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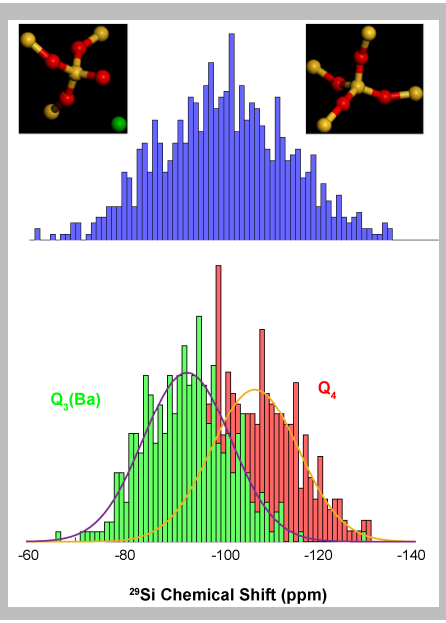

Connecting NMR Spectroscopy Results and MD Simulations of Barium-Silicate Glasses

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Sandia National Laboratories, Albuquerque, NM 87185

Glass and Optical Materials Division Meeting
Madison WI
May 24th, 2016

Sandia National Laboratories

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U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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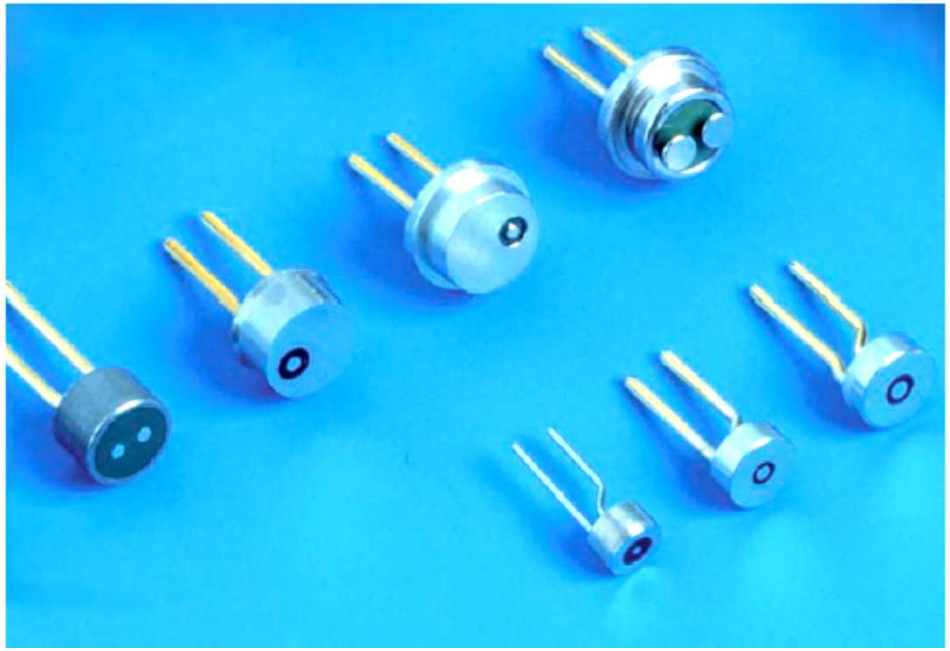
Glass is Used to Bond/Join Materials Sandia's Interest

Glass-Bonding/Joining Applications

- **Glass-Bonded Composites**
  - Glass bonded alumina
  - Low temperature co-fired ceramic (LTCC) electronic packaging
- **Seals**
  - Hermetic glass to metal (Gtm) seals
    - Air bag motors
    - Medical implants
    - Microelectronics
  - Energy Conversion
    - Solid oxide fuel cells (SOFCs)
    - Concentrated solar

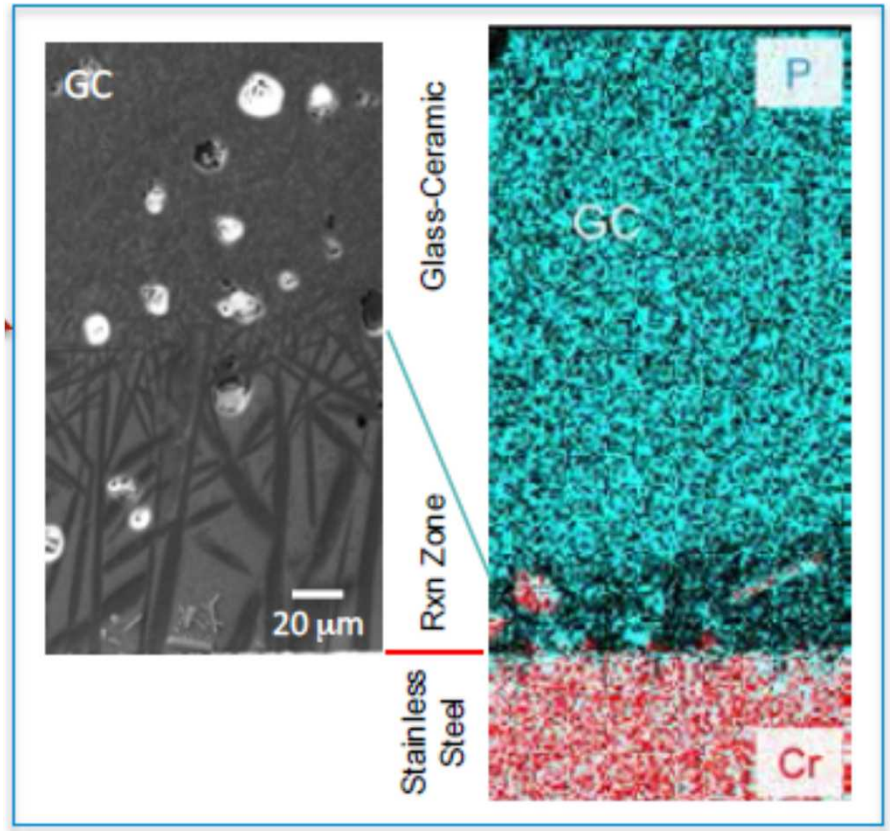


Filled Glass Composite (FGCs)
Glass Processability with Properties of a Ceramic

Glass
- Processability
- Materials Compatibility
- Low/Fixed CTE
- Low Toughness/Crack Tolerance

Glass-Ceramic (GC)
- Toughness/Crack Tolerance
- High/Tunable CTE
- Process Sensitivity
- Reactivity/Instability

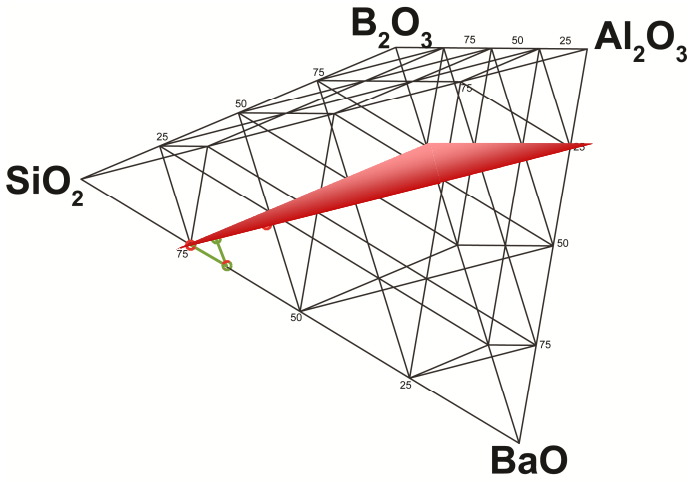
Filled Glass Composite (FGC)
- Process Robustness
- Toughness/Crack Tolerance
- Low to High/Tunable CTE
- Chemical/Structural Stability

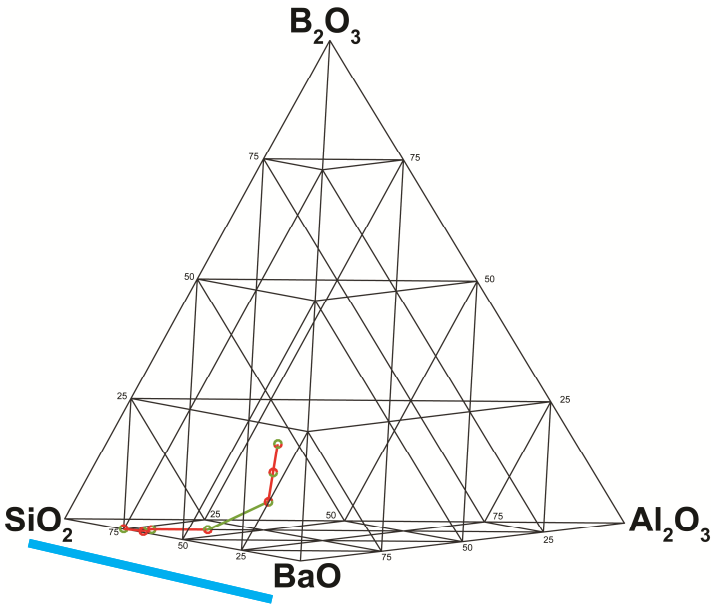


Related Sandia Presentations

Kevin Strong May 24th 11 AM: "Characterizing and Predicting Stress and Structural Relaxation in Glass"

Characterization and Modeling of Chemistry-Structure-Property Relationships



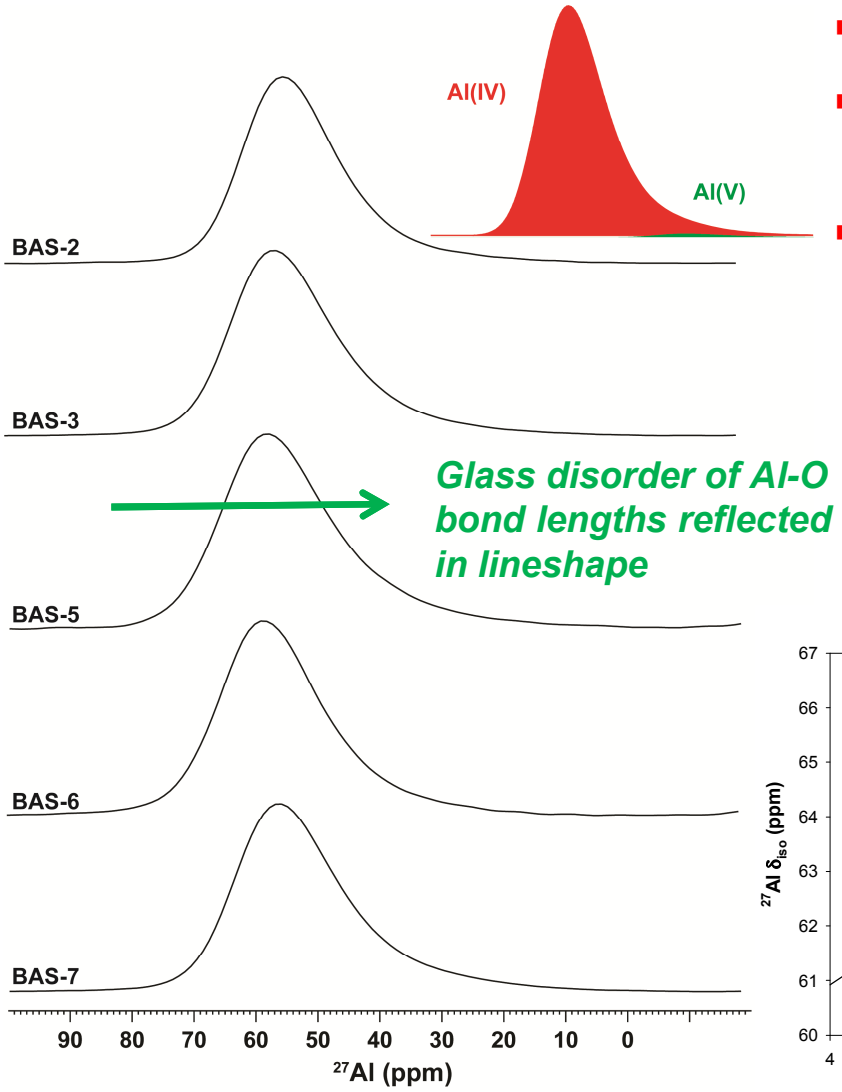


Initial Studies on Simple Boron-Aluminum Modified Barium-Silica Glass

$xBaO$-yAl_2O_3-zB_2O_3-$(100-x-y-z)SiO_2$

Sample	BaO	SiO_2	Al_2O_3	B_2O_3
BAS-1	25.0	75.0	0.0	0.0
BAS-8	33.3	66.7	0.0	0.0
BAS-3	25.0	60.0	15.0	0.0
BAS-5	25.0	46.0	23.0	6.0
BAS-6	25.0	42.0	21.0	12.0
BAS-7	25.0	38.0	19.0	18.0

Characterization – ^{27}Al MAS NMR

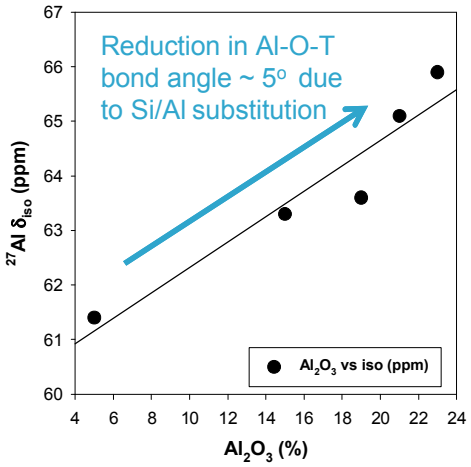


- Predominantly Al^{IV} coordination (> 98%).
- Distribution of local environments reflected in ^{27}Al EFG tensor.
- No significant change in local coordination with variation in modifier and network former concentration.

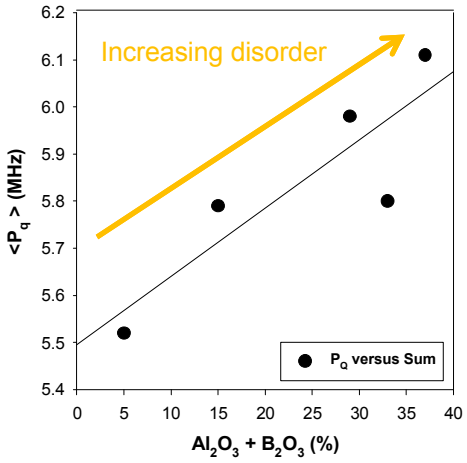
Czjzek Probability Distribution Function

$$P_Q(\nu_Q,\eta)=\frac{1}{\sqrt{2\pi\sigma^5}}\nu_Q^4\eta\left(1-\frac{\eta^2}{9}\right)\exp\left[-\frac{\nu_Q^2\left(1+\frac{\eta^2}{3}\right)}{2\sigma^2}\right]$$

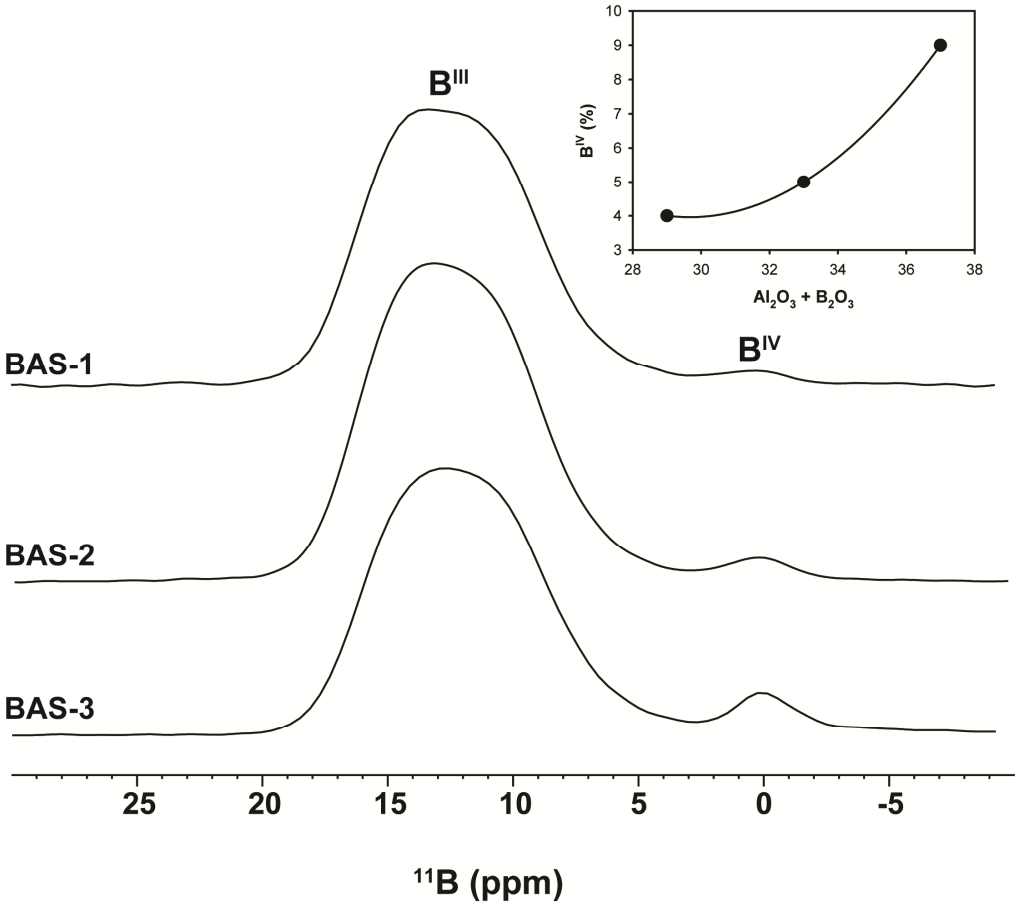
^{27}Al Chemical Shift Variation



Al Quadrupolar Coupling Versus Network Former Concentration

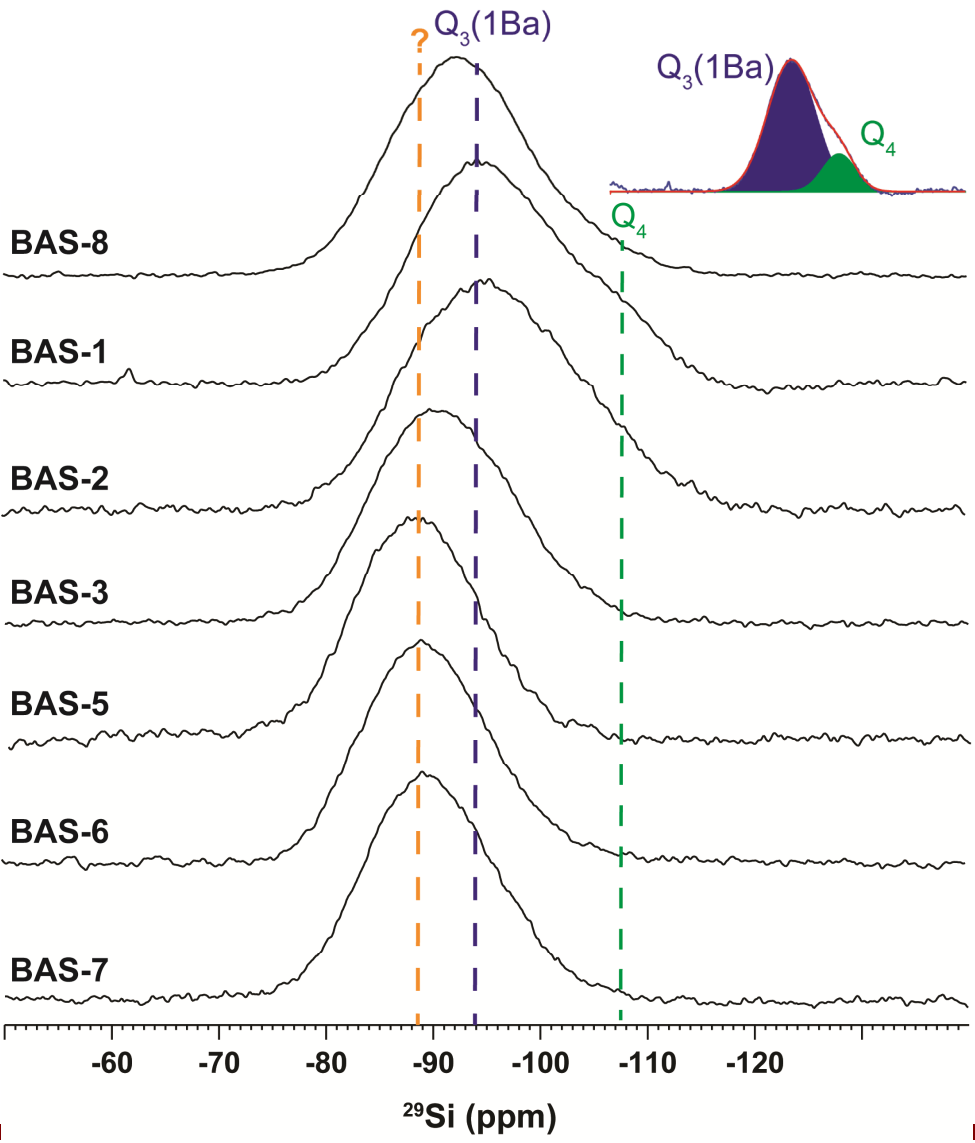


Characterization – ^{11}B MAS NMR



- Trigonal B^{III} coordination (> 90%).
- Slight increase of BIV with increasing B_2O_3 concentration.
- No significant change in local coordination with variation in modifier and network former concentration.

Characterization – ^{29}Si MAS MMR

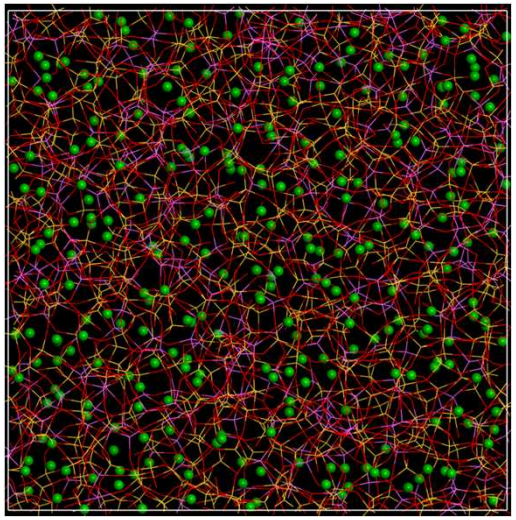


- Changes in the local SiO_4 coordiantion with different Qn speciation.
- Not well resolved and a gradual shift in diso with increasing $A_{l2}O_3$+B_2O_3 concentrations.
- Al and B in 2nd coordination sphere producing a chemical shift change.
- Low resolution seen in other Ba and Ca silicate glasses.

Motivation *for to incorporate results from MD simulation to understand and extract some of these trends.*

Connecting MD Simulations and NMR

BAS-3

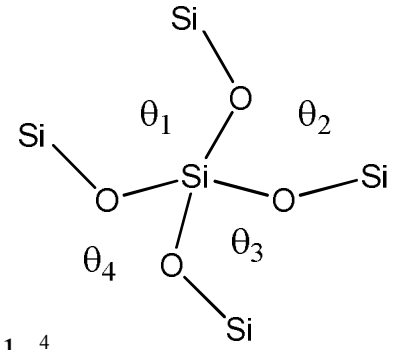


- Goal is to calculate NMR parameters from MD simulations.
- Experimental test of MD simulations.
- Allows assignment of NMR results for different nuclei.
- Can ask question about *specific* next nearest neighbor interaction (Al-O-B, Al-O-Si).
- Explore unique conditions and predict NMR (experimental changes?).
- Possibility to provide feedback for development of force-fields. [1]

[1] Gambuzzi *et al.* Geochimica Cosmochimica Acta (2014) 125, 170-185. Combined CASTEP feedback for MD simulations of Ca-SiO_2-Al_2O_3 glasses.

Approaches: Empirical NMR Correlations

- Prediction of chemical shifts based on local structural parameters: bond lengths, bond order, bond angles, coordination number (CN).
- Original correlation developed from crystalline model compounds.
- Example include ^{17}O, ^{23}Na, ^{29}Si, ^{27}Al NMR chemical shift calculations.
- ^{29}Si NMR correlations well developed (many different examples), and used to extract Bond Angle Distributions (BAD) in amorphous SiO_2.



$$\delta\left(^{29}Si\right) = \frac{1}{4}\sum_{n=1}^{4} F_{\alpha c}(\theta_n)$$

$$F_{\alpha c}(\theta) = -93.12 + 8.66\cos\theta - 22.27\cos 2\theta$$

Mauri *et al.* (2000) Phys. Rev. B, 62, R4786

$$\delta_{TMS} = \frac{1}{4}\sum_{n=1}^{4} F_{b_n}(\theta_n), \quad with \quad F_{b_n=B}(\theta) \text{ or } F_{b_n=Si}(\theta)$$

$$F_B(\theta) = -42.63 - 24.81\cos\theta - 18.20\cos 2\theta$$

$$F_{Si}(\theta) = -31.21 - 10.05\cos\theta - 11.52\cos 2\theta$$

Soleilhavoup et al. (2010) Mag. Res. Chem., 48, S159-S170

- Many not expandable to different cation, CN, or Q_n!
- Require development of multiple correlations!

- **How do you treat the impact of low concentration species?**

- **Is it possible to develop a more empirical relationship?**

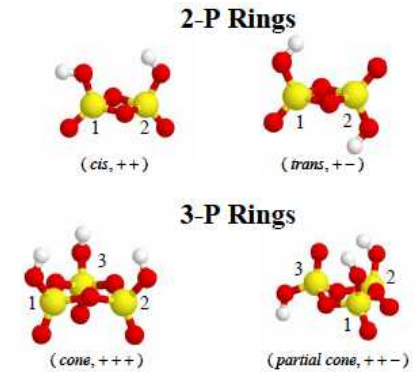
$$s_i = \left(\exp\left[\left(r_0 - r_i\right)/0.37\right]\right)$$

$$\Omega = \sum_{i=1}^{N}\left[s_i\left(1 - 3\cos^2\theta_i\right)/3R_i^3\right]\log D_i$$

$$\delta(^{29}\mathrm{Si}) = 701.6\Omega - 45.7$$

Sherrif et al. (1999) Eur. J. Mineral., 3, 751-768.

Approaches: Quantum Calculations - Clusters



T. M. Alam "Ab Initio Calculations of ^{31}P NMR Chemical Shielding Anisotropy Tensors in Phosphates: Variations Due to Ring Formation", Int. J. Mol. Sci., 3, 888-906 (2002).

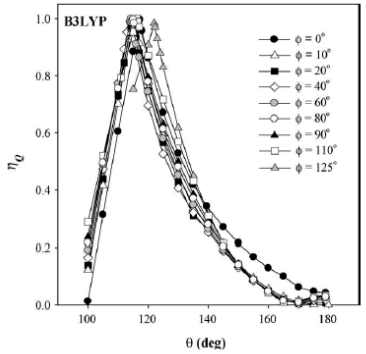
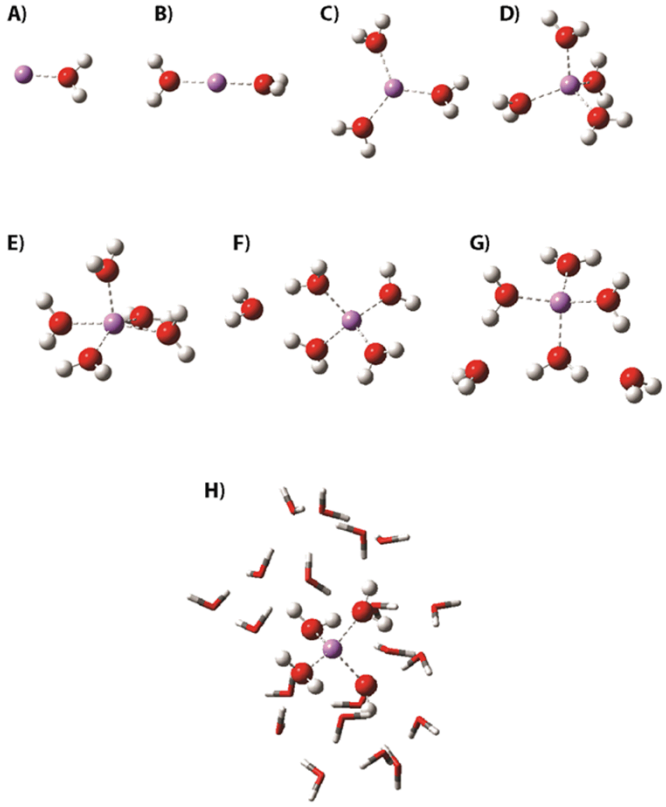


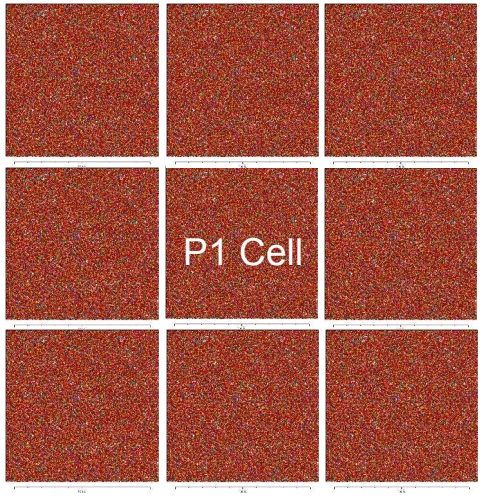
Fig. 3. Variation of the ^{17}O EFG η_Q as a function of the P–O_B–P bond angle (θ) for the bridging oxygen in the $H_4P_2O_7$ cluster are shown. The calculated values for different ϕ configurations are shown for the B3LYP level of theory (See Fig. 1 for definition of the angles).

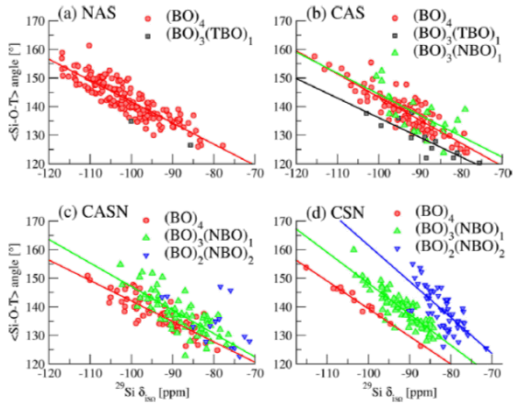
T. M. Alam and J. M. Segall, "Structural Perturbations on the Bridging Oxygen ^{17}O NMR EFG Parameters in Ultraphosphates: An Ab Initio Study", J. Molecular Structure, 674, 167-175 (2004).



T. M. Alam, D. Hart, S. L. B. Rempe, "Computing the ^{7}Li NMR Chemical Shielding of Hydrated Li^+ using Cluster Calculations and Time-Averaged Configurations from *ab initio* Molecular Dynamics Simulations", *Physical Chemistry Chemical Physics*, **13**, 13629-13637, (2011).

Approaches: GIPAW Calculations - Periodic





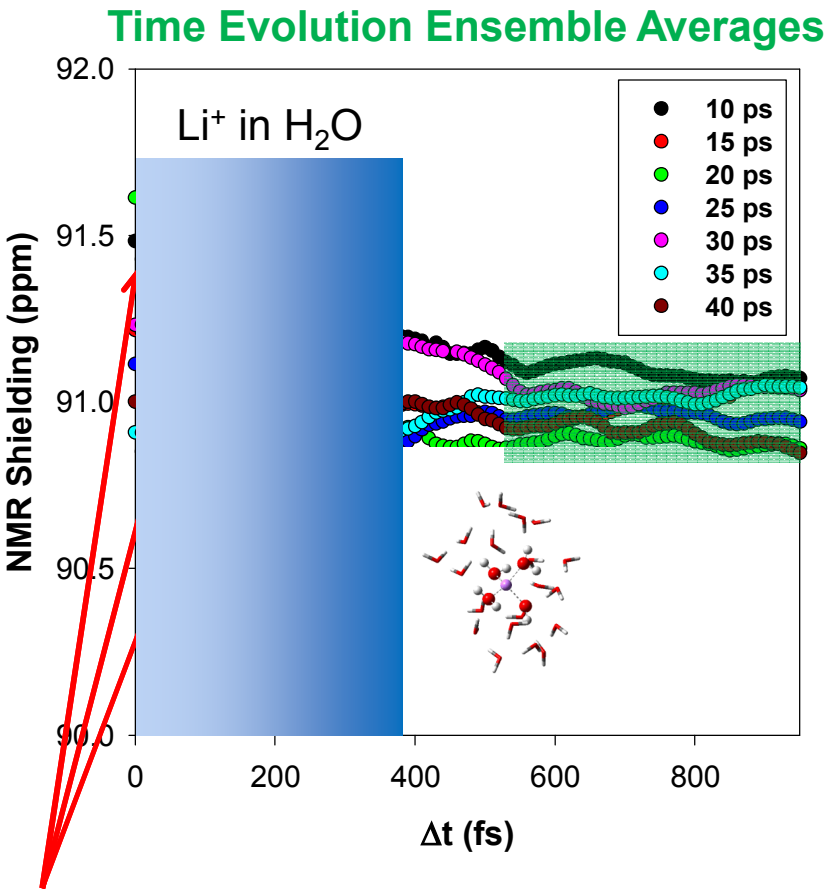
Gambuzzi et al. Geochimica Cosmochimica Acta (2014) 125, 170-185, 'Probing silicon and aluminum chemical environments in silicate and aluminosilicate glasses by solid state NMR spectroscopy and accurate first-principle calculations.

- **GIPAW** (Gauge Including Projector Augmented Wave) method allows direct calculation of NMR tensors in periodic systems. Really developed for crystalline materials – but can be extended to include primitive P1 cells like MD simulations.
- ***State of the art for NMR of glass simulations!*** No need for model systems, no needs for cluster extractions – direct quantum level calculations of ALL nuclei.
- Most commonly Implemented in CASTEP program ($$, UK).
- Computational expensive – as MD cell size **(limited)** increases calculation becomes very time consuming (impacts on averaging).
- More recent examples in glass use smaller P1 cells and develop empirical relationships….**future direction!**

Issues: Extraction of Average Chemical Shifts from MD

- Time and ensemble averaging over the configurations obtained during MD simulations can provide a more accurate result in calculation of the NMR chemical shift.
- Typically, need to average the NMR shielding over an "appropriate" time scale (auto correlation time) for the NMR observable.
- This time scale is NOT known *a priori.*
- NMR time scale is NOT the same as the decay time for the energy auto correlation function.
- May require thousands of calculations to simply determine the appropriate NMR time scale.
- Long term fluctuations may not be captured in a simple auto correlation averaging. This may not be an issue for small molecules, but could represent an issue for large complexes or surface adsorption.

T. M. Alam, D. Hart, S. L. B. Rempe, "Computing the ^{7}Li NMR Chemical Shielding of Hydrated Li^{+} using Cluster Calculations and Time-Averaged Configurations from *ab initio* Molecular Dynamics Simulations", *Physical Chemistry Chemical Physics*, **13**, 13629-13637, (2011).



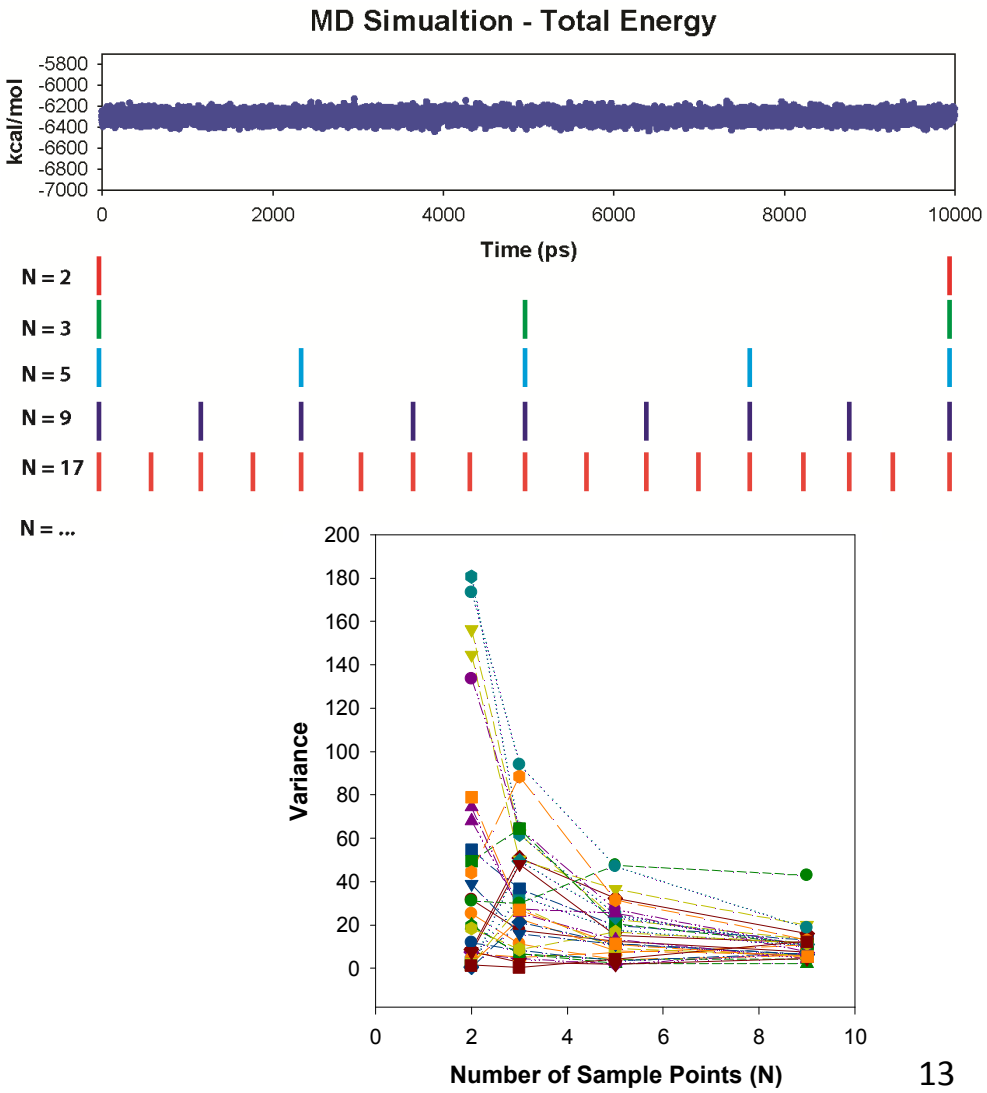
Even the ***ensemble*** averages (64 Li) vary on starting time slice!

Time period to approach local average chemical shift.

Finally converge on a similar NMR chemical shift.

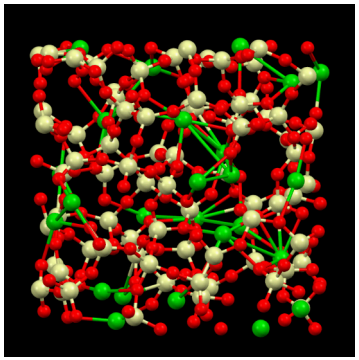
A Solution: Extraction of Chemical Shifts from MD Simulations

- Implemented a **"halfing" sampling method** to improve the speed and performance of the time and ensemble averaging of the NMR calculations.
- By monitoring the variation of the standard deviation it is possible to determine when enough sampling points have been averaged.
- Sample over the entire time series, incorporates longer term fluctuations.
- Continue to develop this interface to improve the speed and compatibility with MD simulations from different sources.
- **Still requires calculation from multiple time slices to obtain a representative chemical shift prediction.**
- **Need to consider computational speed limitations!**



Issues:
Calcualtion Time and Statstics

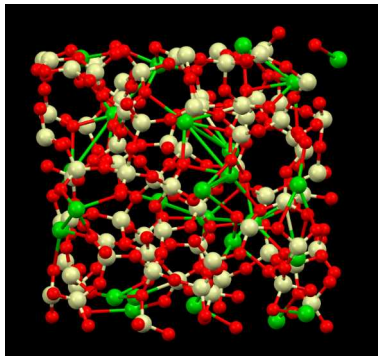
275 atoms



MD Snap Shot (Energy Relaxed)

Plane Wave Periodic Structure Calculation

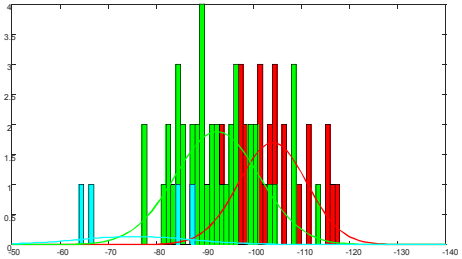
~ 1 week calculation



Geometry Relaxed

Empirical NMR Shielding Calculation

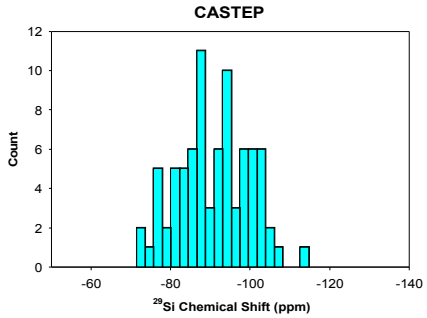
(~ 1 s)



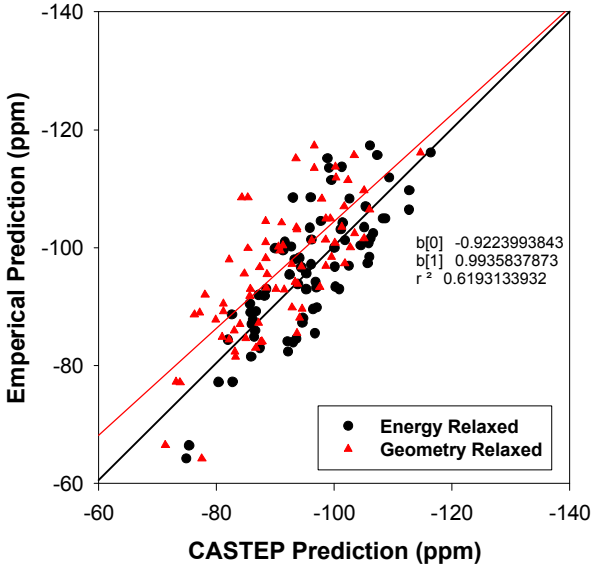
GIPAW CASTEP NMR Shielding Calculation

(~ 1 day)

75 Si atoms

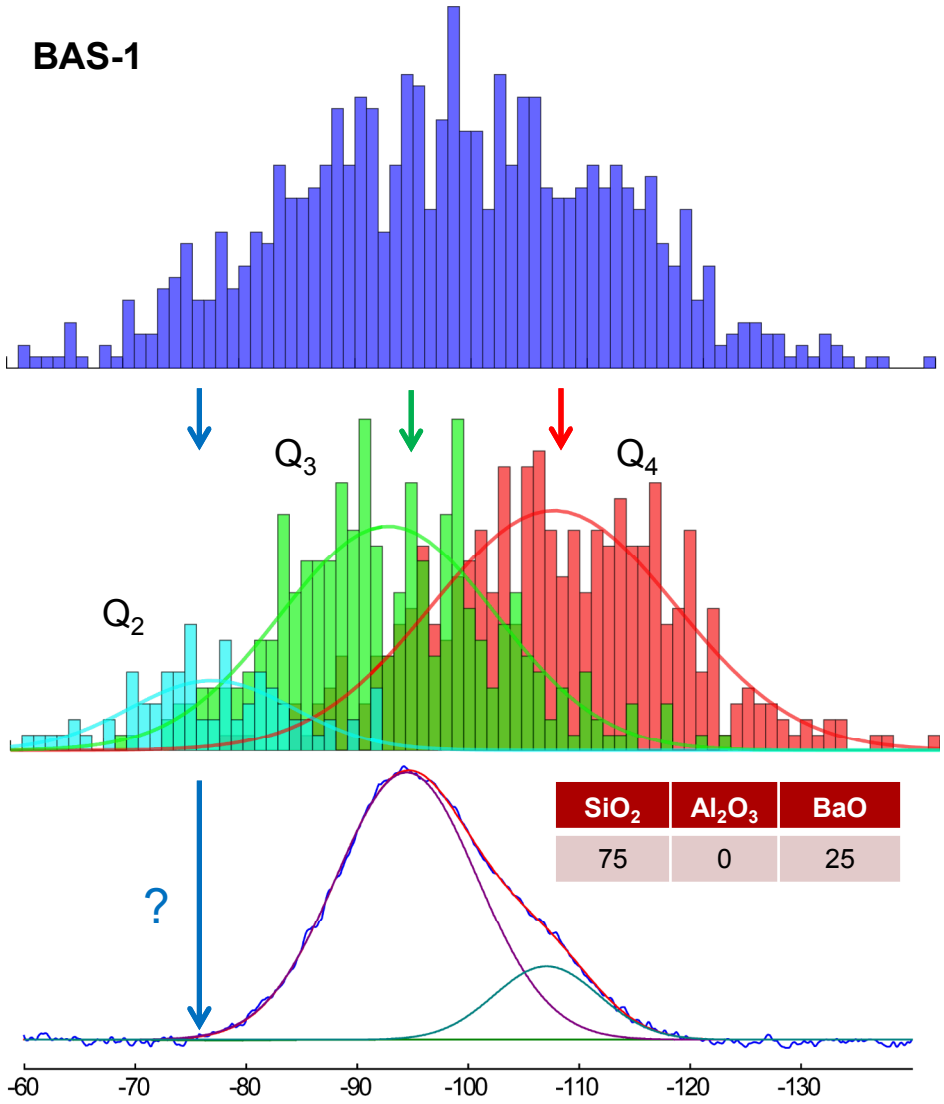


Prediction Correlations



- Larger size MD snap shot computationally demanding. If scales as **~N^2 a 3000** atom calculation would require ***119 days for NMR calculation and 119 weeks*** for geometry relaxed calculation!
- ***Larger size is required for improved statistics.***
- What can be modified in empirical relationship to improve correlation?
- Sampling scheme for MD would also improve statistics.

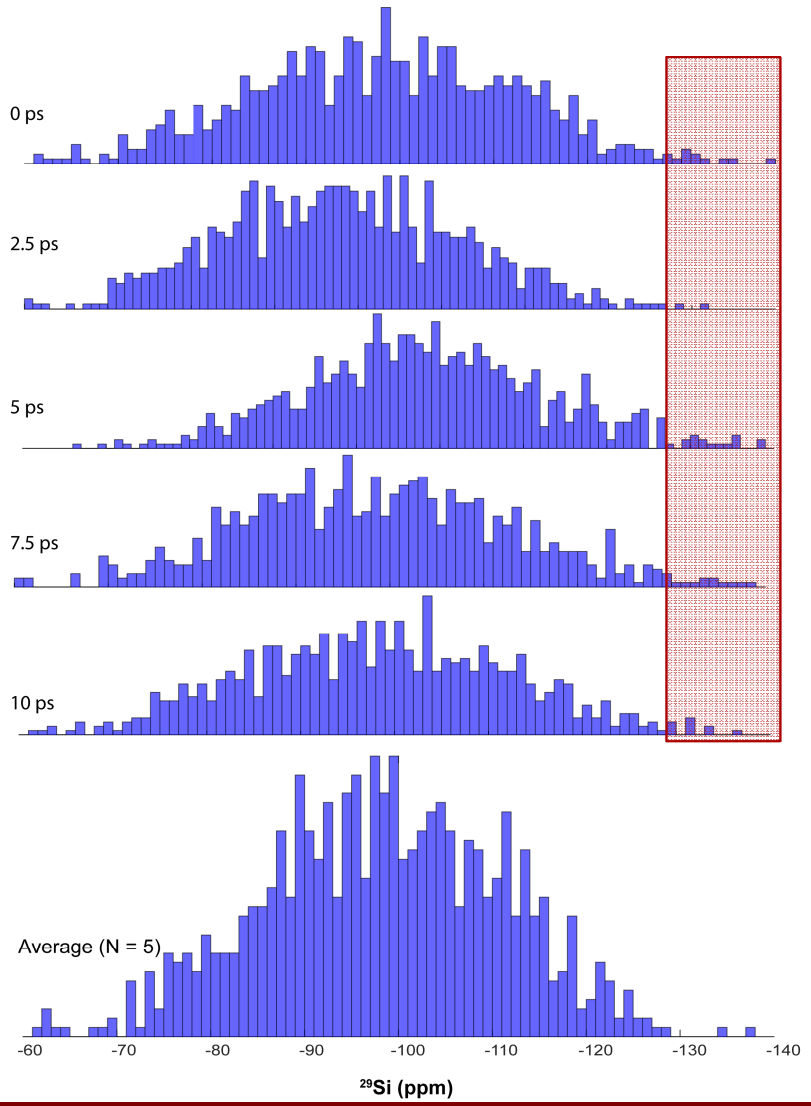
^{29}Si NMR Shift Calcualtions: Empirical

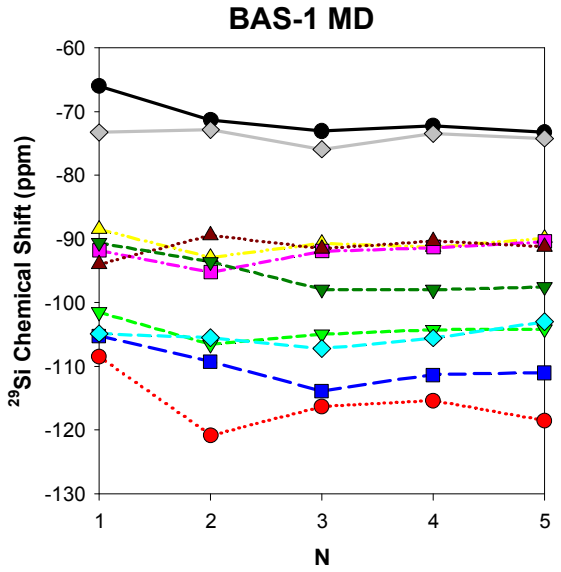


- Veryfast! (~1s for 3000 atoms).
- The mean chemical shift for each Q_n species is correctly predicted.
- Allows for more reliable deconvolution for non-standard compositions.
- The MD simulation over estimates Q_2 concentration, which is essentially not observed in the experimental NMR.
- MD simulation appears to predict a larger distribution on Q_n resonances than observed experimentally.
- (Ongoing) Useful in understanding and deconvolute the ^{29}Si chemical shifts with ^{27}Al and ^{11}B added (not clearly resolved in the ^{29}Si NMR line shape).

Sherrif et al. (1999) Eur. J. Mineral., 3, 751-768.

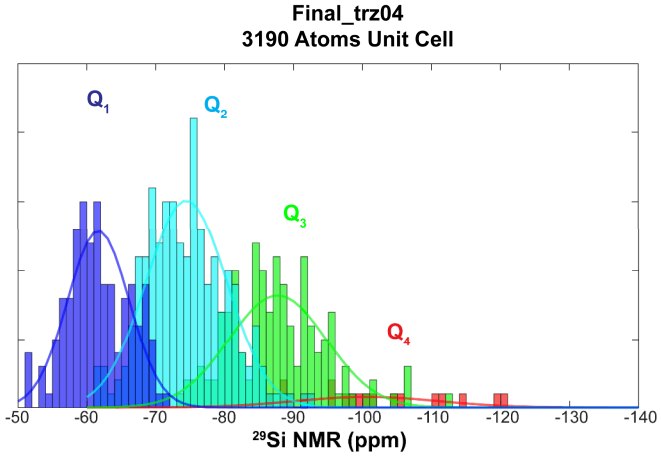
Averaging Over MD Time Series

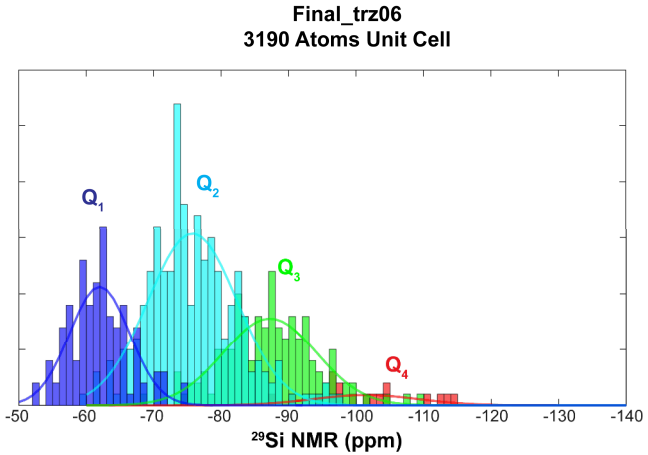


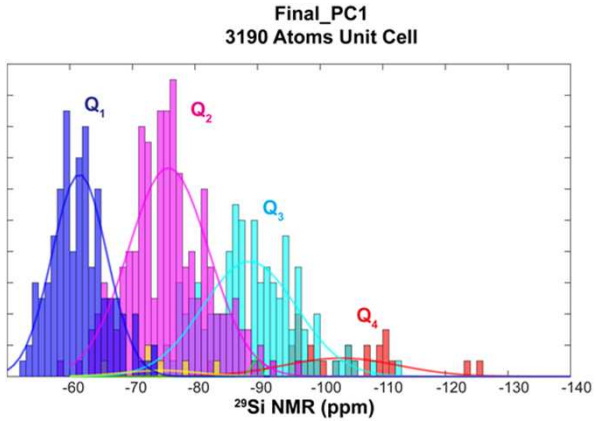


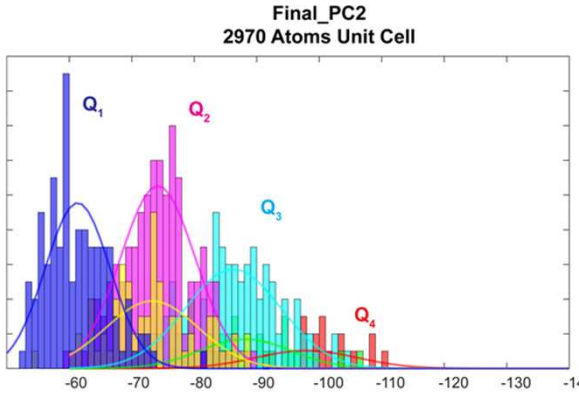
- Time averaging removes chemical shift of strained geometries.
- Slight reduction in distribution width for each Q_n species. Needs more averaging?
- Speed of empirical calculation actually allows for larger averaging set. Could be done over entire time series. (Future effort).

Variation with Cation Compositions



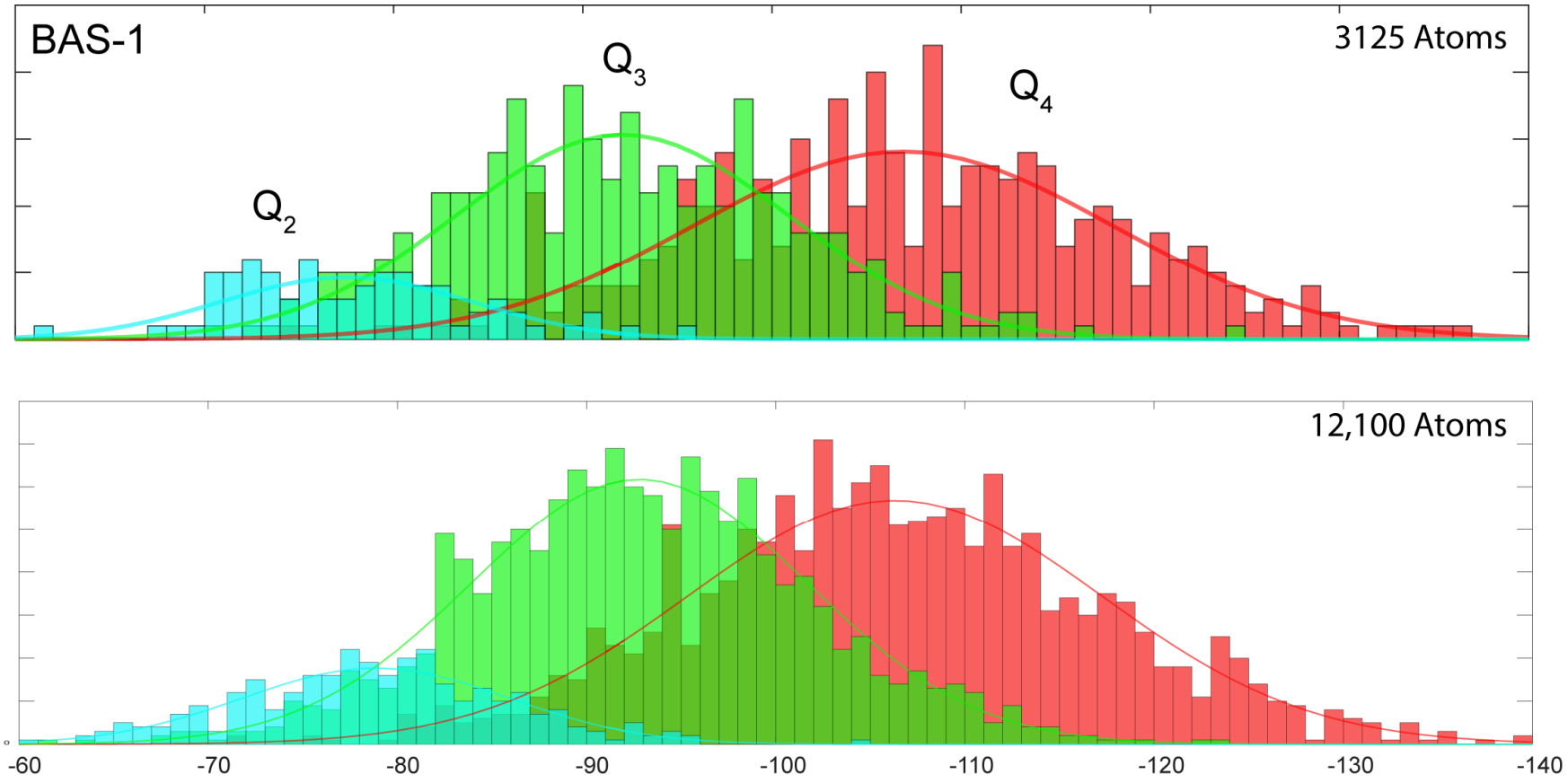




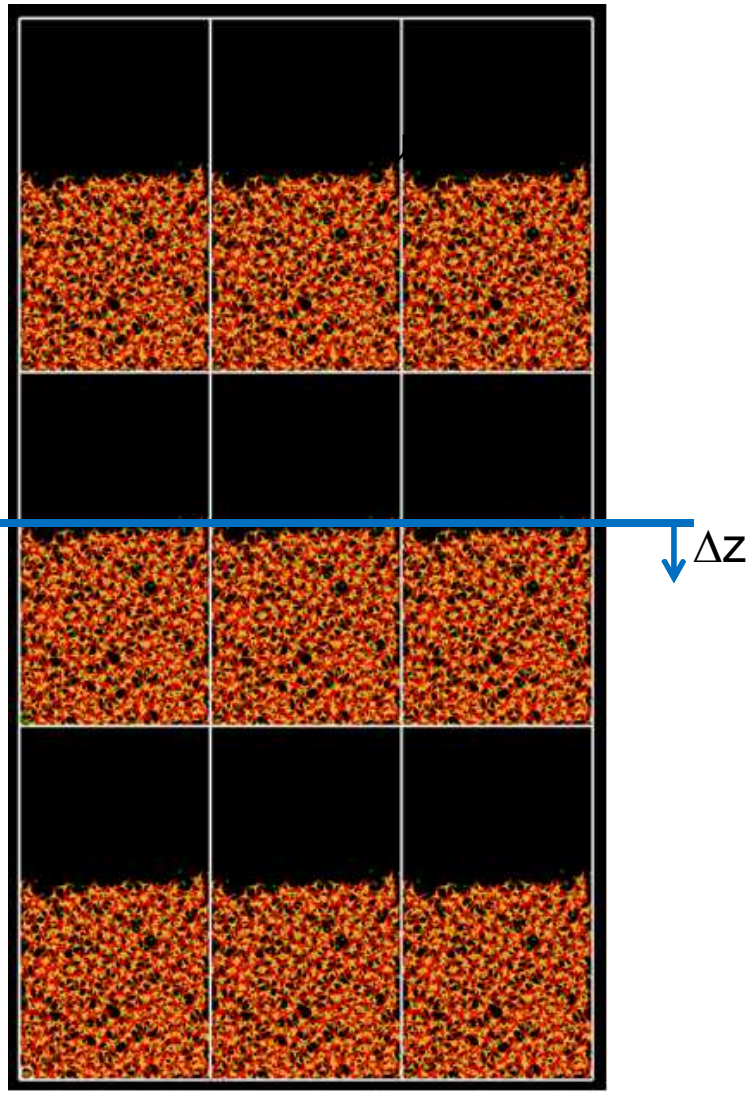


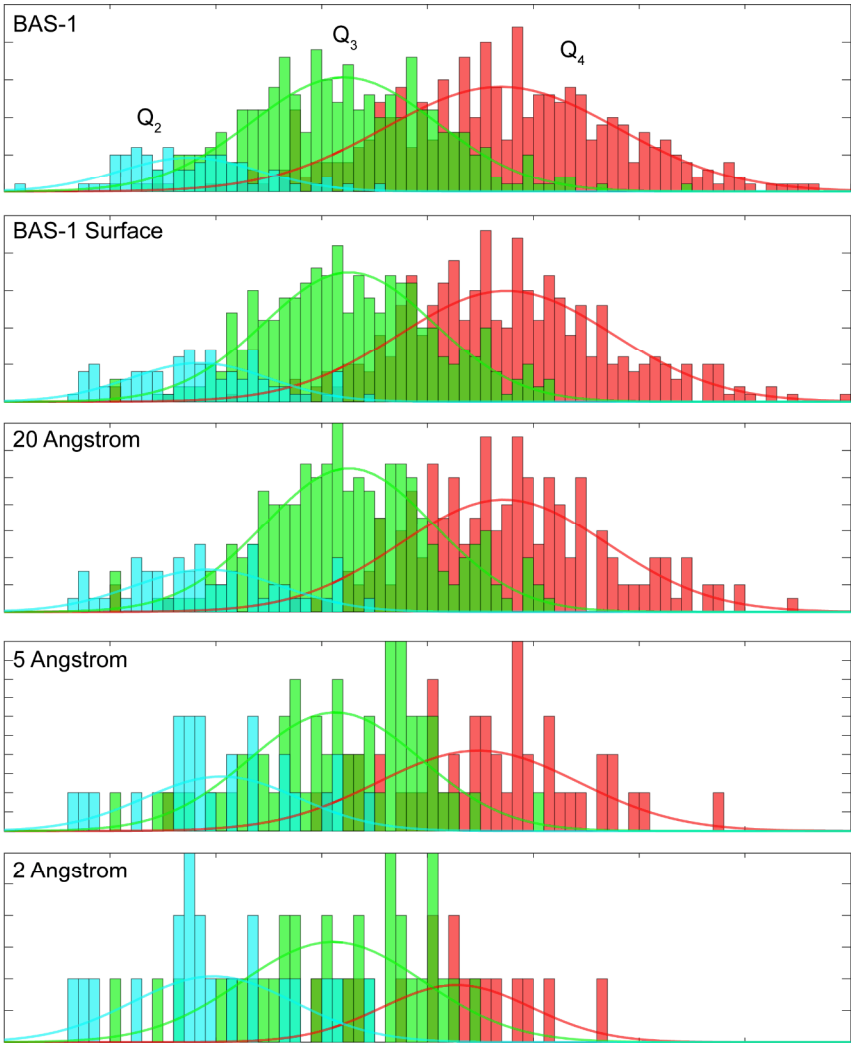
	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O
BAS-1	75	0	25	0	0	0	0
PC1	50	0	10	0	0	40	0
PC2	50	0	30	0	0	20	0
TRZ04	50		10			10	30
TRZ06	50		10			30	10

How Large Can We Go?

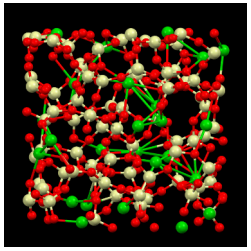


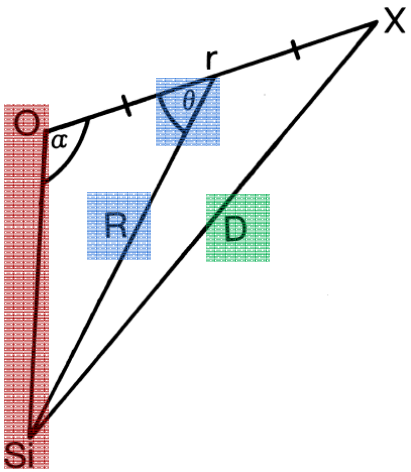
Simulation of Vacuum Surface

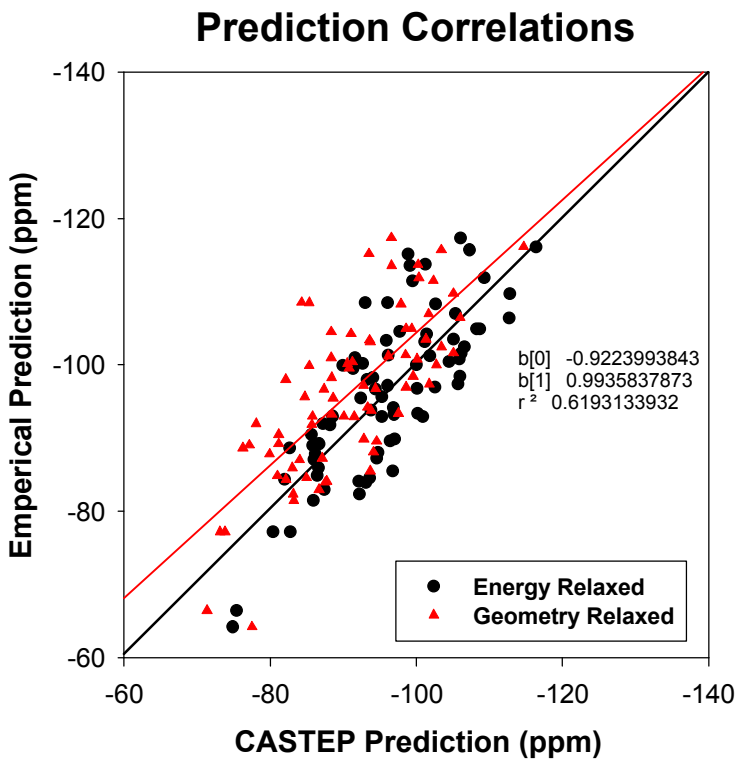




Empirical Correlations







$$s_i = \left(\exp\left[\left(r_0 - r_i\right)/0.37\right]\right)$$

$$\Omega = \sum_{i=1}^{N}\left[s_i\left(1-3\cos^2\theta_i\right)/3R_i^3\right]\log D_i$$

$$\delta(^{29}\mathrm{Si}) = 701.6\Omega - 45.7$$

Sherrif et al. (1999) Eur. J. Mineral., 3, 751-768.

- **Larger size MD snap shot computationally demanding. If scales as ~N^2 a 3000 atom calculation would require 119 days for NMR calculation and 119 weeks for geometry relaxed calculation!**
- **Larger size is required for improved statistics.**
- **What can be modified in these empirical relationships to improve correlation?**

Conclusions and Future Efforts

- **Have developed code for the empirical calculation of ^{29}Si NMR chemical shifts from MD simulation structures.**
- **Allowed for improved NMR assignments, and identification of unique signatures.**
- **Reveals some discrepancies between MD predicted structures and experimental NMR results.**
- **Demonstrated equivalence with GIPAW plane wave periodic calculations.**
- **Have been able to address very generalized compositions and larger sizes!**
- **Continue improvements of empirical relationships based on GIPAW simulations.**

Acknowledgements

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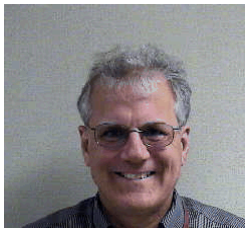
Todd Zeitler (Sandia) – All things MD

Kevin Ewsuk (Sandia) – Program Lead



Thanks for your attention…….

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