

# Exploring the Role of Phosphate Structural Distortions on the Sodium Jump Dynamics in NASICON Phases

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Photograph by Sarah K. McIntyre

## INTRODUCTION

Sodium ion conducting solids continue to be explored for future electrochemical energy storage applications. In particular, Sodium Superionic Conductor (NASICON) materials are being actively pursued due to their known high ionic conductivity. The conductivity of NASICON-type materials is directly proportional to the Na<sup>+</sup> carrier mobility (Na jumps), and is typically described as being controlled by structural restrictions along the conduction pathway, which is commonly referred to as the "bottleneck" region. It has been shown that for NASICON-type structures containing cations of different sizes, the PO<sub>4</sub> tetrahedra that bridge/link the ZrO<sub>6</sub> octahedra are distorted. These local PO<sub>4</sub> environments and distortions and not always clearly identified using XRD, yet can influence the Na cation conductivity. It has been suggested that while XRD may show an increase in the size of the bottleneck opening as a function of NASICON composition, local distortions can counteract this by modulating the Na<sup>+</sup> jump pathway. Experimental techniques that can measure both the local molecular-level jump-motions and the local environments would provide additional insight into the role of structural distortions and phase impurities on the observed conductivity in NASICON materials. In this presentation, the multiple sodium and phosphate environments and structural distortions produced by different sol-gel syntheses and processing conditions were evaluated using <sup>29</sup>Si, <sup>23</sup>Na and <sup>31</sup>P magic angle spinning (MAS) NMR spectroscopy. It was observed that the primary local structural distortion occurs in the PO<sub>4</sub> tetrahedra, while the SiO<sub>4</sub> tetrahedra showed relatively little variation. The impact of PO<sub>4</sub> distortions on the local Na dynamics were probed by variable temperature solid state <sup>23</sup>Na NMR spectroscopy, where the temperature dependence of the <sup>23</sup>Na spin-lattice relaxation rates (R1 = 1/T<sub>1</sub>) allowed the Na jump rates between different cation sites in lattice and the corresponding activation energies to be determined. It was found that for phases near the optimal conductive Na<sub>3</sub>Zr<sub>2</sub>PSi<sub>2</sub>O<sub>12</sub> composition that slight changes in the synthesis and processing conditions produced large variations in the phosphate speciation and degree of structural distortions. These differences in the phosphate environment were shown to ultimately impact the Na jump dynamics. The NMR based Na<sup>+</sup> jump rates are discussed with respect to conductivity results.

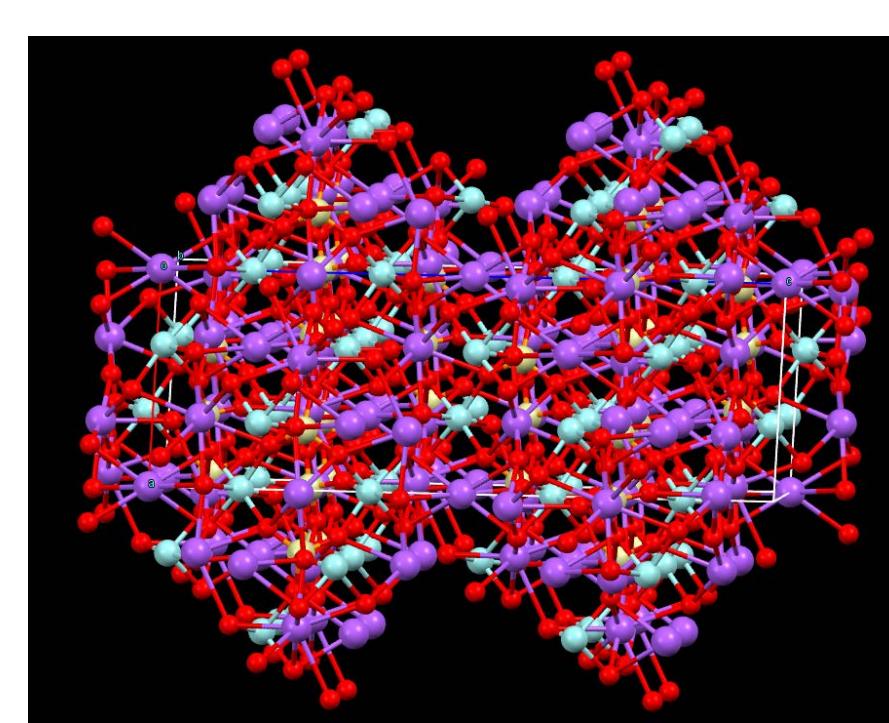
## MATERIALS

- The nominal Na<sub>3.0</sub>Zr<sub>2</sub>PSi<sub>2</sub>O<sub>12</sub> NASICON materials were prepared using a sol-gel procedure utilizing zirconium butoxide, tetraethyl orthosilicate, sodium phosphate tribasic and sodium acetate,
- The resulting gel was calcined at 800 °C.
- To address Na composition impact a 1% and 2% excess material (i.e. Na<sub>3.03</sub> and Na<sub>3.06</sub>) were also prepared.
- To address processing temperature/duration effects the base material was further treated at 1000, 1100 or 1250 °C for 12 or 40 hours.
- The commercial Ceramatek Inc. NASICON material (Salt Lake City, UT) was used as received and is nominally Na<sub>3.0</sub>Zr<sub>2</sub>PSi<sub>2</sub>O<sub>12</sub>, but contains additional proprietary components as additives.

## NMR SPECTROSCOPY

- All solid state NMR spectra were obtained on a Bruker Avance I using a 4 mm MAS NMR Probe at 162.0 MHz (<sup>31</sup>P), 158.7 MHz (<sup>23</sup>Na) and 79.5 MHz (<sup>29</sup>Si).
- Multiple Quantum (MQMAS) NMR experiments were obtained with a 3 pulse sequence followed by t<sub>1</sub> shearing.
- High temperature <sup>23</sup>Na MAS NMR spectra were collected using a DOTY Scientific (Columbia, SC) DPI 7 mm probe spinning at 4 kHz. A standard inversion recovery pulse sequence was used to determine the spin-lattice relaxation time (T<sub>1</sub>), with 32 inter-pulse relation delays and 8 to 16 scan averages.

- 2 Na site in crystal structure.
- Only 1 site typically occupied in NASICON.
- Na(1) sites along channels.
- Sol-gel material multiple Na sites.



## RELAXATION THEORY

- The <sup>23</sup>Na NMR spin lattice relaxation times (T<sub>1</sub>) are sensitive to jump dynamics that are on the order of the inverse of the NMR Larmor observed frequency (ω<sub>0</sub>) and are inversely related to the spin-lattice relaxation rates (R<sub>1</sub>) through the spectral densities J<sub>m</sub>(ω<sub>0</sub>).
- The simplest spectral density is the Bloembergen, Purcell and Pound (BPP) model and describes a random motion containing only a single jump rate (k) or correlation time τ<sub>c</sub> (=1/k).

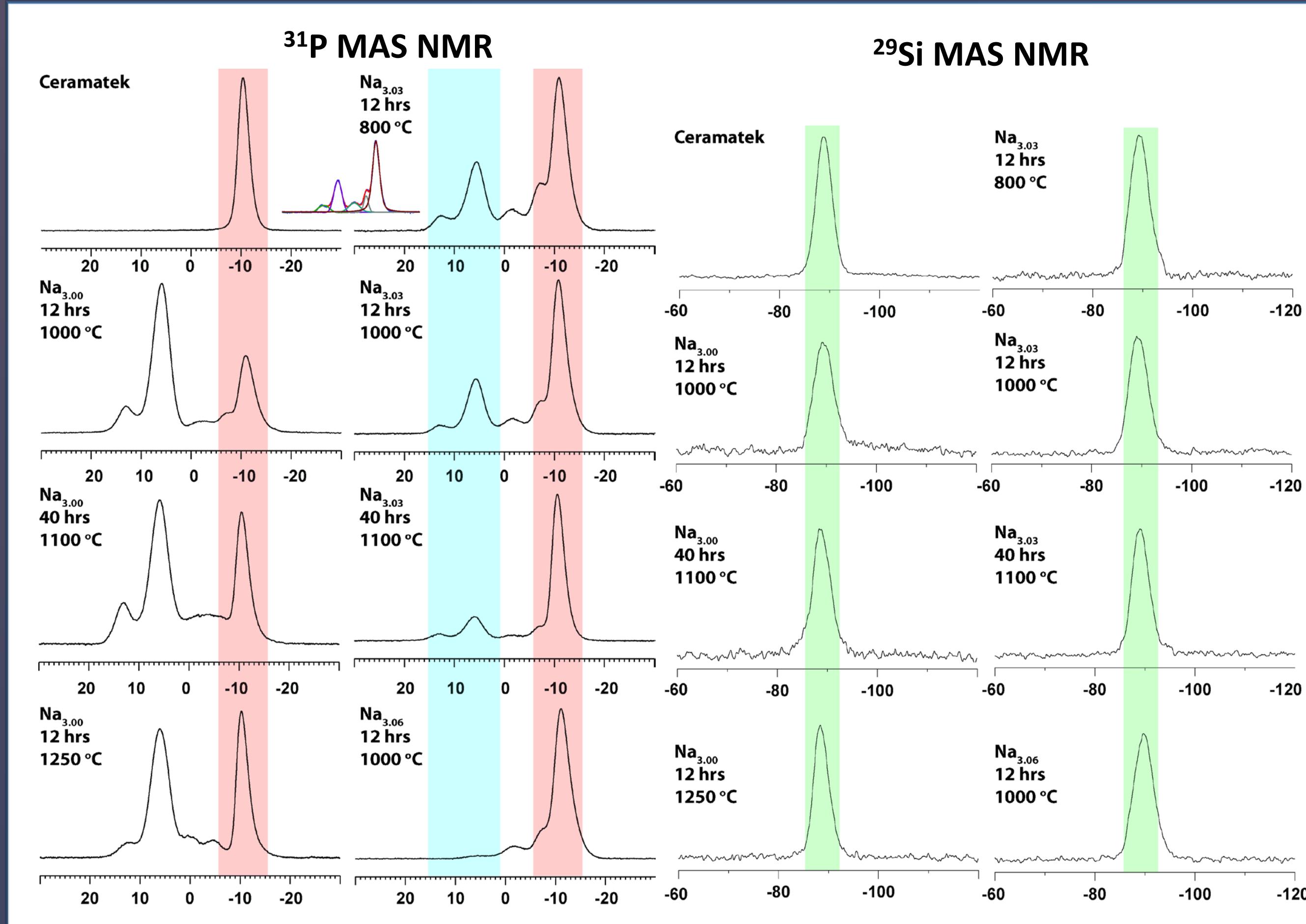
$$\text{BPP} \quad \text{Arrhenius} \quad R_1 = \frac{1}{T_1} = K_Q [J_1(\omega_0) + 4J_2(2\omega_0)] \quad J_n(n\omega_0) = \frac{2\tau_c}{1 + (n\omega_0\tau_c)^2} \quad \tau_c = \tau_0 \exp(E_a/k_B T)$$

- A distribution in the activation energies probabilities P(E<sub>a</sub>) can be assumed, with the observed NMR T<sub>1</sub> relaxation being an weighted average.

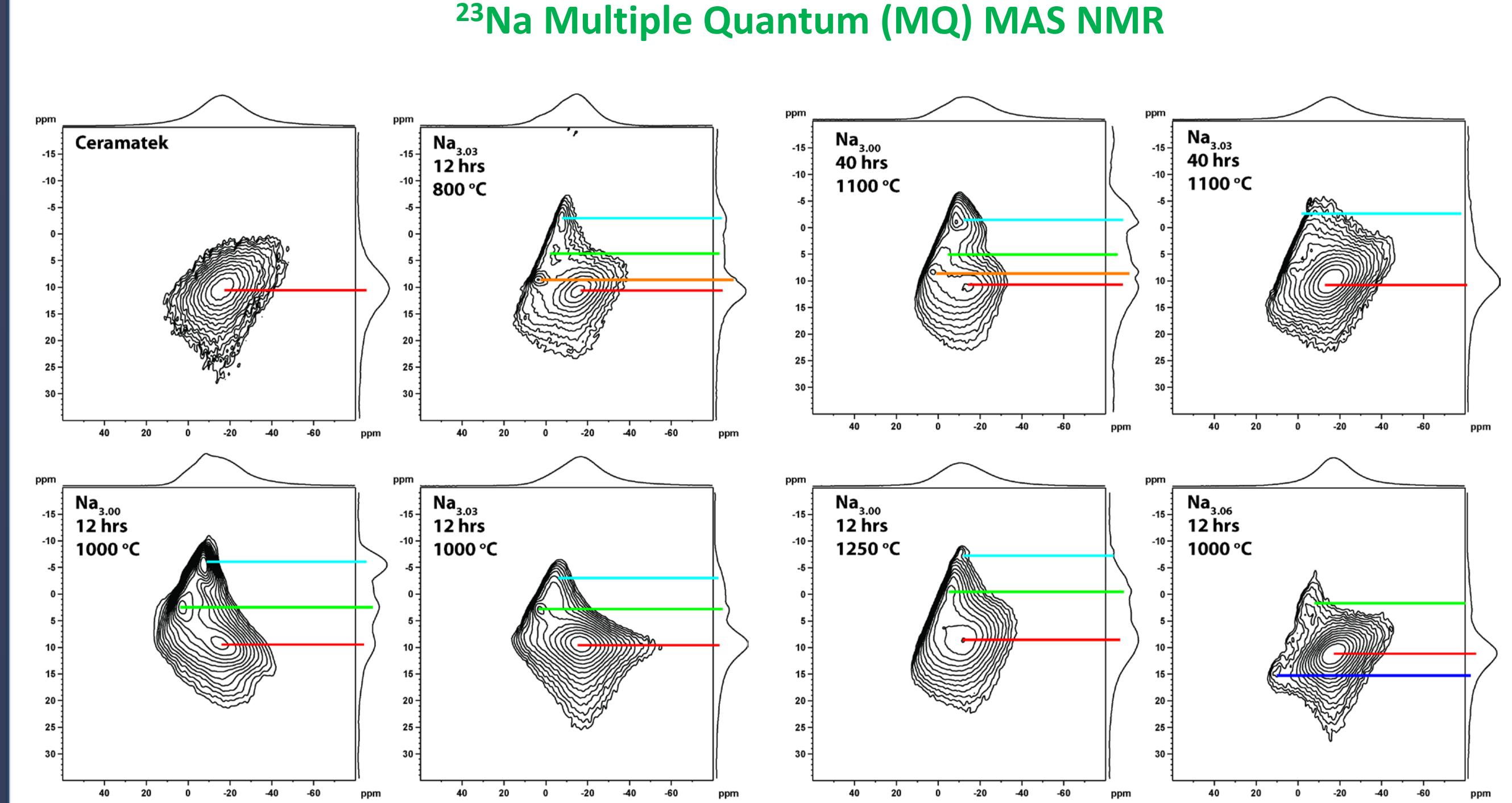
$$\text{Distribution in } E_a \quad R_1 = \frac{1}{T_1} = K_Q \int_0^\infty P(E_a) [J_1(\omega_0) + 4J_2(2\omega_0)] dE_a \quad E_{\text{BPP}} = k_B T \ln(\tau_c/\tau_0)$$

$$\text{Gaussian Distribution} \quad P(E_a) = \frac{1}{\sigma_a \sqrt{2\pi}} \exp\left[-\left(E_a - E_a^0\right)^2 / 2\sigma_a^2\right]$$

$$\text{Cole-Davidson (Cut-off correlation time)} \quad J_{CD}(n\omega_0) = \frac{2 \sin[\beta_{CD} \arctan(n\omega_0)]}{n\omega_0 [1 + (n\omega_0\tau_{CD})^2]^{\beta_{CD}/2}} \quad E_a(CD) = k_B T * \ln(\tau_{CD}/\tau_0)$$

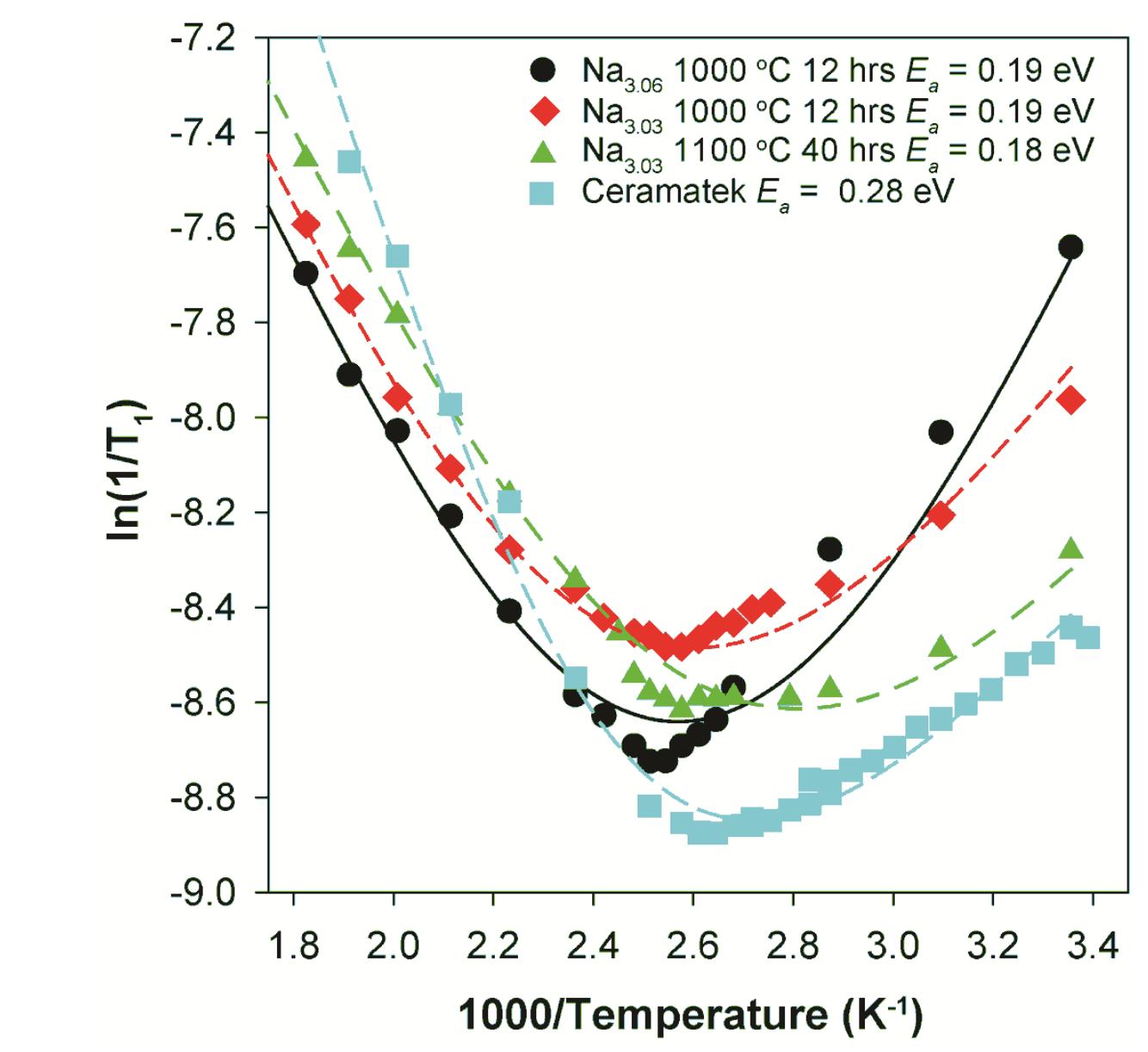
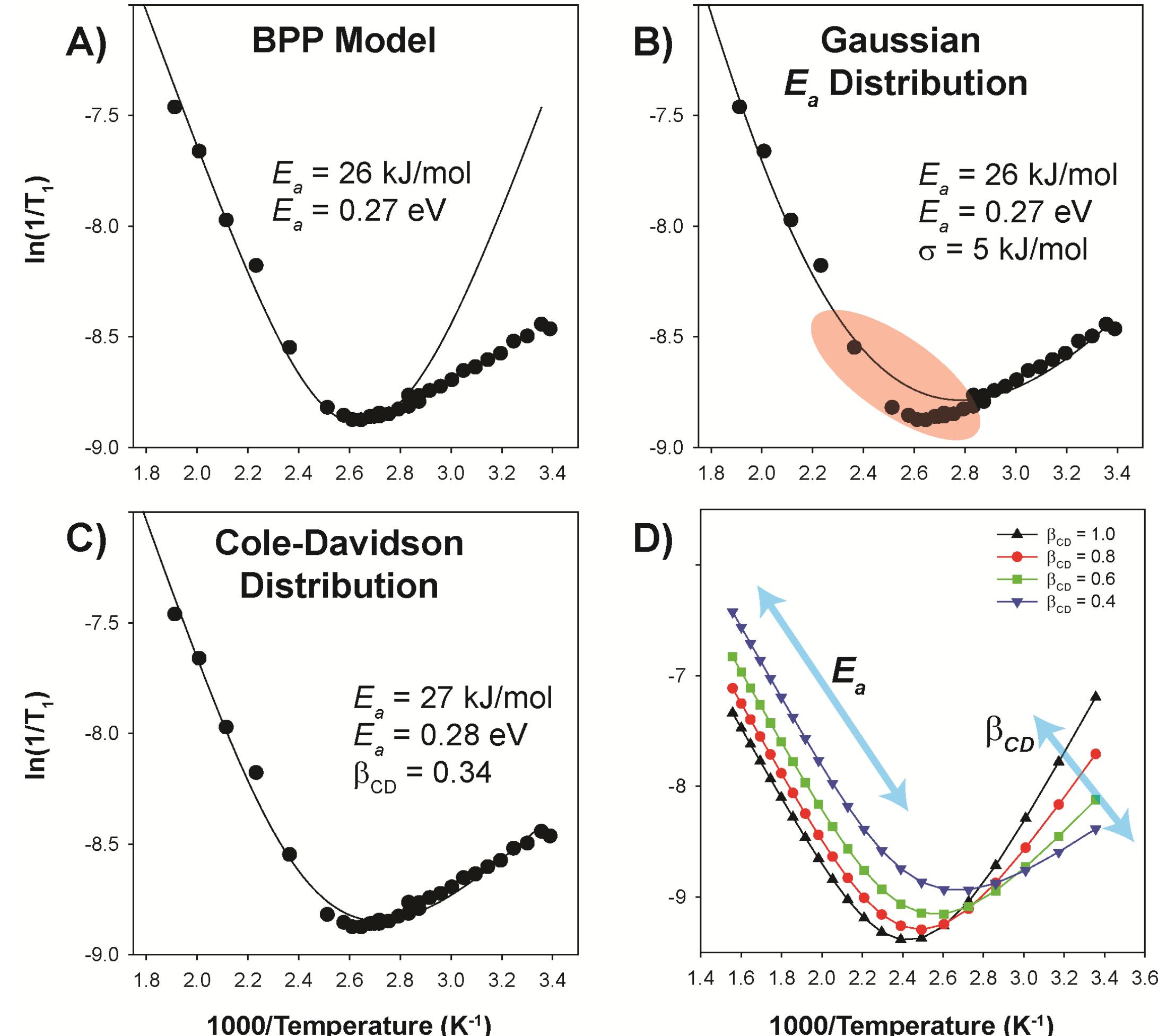


- Sol-gel derived material had disordered phosphate tetrahedral environments.
- Impact on Si tetrahedral sites is minimum.
- <sup>1</sup>H-<sup>31</sup>P and <sup>1</sup>H-<sup>29</sup>Si cross polarization (CP) results demonstrate the presence of proton containing phases in materials.
- Proton most associate with disordered phosphate phases.
- <sup>23</sup>Na results reveal between 1 and 5 different Na environments depending on processing conditions.



## High Temperature <sup>23</sup>Na Relaxation Studies

- Have demonstrated that the T<sub>1</sub> relaxation reflects the Na jump dynamics
- Results show that a single jump rate (BPP) model is inadequate.
- All materials show a distribution of Na jump rates.

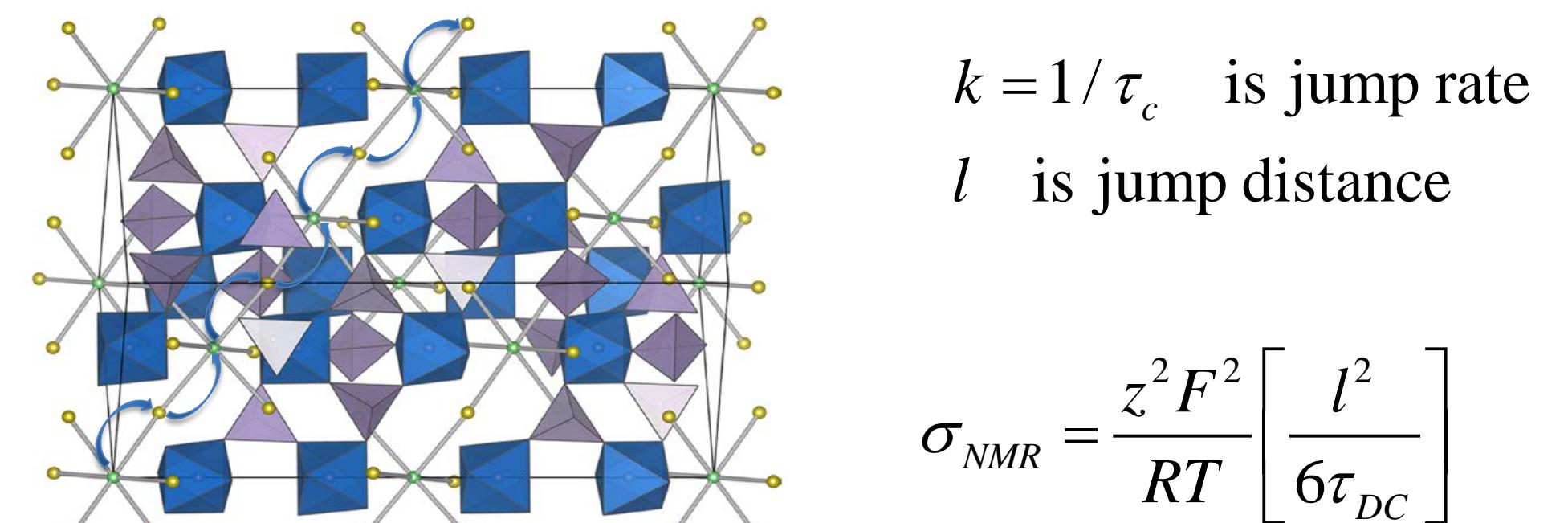


- The distributions of Na jump rates is impacted with composition and processing conditions.
- Materials that reveal the Na site composition closest to the Ceramatek NASICON material have similar (i.e. approaching) relaxation behavior.
- The single Na site at δ<sub>iso</sub> at ~+10.9 ppm is highly disordered and gives rise to the most enhanced <sup>23</sup>Na relaxation.
- This site also has a larger Na jump rate distribution.

## Connecting Na Jump Rates to Conductivity

$$\sigma = \frac{z^2 F^2}{RT} [D_+ + D_-] = \frac{z^2 F^2}{RT} D_{Na^+}$$

$$D = \alpha l^2 k = \alpha l^2 / \tau \sim l^2 / 6\tau$$

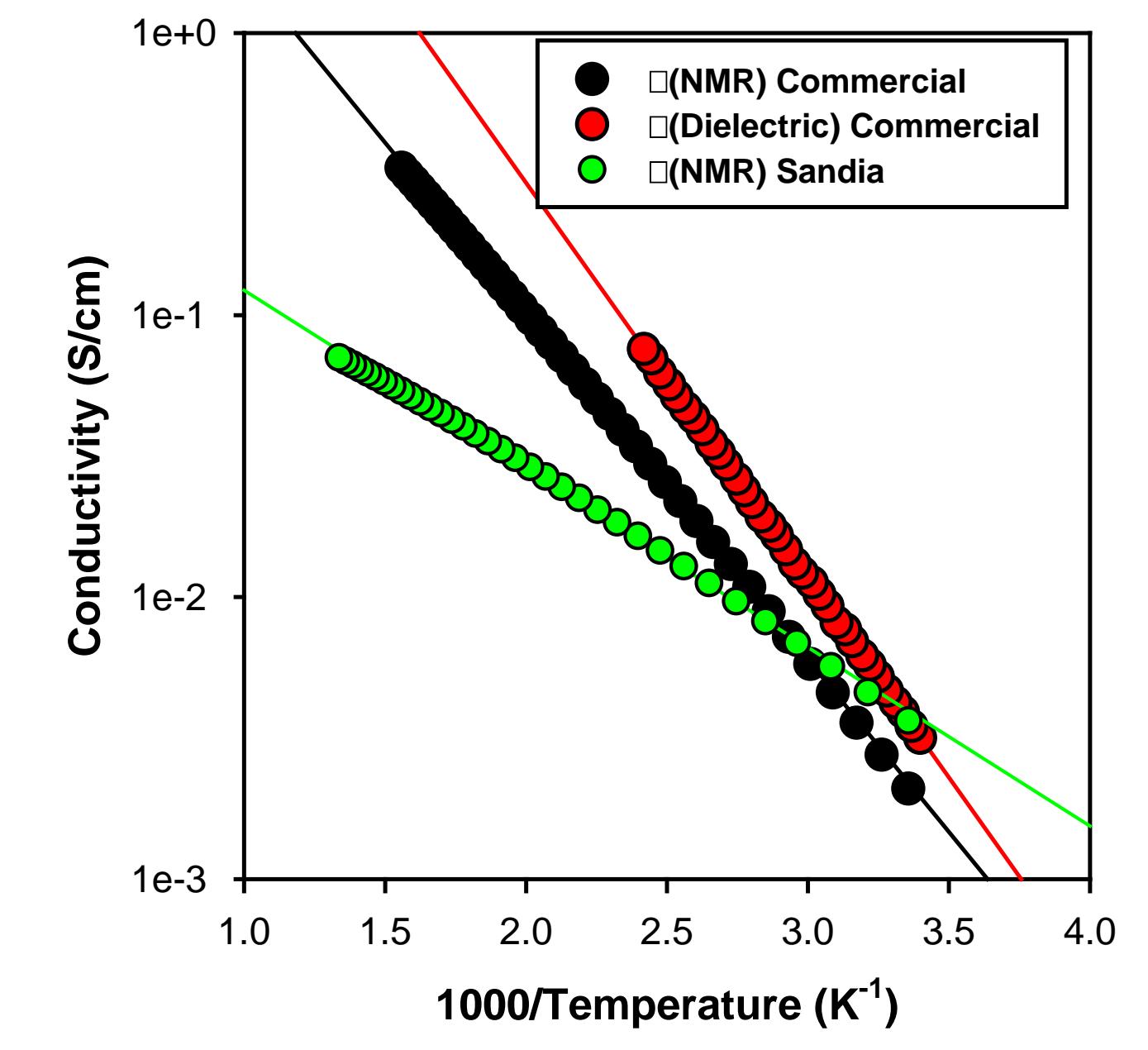


$$k = 1/\tau_c \text{ is jump rate}$$

$$l \text{ is jump distance}$$

$$\sigma_{NMR} = \frac{z^2 F^2}{RT} \left[ \frac{l^2}{6\tau_{DC}} \right]$$

## NMR Predicted Conductivity versus Dielectric Na<sub>3</sub>Zr<sub>2</sub>PSi<sub>2</sub>O<sub>12</sub>



## CONCLUSIONS

- Have demonstrated that processing condition significantly impact the local disorder and multiple phases in sol-gel preparation of NASICON materials.
- The disorder is apparent in the multiple phosphate tetrahedral environments and the presence of multiple Na environments.
- High temperature <sup>23</sup>Na NMR T<sub>1</sub> relaxation experiments can be used to directly measure the Na jump rates.
- The <sup>23</sup>Na relaxation experiments also prove that distributions in the Na jump rates are present for all of these NASICON materials.

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