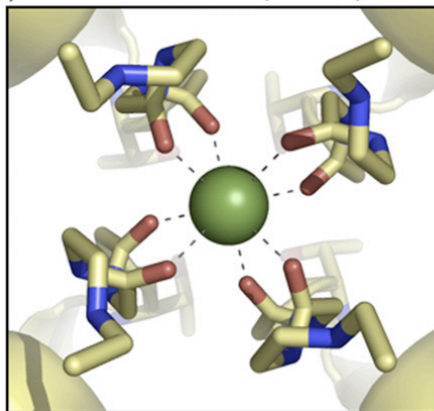
- higher flux at low applied pressure
- biomimetic design more **efficient**

Nature Materials Letts (in prep)
Provisional Patent #SD-1175
Award for Excellence, LDRD (2010)

Mechanisms of Selective Ion Transport in Biological Pores: K^+ vs Na^+

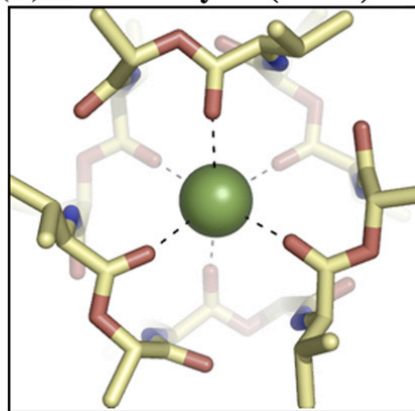


(a) **K-Channel (8-fold)**

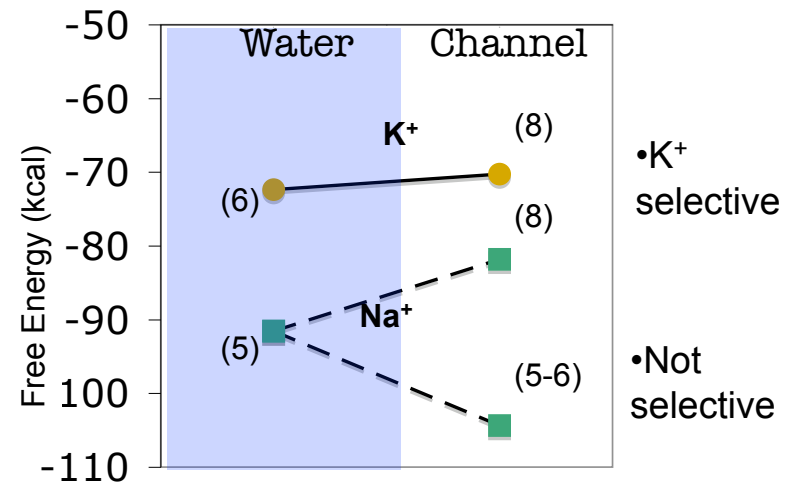


1) Over-coordinated binding sites tuned by surrounds

(b) **Valinomycin (6-fold)**



2) Specific cavity size in binding site

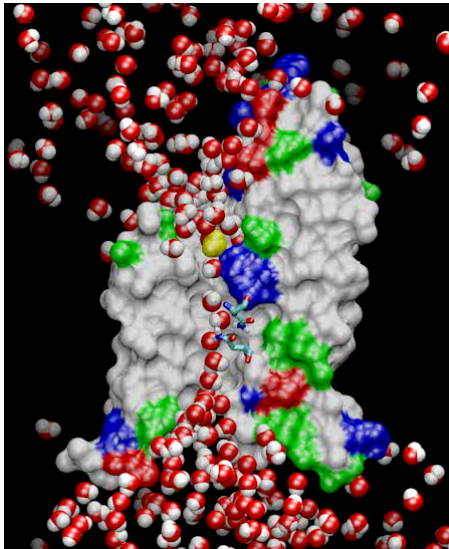


Biophys J (2007)
J Mol Bio (2008)
J Am Chem Soc (2008)
J General Physiology (2011)

Subtle structure-function relationships resolved by simulation & verified by experiments. **Can we translate to inorganic pores?**

Computational Materials Science for Desalination Membrane Design

Natural Water Channel



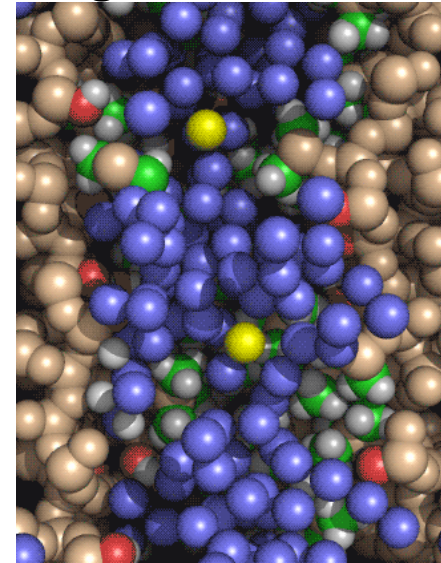
(Tajkhorshid & co)

Bio mechanisms



Engineering solutions

Inorganic Water Channel



(Desal Team, Sandia)

- Solve important material design problems by understanding & mimicking nature:
 - **Water-Energy** (mineral water, efficiently)
 - **Energy-BioBatteries** (charge separation, fast, selective transport)

Biology ↔ **inorganic nanostructures**
Quantum modeling ↔ **experiments**

Acknowledgements



- **Funding**

1. DOE: Sandia's Water Desalination Program
2. DOE: Sandia's LDRD program (ECIS)
3. NIH: National Nanomedicine Center

- **Compute time (~ 300,000 hours cpu)**

1. Sandia Computing: Thunderbird, Red Sky
2. National Center of Supercomputing Applications (NCSA), UIUC

- **Collaborative Teams of Sandia & UNM Staff, Postdocs, and Students**

PI: Susan Rempe

- Jeff Brinker
- Kevin Leung
- Ying-Bing Jiang (UNM postdoc → UNM)
- David Rogers (postdoc)
- Shaorong Yang (UNM postdoc → CNM)
- Seema Singh (UNM postdoc → SNL)
- Dubravko Sabo (postdoc → NYU)
- Sameer Varma (postdoc → IIT)
- Chris Lorenz (postdoc → King's College)
- Caroline Rempe (UNM student)
- Todd Alam
- Peter Feibelman
- Zhu Chen (UNM grad student)
- Tom Mayer (project manager)
- John Merson (project manager)

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