

NMR Crystallography of Mixed-Metal Phosphates

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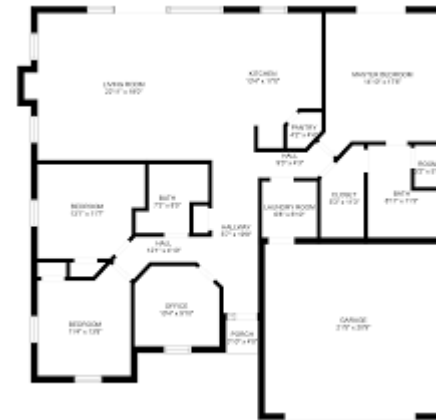
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NMR Crystallography

- Imagine a periodic crystalline sample...

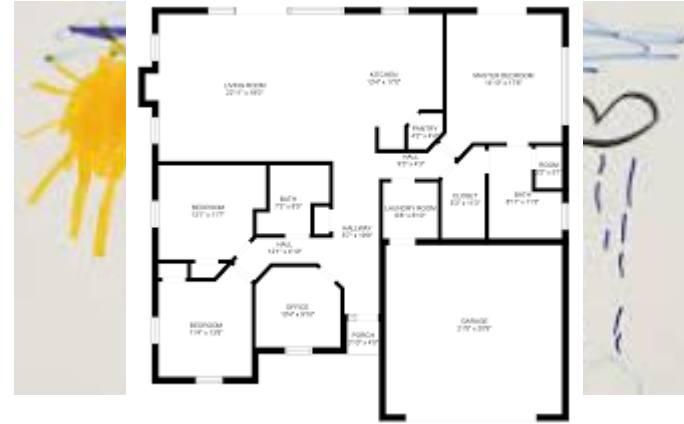


- A crystallographer would describe this in terms of the periodic repeat unit
- Crystal structures allow measurement of distances and angles to high precision (according to crystallographers)



NMR Crystallography

- But we know many samples contain disorder (motion, different orientations, different ions on the same site, different sites for the same ion...)



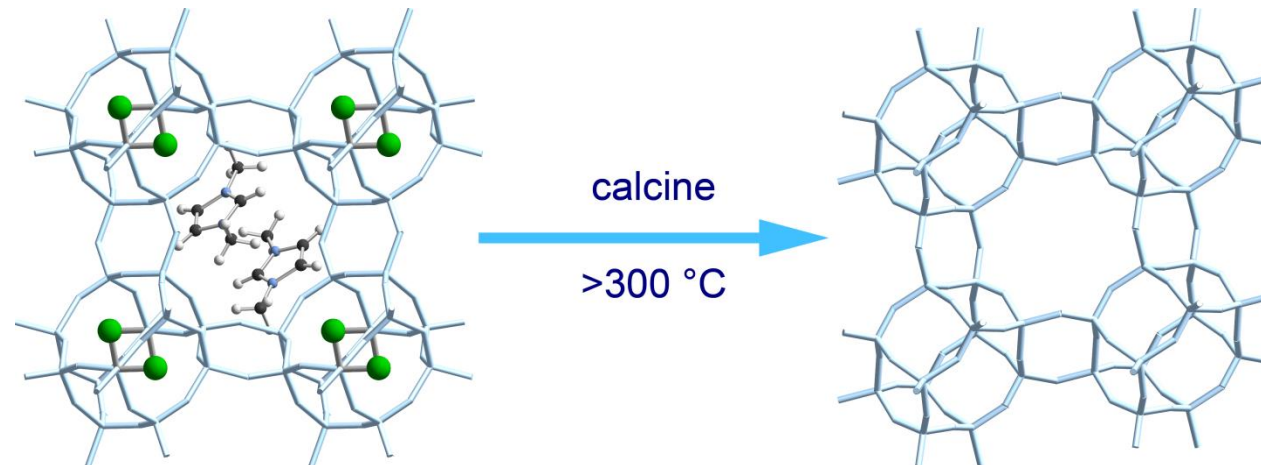
- NMR spectroscopy only shows element specific local details



- NMR crystallography seeks to connect the two, often via computation, to provide a richer picture of the structure-disorder-property relationships necessary to understand the material

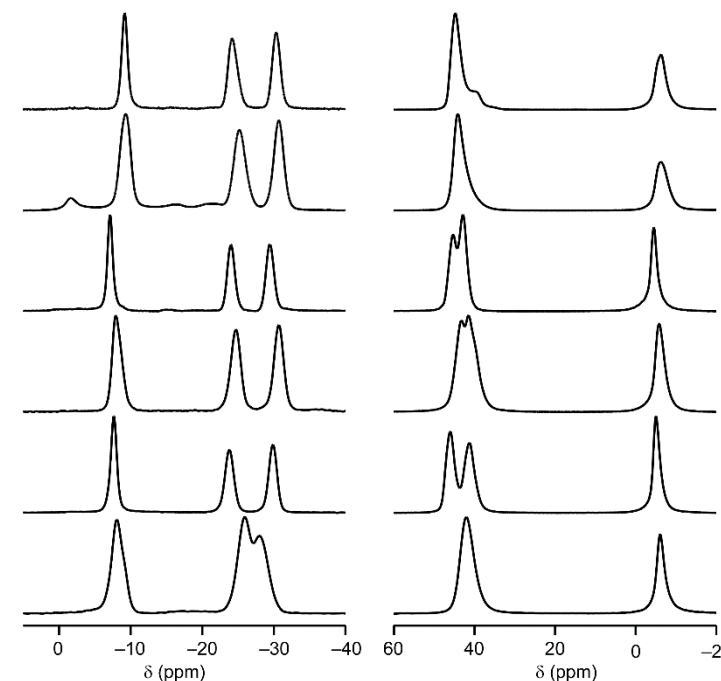
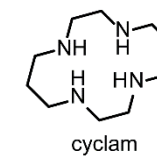
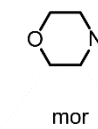
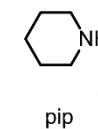
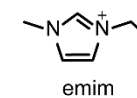
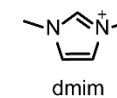
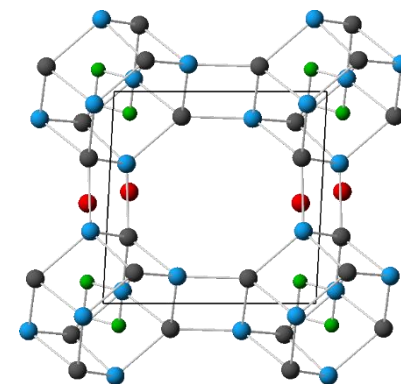
Metallophosphates

- Charge-neutral MPO_4 framework ($M = Al, Ga$) with alternating MO_4 and PO_4 tetrahedra
- Topology is guided by cationic structure-directing agents (SDAs)
- Charge of the SDA is balanced by OH or F anions bound to M, giving 5- or 6-coordinate sites
- Calcination removes SDA and anions; for GaPOs the calcined framework may be unstable



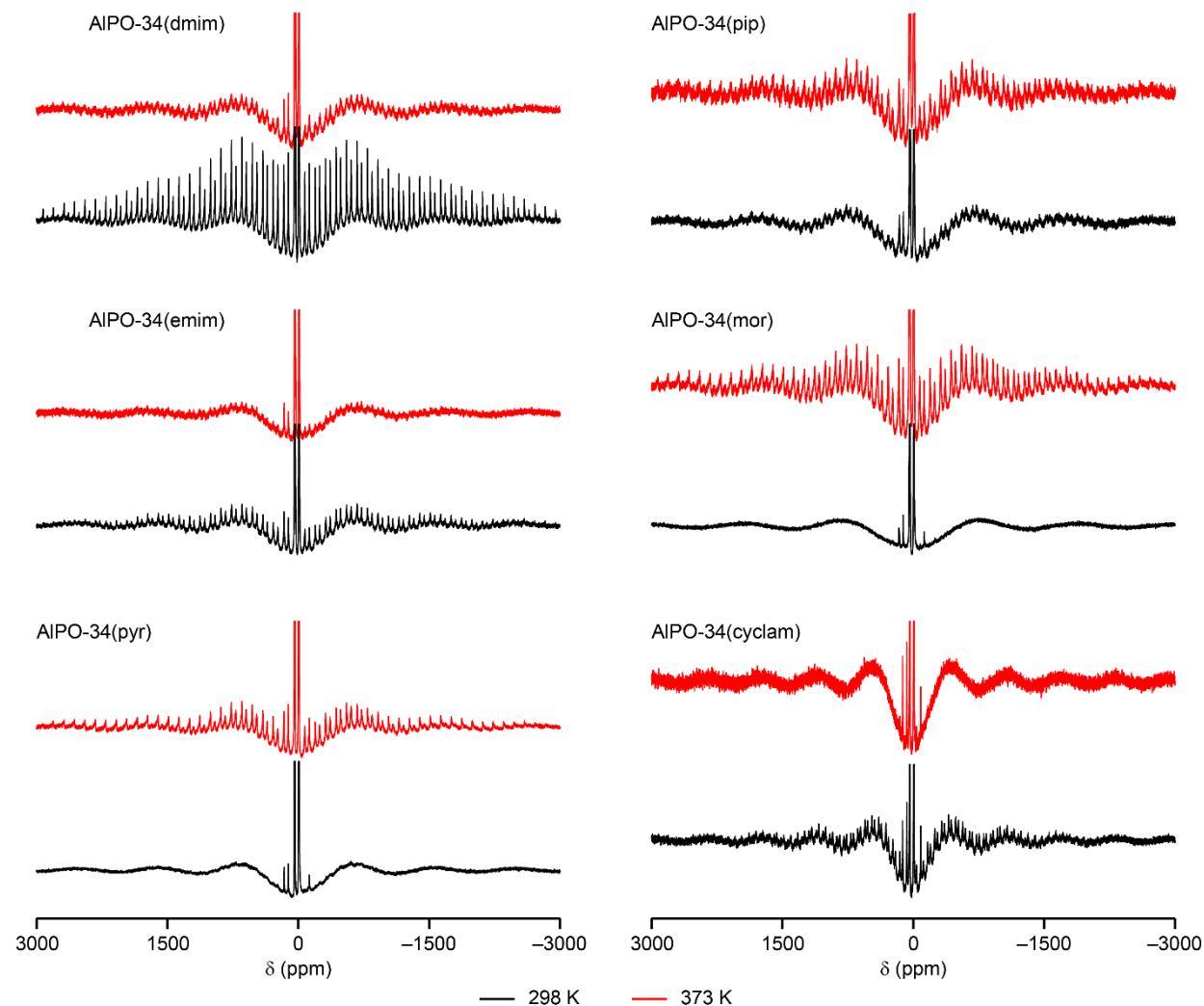
AIPO-34

- Started with CHA type AIPO-34 as a simple model system
- Thermodynamically quite stable so can form with several SDAs
- Attempting to understand this templating effect
- NMR spectra agree with crystal structures – three P sites, three Al



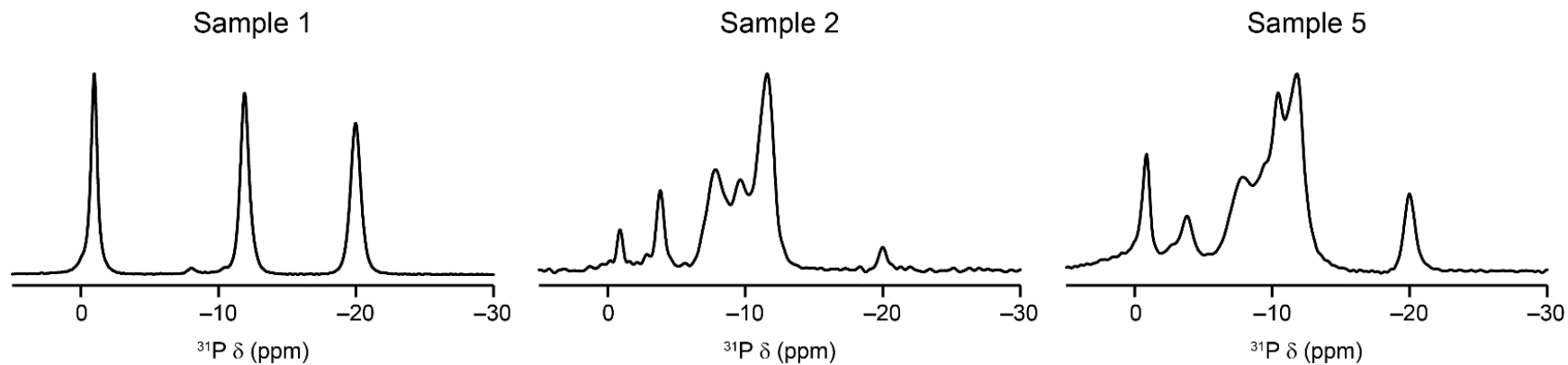
AIPO-34

- Some crystal structures show disorder
- Static or dynamic disorder?
- In NMR, motion on the timescale τ_c interferes with interactions of magnitude $\omega \approx 1/\tau_c$ so that maximum interference (broadening) at $\omega\tau_c \approx 1$
- ^{27}Al satellite transitions are MHz wide so we don't normally look at them; here we see variation in linewidth with T



GaPO-34

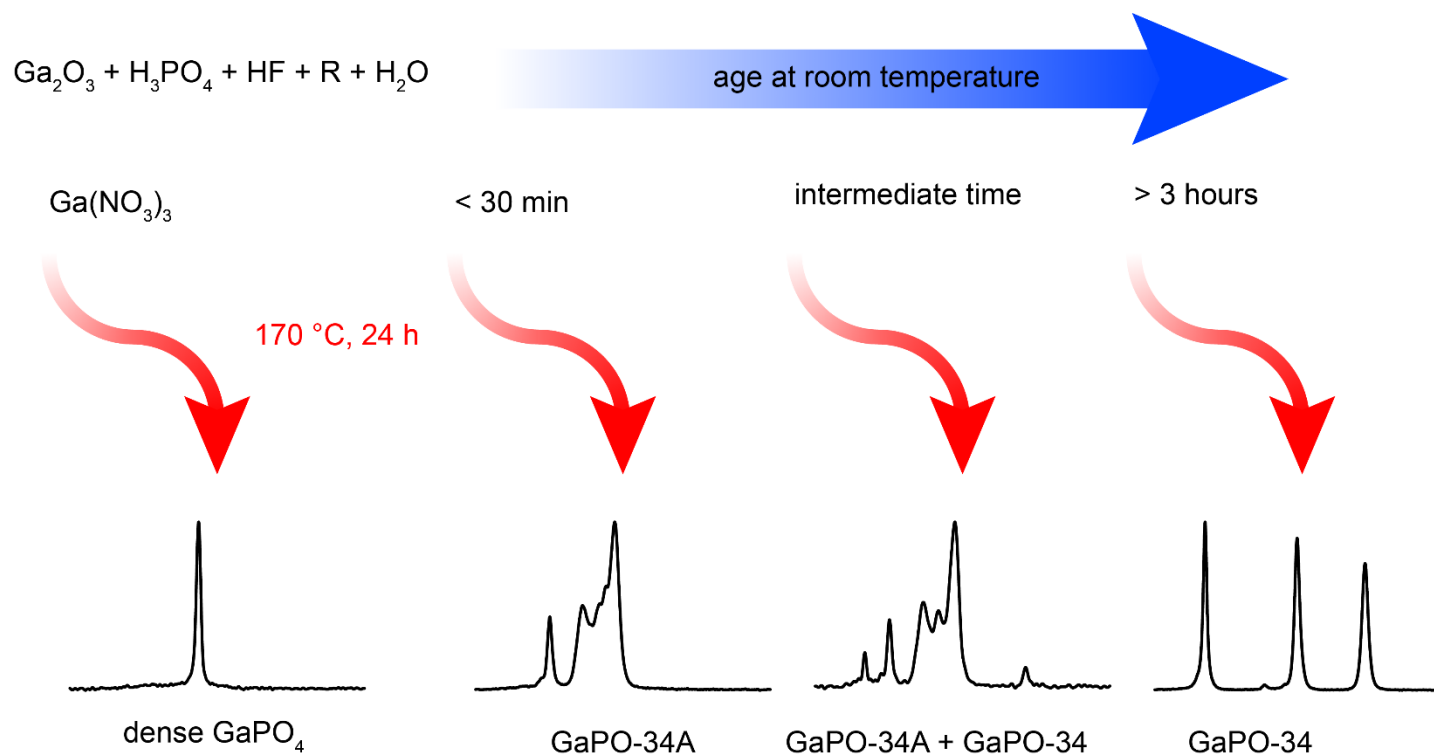
- The Ga analogue, GaPO-34 displays a similar templating effect (mim or pyr SDAs)
- Very hard to make pure samples



- Two common impurities, GaPO_4 berlinite (quartz type) and unidentified phase, “GaPO-34A”

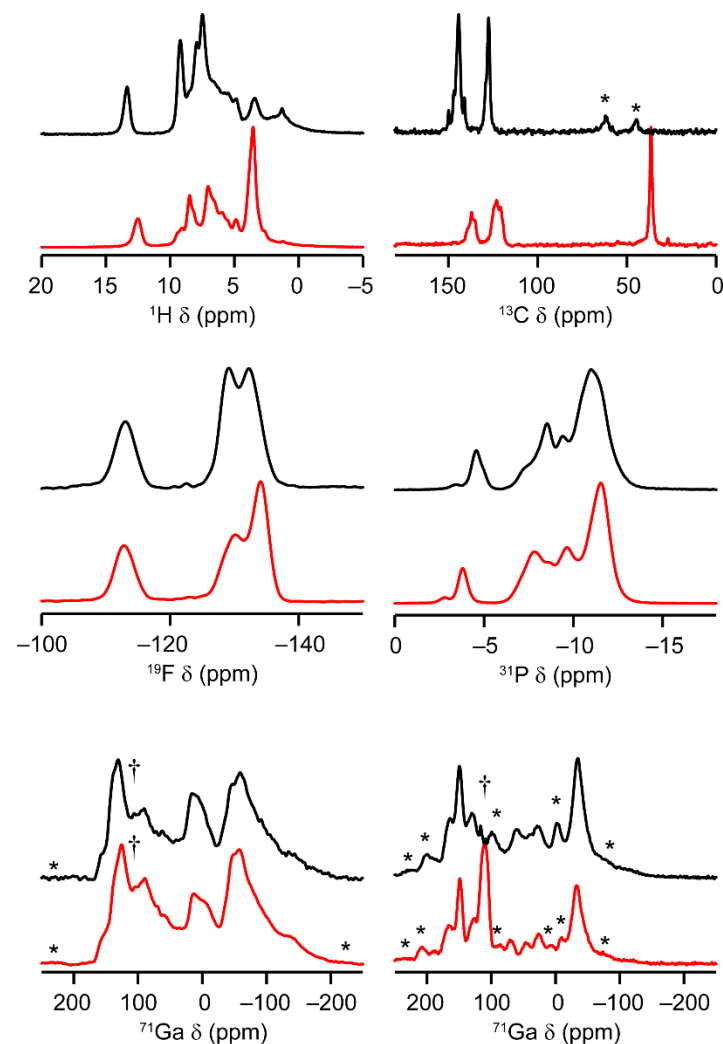
GaPO-34A

- The key to preparing single-phase samples is gel ageing time before heating



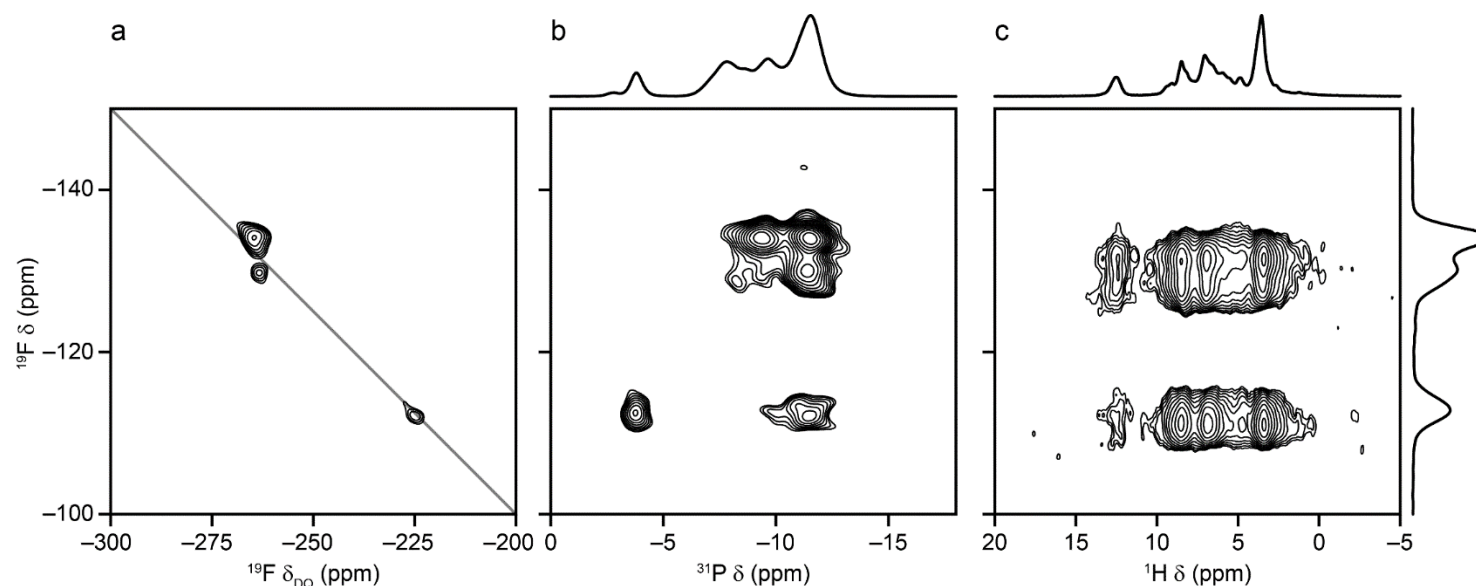
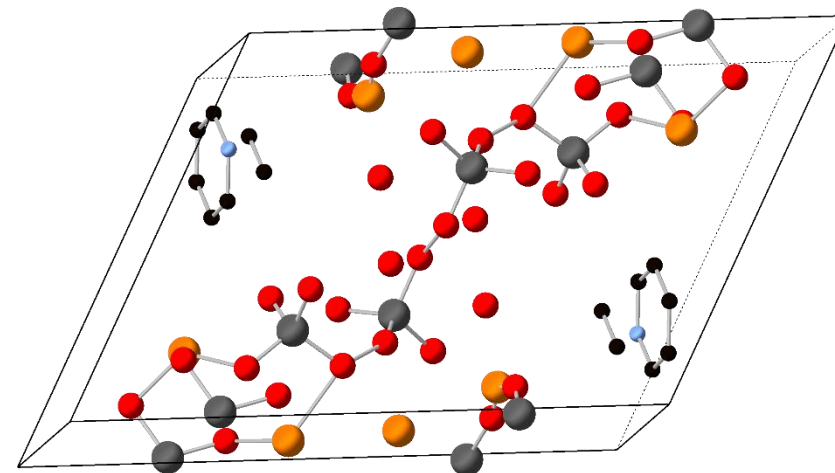
GaPO-34A

- When we teach students to interpret NMR data step one is “how many peaks?”
- Step two is “where are the peaks?”, which is a bit more useful
- Step three, “how much of each peak?” doesn’t work well without knowing the answer to step one...
- Rough integrals give 6-ish P and 7-ish Ga
 - Makes no sense for a GaPO_4 material
 - Agrees roughly with elemental analysis



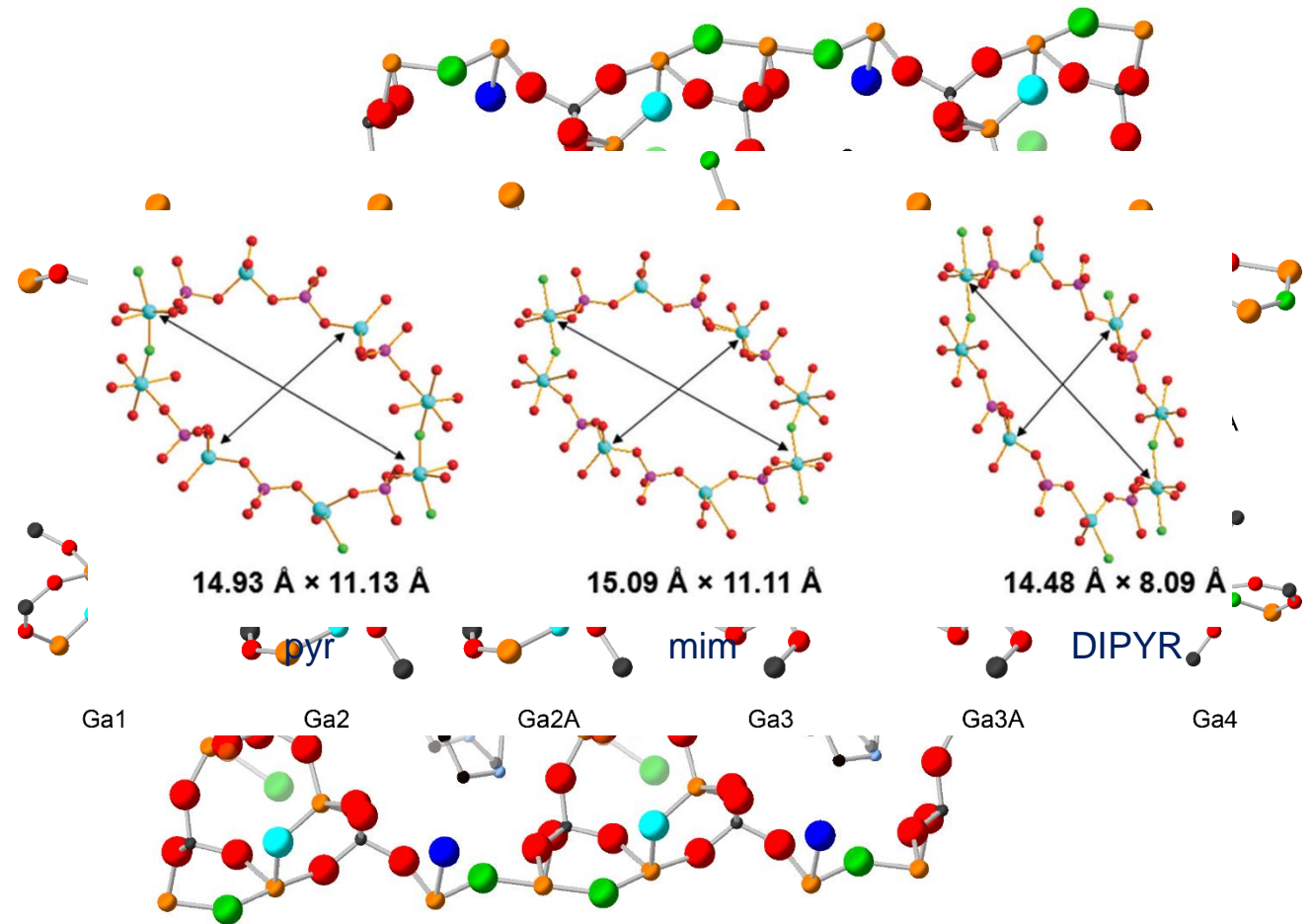
GaPO-34A

- Early crystal structure didn't make much sense either
 - the POOP structure
- Range of 2D NMR spectra gave us little snippets of information but still didn't really understand what was going on



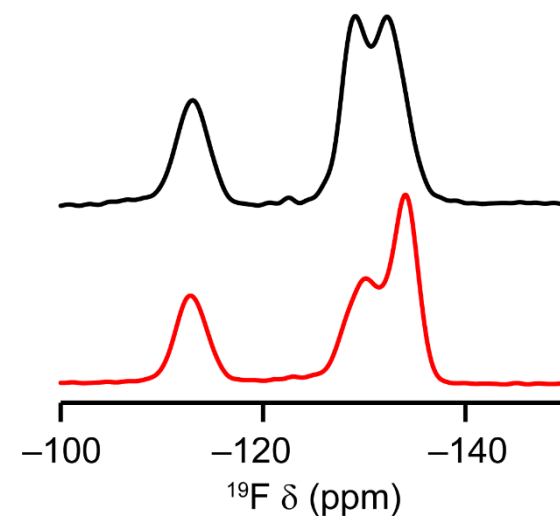
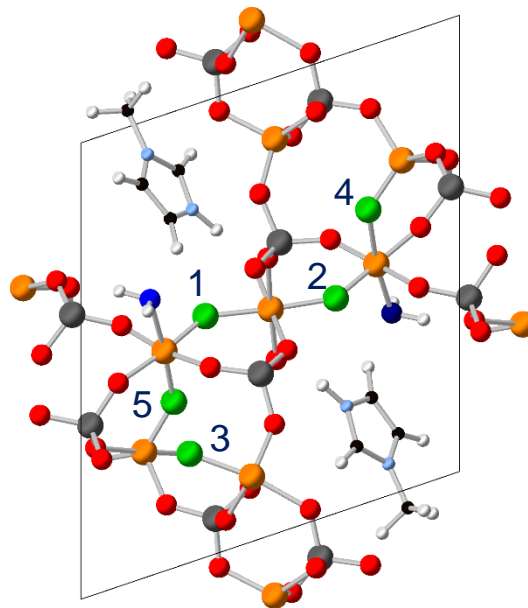
GaPO-34A

- Elemental analysis gives a formula of $\text{Ga}_7\text{P}_6\text{O}_{24} \cdot 2(\text{OH}) \cdot 3\text{F} \cdot 2(\text{H}_2\text{O}) \cdot 2\text{R}$
- GaPO-34A forms small crystals so structure determination needed synchrotron diffraction
- Framework topology is the same as DIPYR-GaPO, but very distorted
- Contents of the unit cell are very disordered
 - fractional occupancy
 - positional disorder
 - variable coordination number



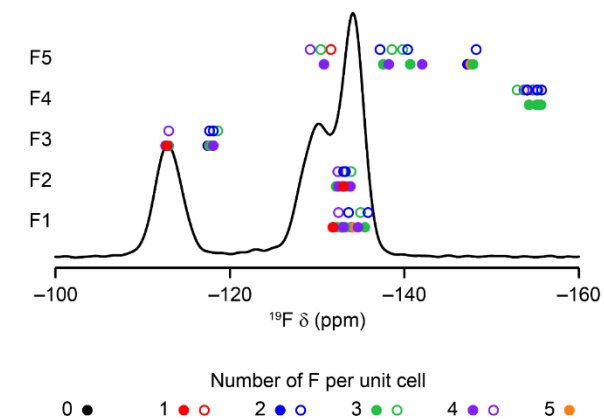
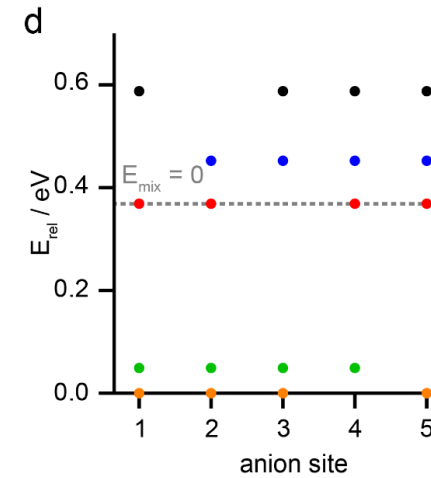
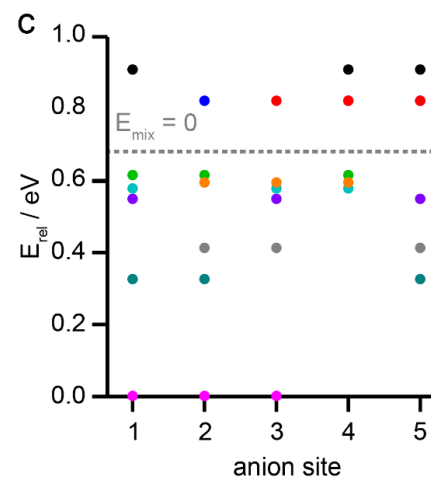
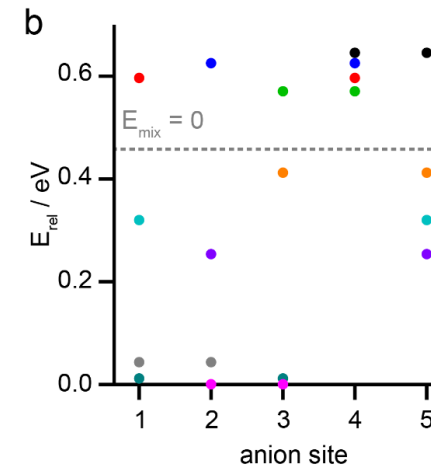
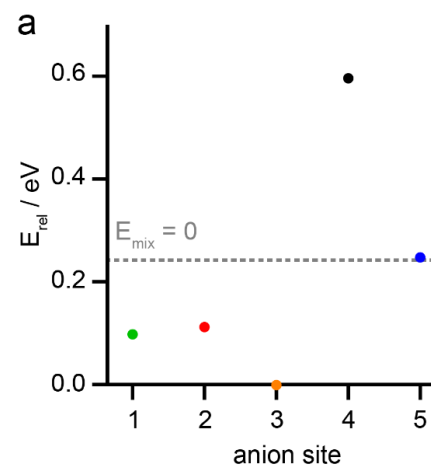
GaPO-34A

- I'm going to skip the full story and give you some edited highlights...
- Five anions distributed across six sites in $\text{Ga}_7\text{P}_6\text{O}_{24} \cdot 2(\text{OH}) \cdot 3\text{F} \cdot 2(\text{H}_2\text{O}) \cdot 2\text{R}$
- Sites 1-4 always occupied, one of 5 and 6 occupied
- Three signals in ^{19}F NMR spectrum
- Some F/OH ordering?



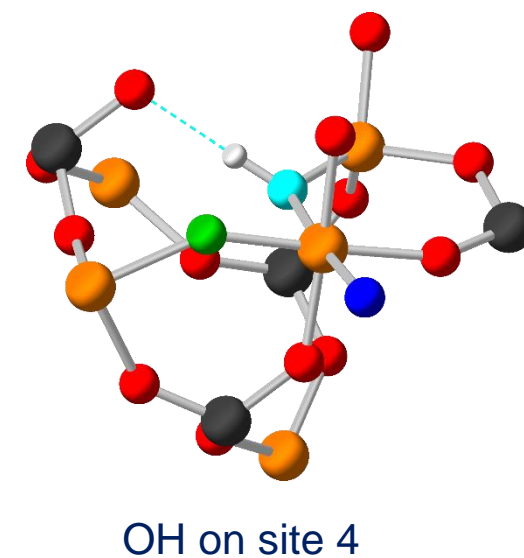
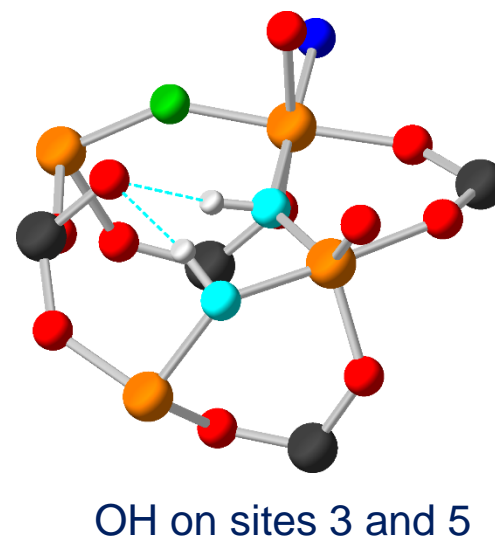
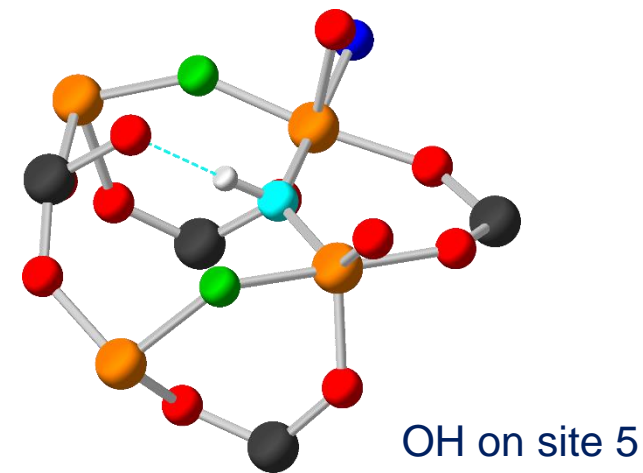
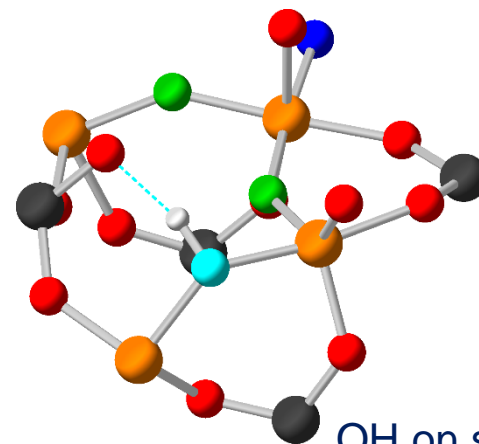
GaPO-34A

- Generated an ensemble of structures from OOOOO to FFFFF
- Used DFT to calculate the relative energies of different anion configurations
- F on sites 1, 2 and 3 is strongly favoured
- Calculated ^{19}F shifts agree with experiment



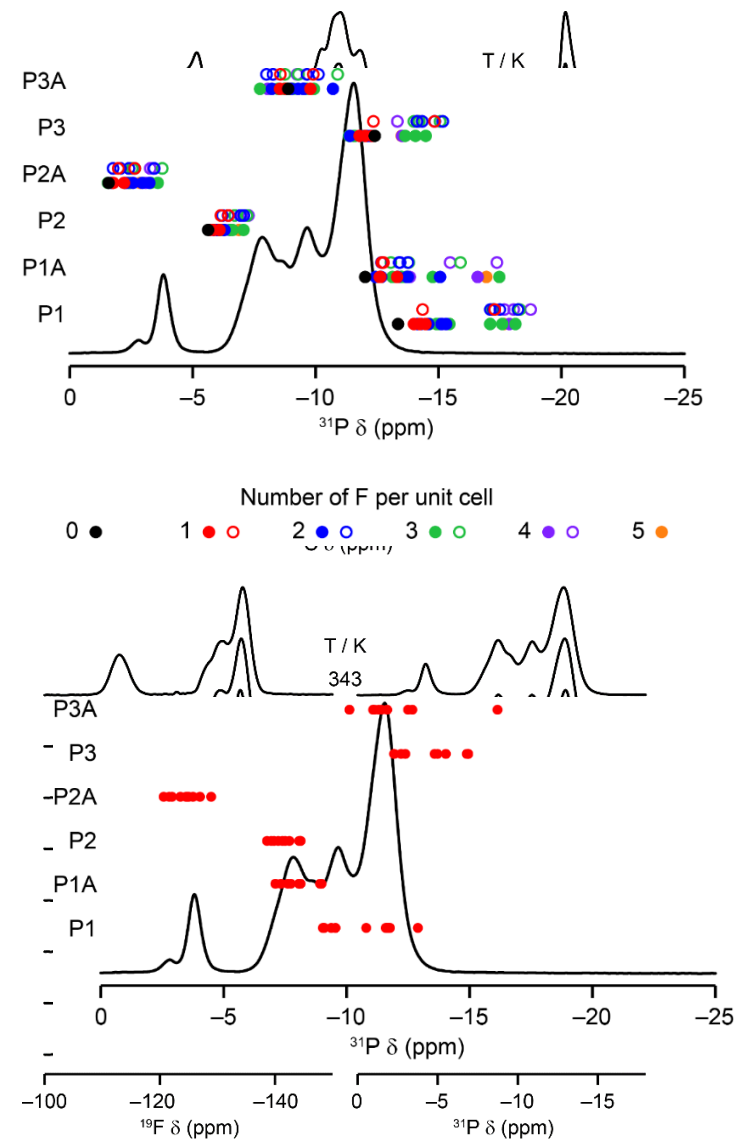
GaPO-34A

- O-H...O hydrogen bonding explains unfavourability of fluorinating sites 4 and 5
- OH on 3 and 5 compete to hydrogen bond to the same framework O
- O5H...O is more favourable than O3H...O (so F3 is better than F5)
- Fluorinating site 4 results in loss of stable O4H...O hydrogen bond, so is strongly disfavoured



Dynamics in GaPO-34A

- Variable-temperature NMR spectra show changes
- Perhaps exchange between different orientations of the SDA
- Possibly H₂O motion (reorientation or bulk movement)
- Explains why F1 and F2 have much shorter T₁ relaxation times than F3 (which is hidden away from the SDA)
- Perhaps explains poor agreement between experimental and calculated ³¹P spectra

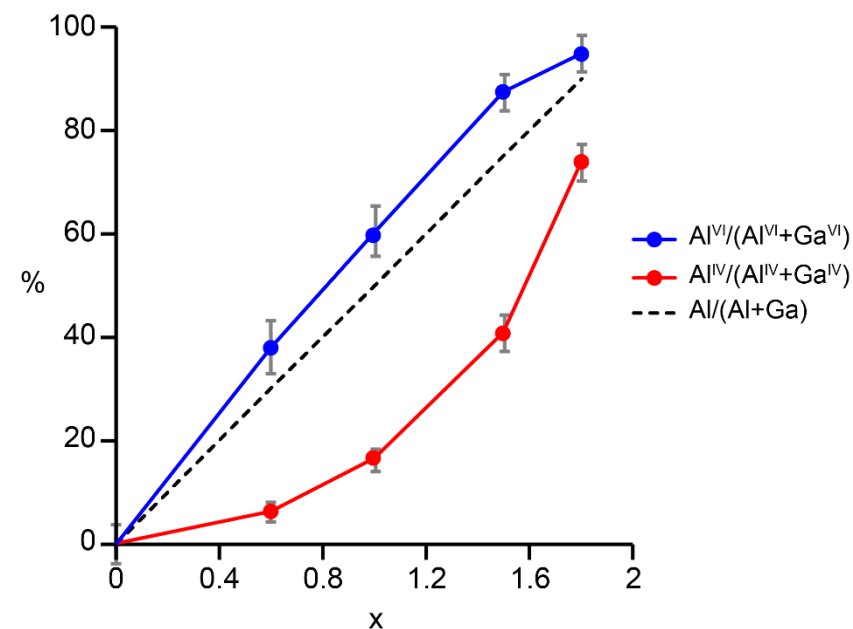


GaPO-34A Conclusions

- Very complicated material
 - hard to make pure (kinetic product)
 - dynamic disorder of the SDA and water
 - occupational disorder of the anions (occupancy of site 5 or 6?)
 - compositional disorder of the anions (OH or F?)
- No wonder it doesn't form large single crystals!
- Neither NMR nor diffraction can tell the whole story on their own
- We can get a surprising amount of detail about the underlying principles of what's going on in the structure by using an NMR crystallographic approach

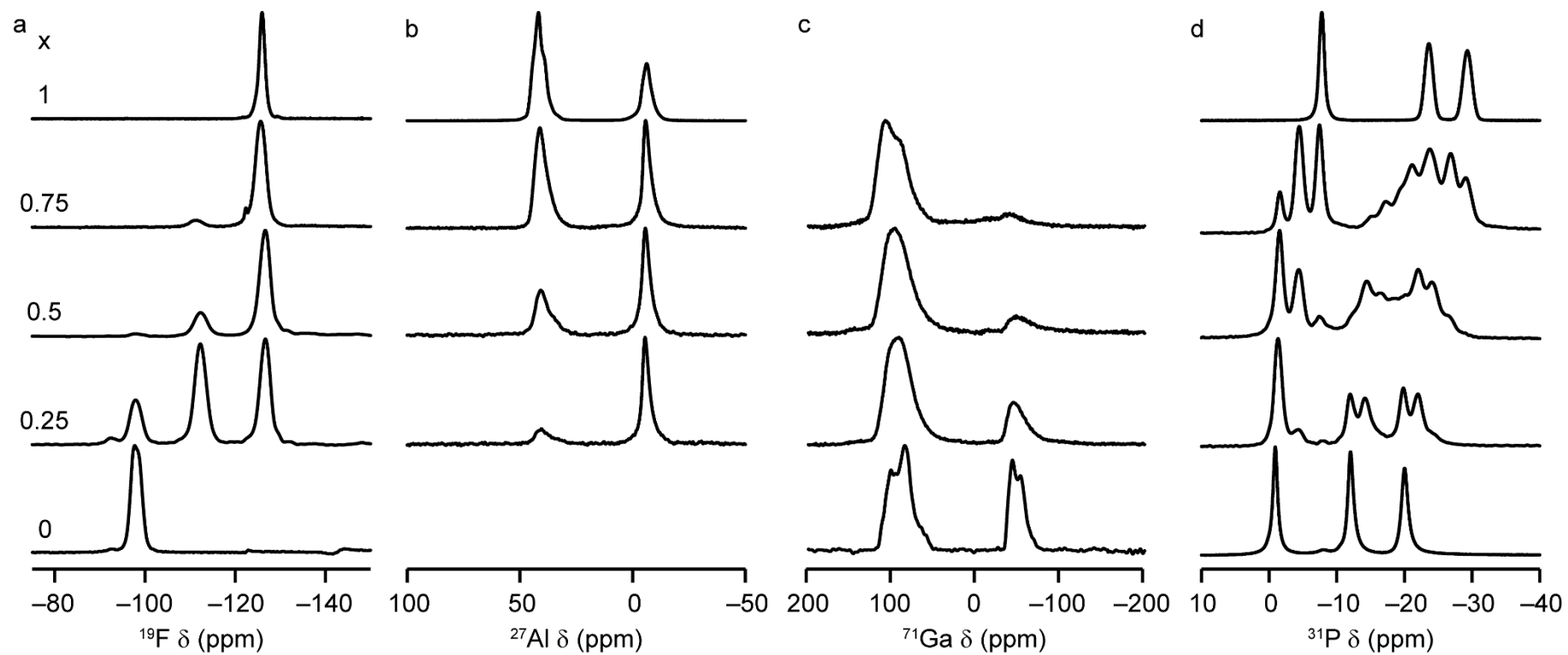
AlGaPO-34

- Combined another project on mixed metal oxides for catalysts/catalyst supports with ongoing work on phosphates
- Mixing metals in materials often leads to a combination of their properties
- A good model system with NMR-friendly nuclei to develop NMR crystallographic methods
- NMR of the oxides showed a preference for octahedral Al and tetrahedral Ga



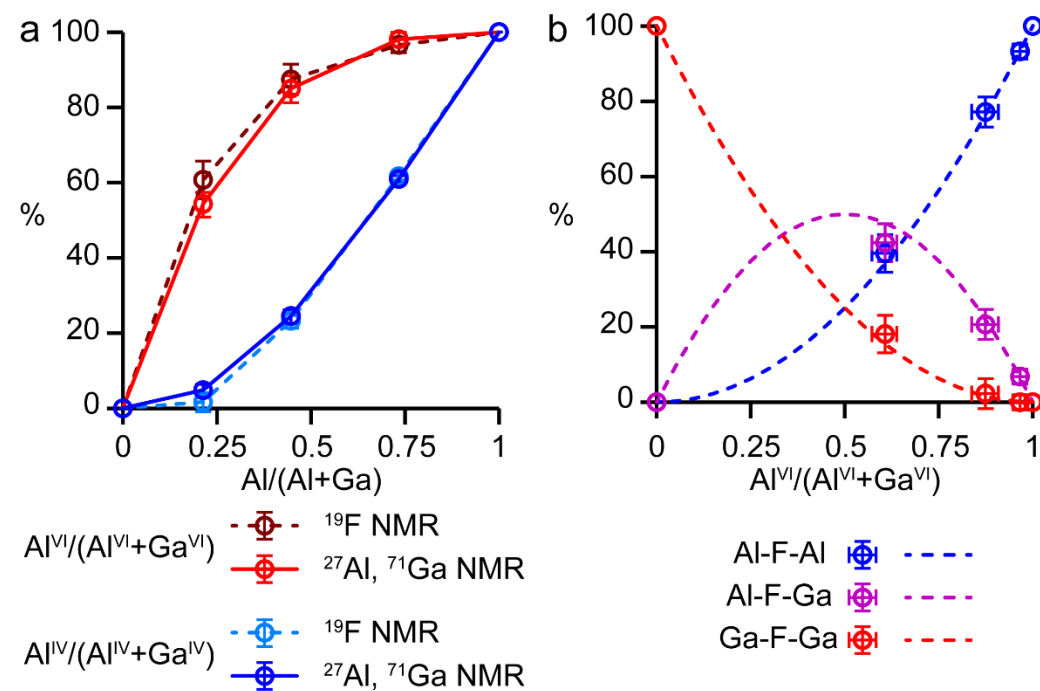
AlGaPO-34

- NMR spectra are fairly straightforward to interpret



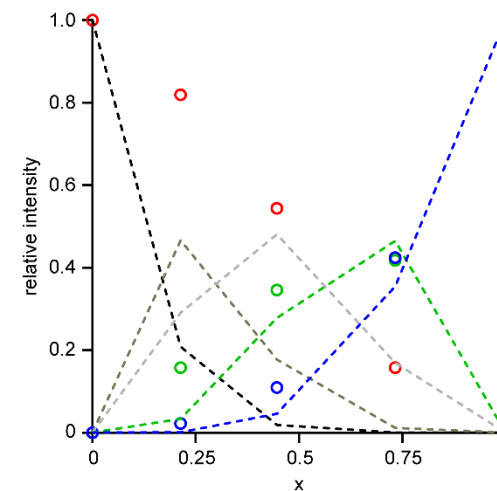
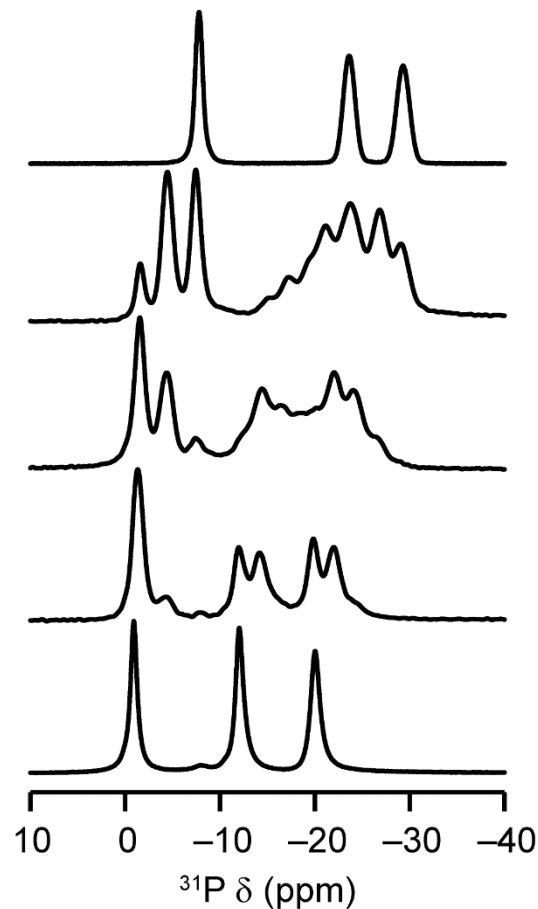
AlGaPO-34

- Even more extreme preference for octahedral Al and tetrahedral Ga here
- More ionic MO_4F_2 here rather than MO_6 in oxides
- ^{19}F intensities can be used to probe M-F-M linkages but show no preference for clustered Al-F-Al/Ga-F-Ga or mixed Al-F-Ga



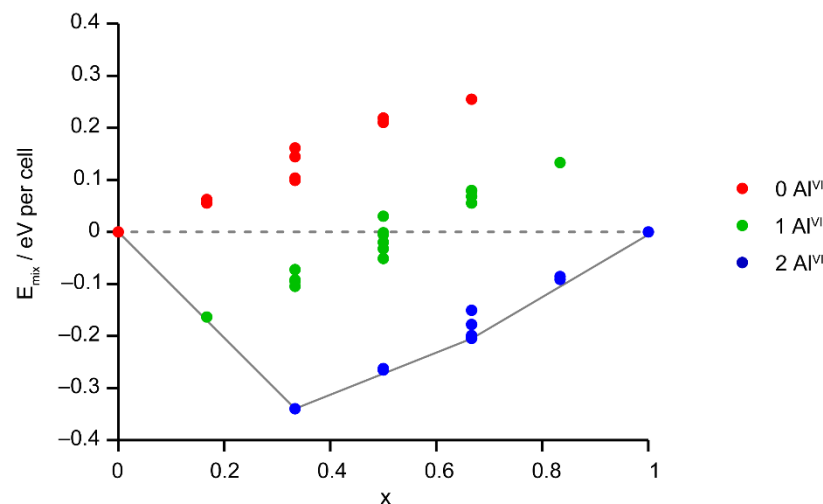
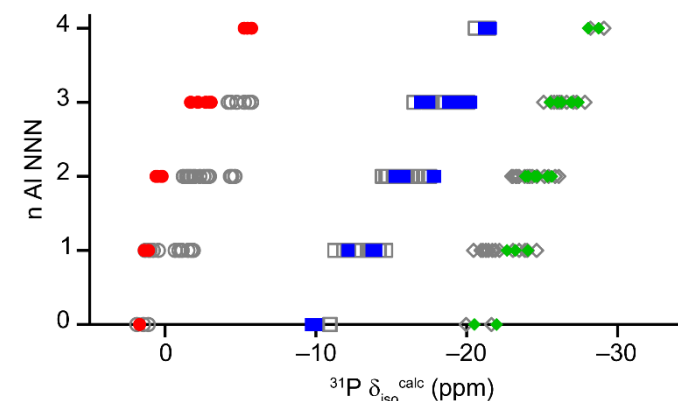
AlGaPO-34

- At first glance, ^{31}P lineshapes look like the ^{29}Si signals for zeolites with $\text{Si}(n\text{Al})$, $0 \leq n \leq 4$
- However, there aren't enough peaks for that for P1
- We can predict intensities for each $\text{P}(n\text{Al})$ signal
- Good agreement with experiment when we combine intensities for $\text{P}(0-2\text{Al})$



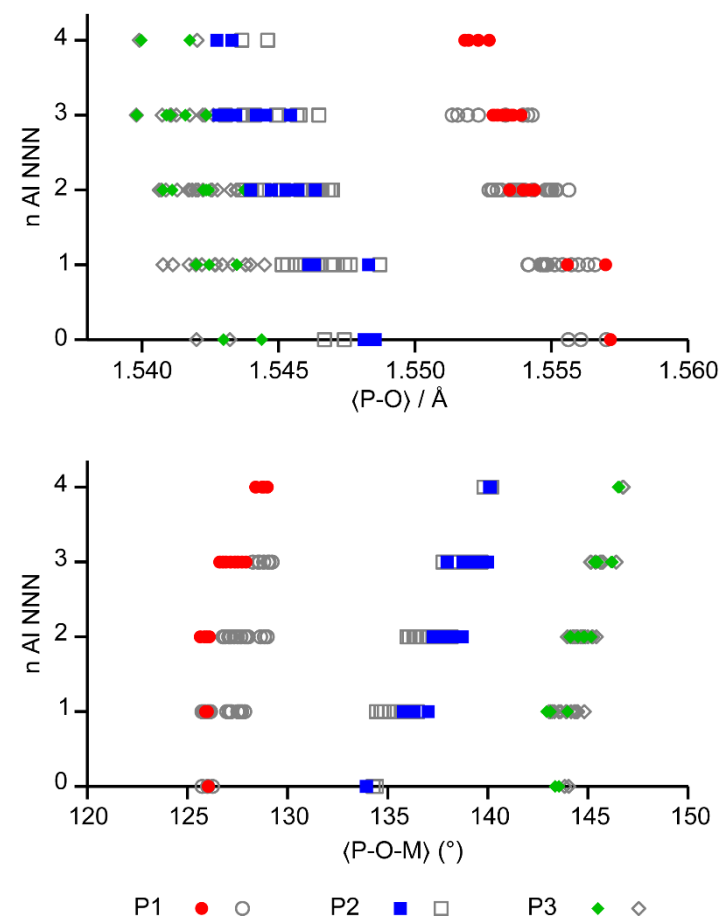
The CHA Framework

- DFT predicts reasonably consistent steps in ^{31}P shift for each extra NNN Al
- Are we seeing all of the structures?
- Convex hull shows a preference to maximise the number of octahedral Al
- Agreement with experiment is much better when considering only lowest energy structures



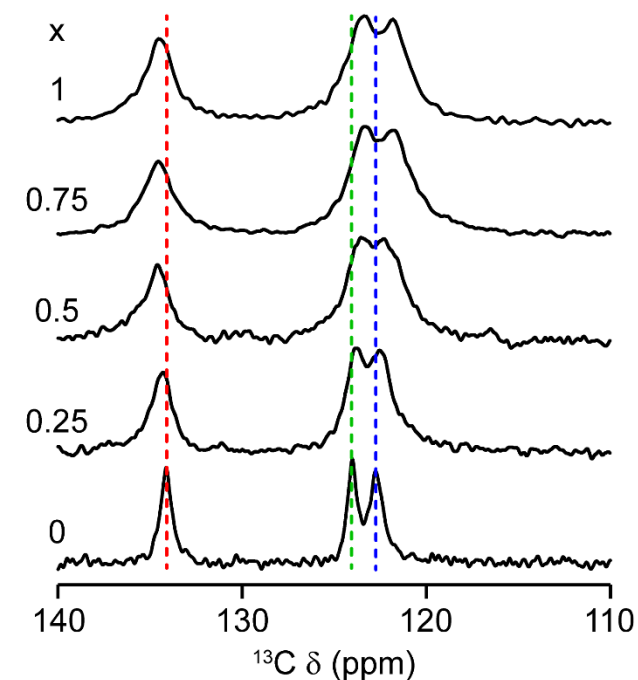
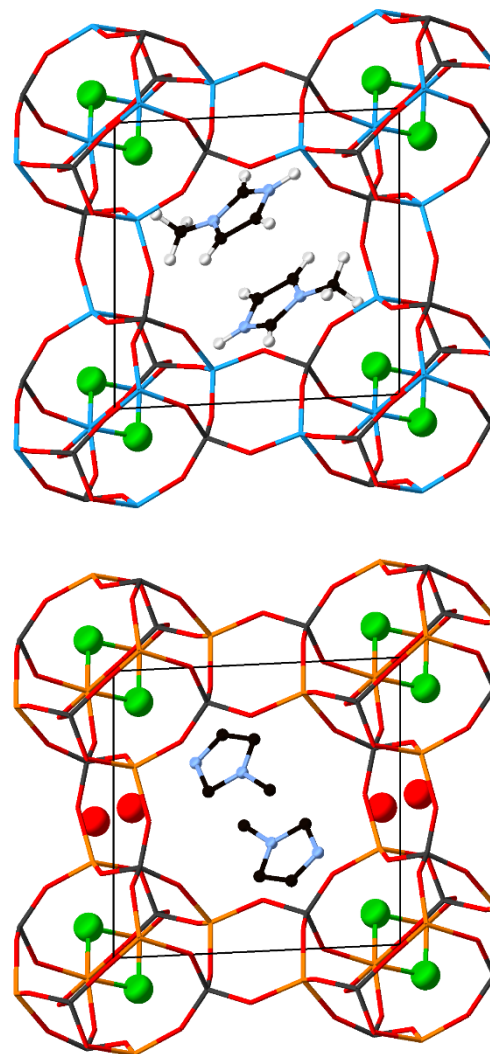
The CHA Framework

- Looking at the optimised (not experimental) local structure, we can see that the P-O bond length changes very slightly (~ 0.01 Å) but the mean P-O-M angle is the same for P1(0-2Al)
- We have previously shown for AlPOs that the ^{31}P shift is sensitive to both the mean P-O length and the mean P-O-Al angle
- Atomic arrangement is driven by octahedral site occupancy but NMR shifts are driven by tetrahedral site occupancy, which has a bigger effect on the structure!



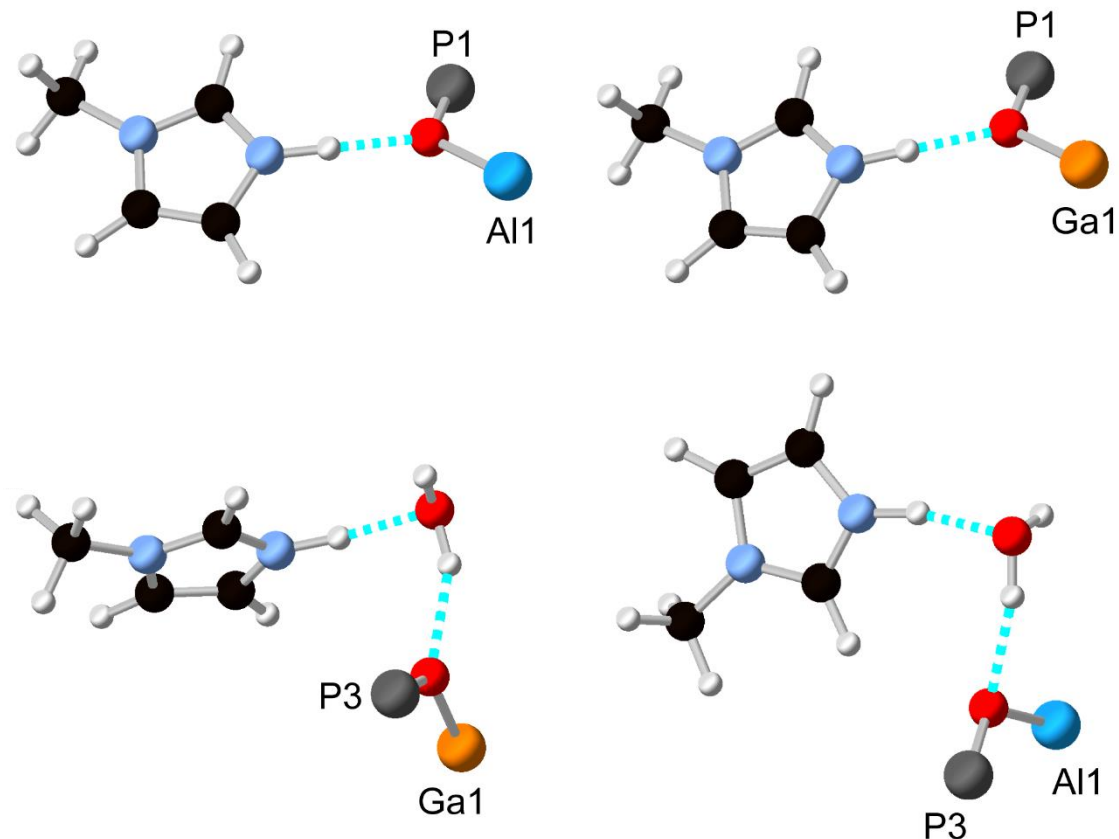
The CHA Framework

- The SDA was refined in two different orientations in the AIPO and GaPO end members
- ^{13}C CP MAS shows small changes but masked by broadening
- Is there a fundamental reason for this difference or just different static snapshots of a dynamic molecule?



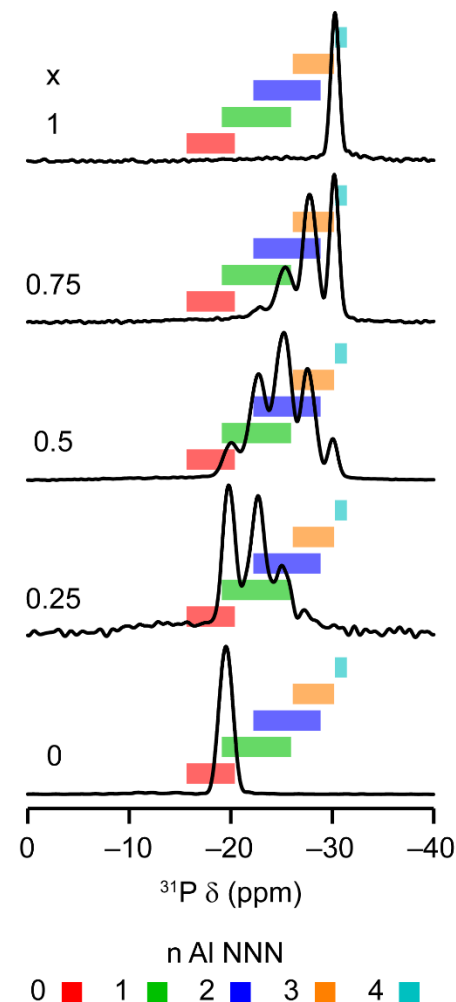
The CHA Framework

- Again, hydrogen bonding seems to drive local arrangement of molecules in the pores
- Different framework O involved in hydrogen bonding if water is present/absent
- We'd expect dynamics but haven't confirmed that yet
- Demonstration of how small molecules may interact with the pore wall during catalysis and how subtle changes in charge on O may affect this



The CHA Framework

- Calcination causes increase in symmetry from $P-1$ to $R-3$
- Single P site, which will have an environment that is a superposition of the environments from P1, P2 and P3 from before
- This time the spectra look like there is a random distribution of cations even though we know that's not where we started
- Predictions for the starting arrangement of cations also agree well



Conclusions

- NMR alone isn't enough to understand the most complicated of materials. Crystallography on its own isn't very useful for this either
- By combining the two and linking them via DFT, it is possible to get surprisingly detailed insight into the physical phenomena behind *why* structures behave the way they do
- Disorder isn't always random
 - F/OH disorder in GaPO-34A has favourable hydrogen bonding arrangements
 - Ga/Al disorder in AlGaPO-34 favours octahedral Al but not exclusively
 - still working on the dynamic disorder!

Acknowledgments

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