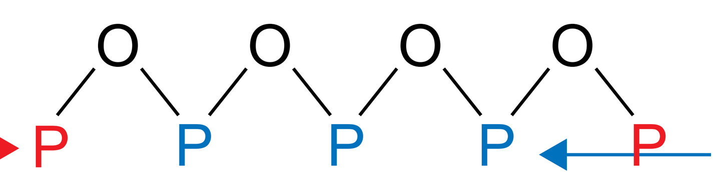
# Probing the Structures of Phosphate Glasses by Solid State NMR

**Nathan Barrow**
Supervisors: Dr Diane Holland, Dr Steven P Brown
Department of Physics, University of Warwick, U.K.

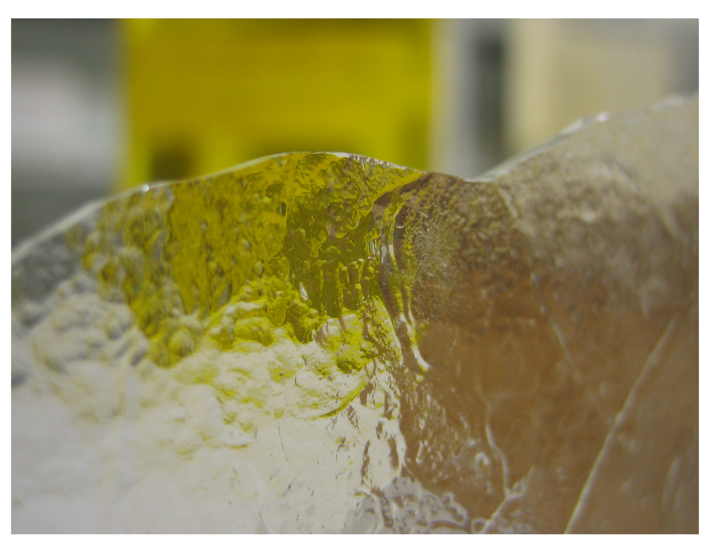
## Cadmium Phosphate Glass

The glass is made up of Phosphorus atoms connected together with bridging Oxygens. These chains are amorphously arranged, forming a glass. Characterising such disordered solids is difficult. The reason for analying the atomic level structure is because the macroscopic properties emerge from this underlying structure.

$Q_1$ - connected to 1 Oxygen




$Q_2$ - connected to 2 Oxygens


A Photograph of the glass created

Uses of Phosphate glasses:

High level nuclear waste encapsulation. (As a good solvent with very low internal ion diffusion when solid)

Lasers (By doping with Nd3+)

Biomedicine (Bone growth, Joint protheses, that are stronger and more biocompatible, Bone cement and repair, Dental implants that are stronger than normal teeth)

## Making the Glass


Mixing together the reactants

$xCdCO_3 + 2(1\text{-}x)H_3PO_4$

Cadmium Carbonate + Phosphoric acid

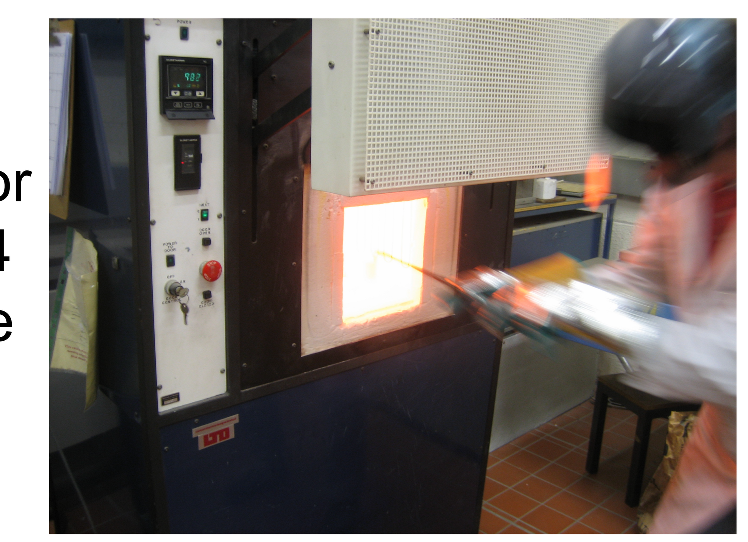
↓

$xCdO{\bullet}(1\text{-}x)P_2O_5 + CO_2 + 3H_2O$

Cadmium Pyrophosphate + Carbon Dioxide + Water

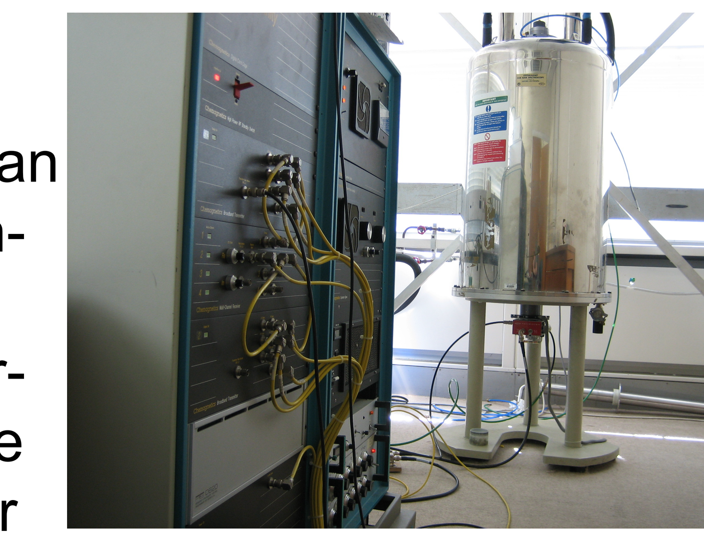
The first stage is carefully weighing the reactants, then slowly mixing them in a beaker.

Secondly, the powdery mixture is put into a furnace that heats up to 1100°C and holds there for a varying amount of time from 4 to 28 hours. The molten mixture is then poured onto cold metal and splatted to cool it quickly into a glass.

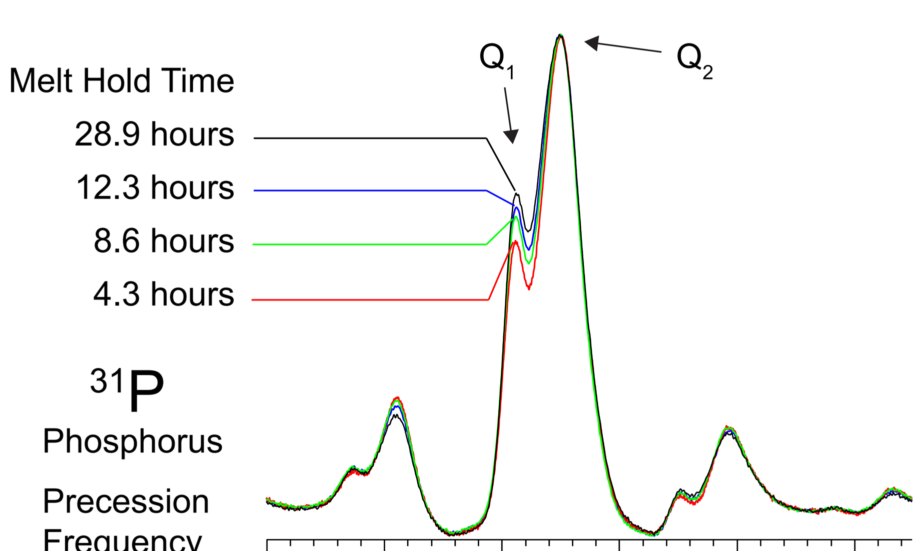

Taking the glass out of the furnace

## Nuclear Magnetic Resonance

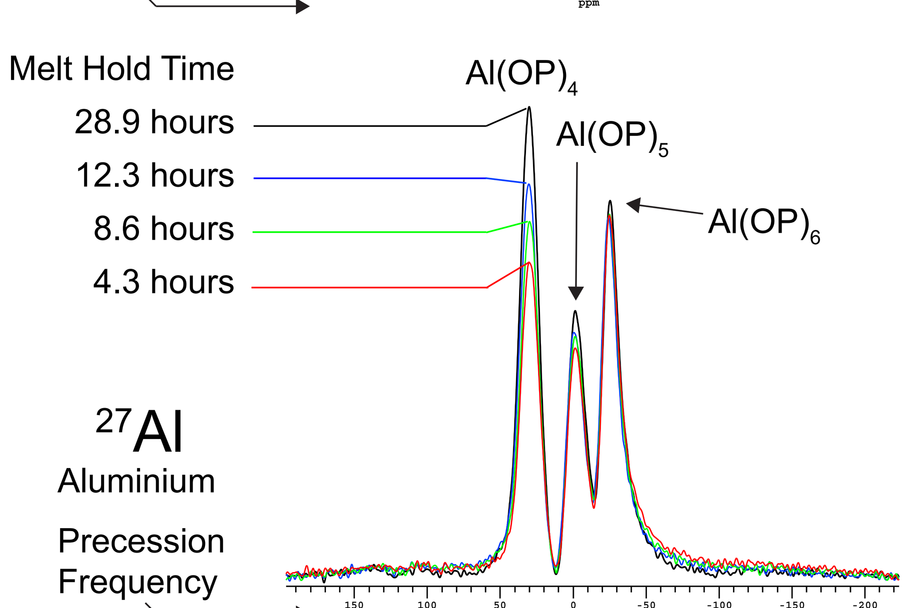
NMR uses a superconducting magnet to generate magnetic fields 250,000 times greater than the Earth's. NMR probes the inherent magnetic properties of atomic nuclei. The strong external magnetic field causes these magnetic moments to rotate, or precess, around the magnetic field. NMR Spectroscopy measures the frequency of this precession. This is a powerful probe of the chemical structure because the exact frequency is very sensitive to the surrounding electrons, which are also magnetic particles. NMR can show the through-bond and through-space connectivies because atomic nuclei are affected by other atomic nuclei.


An NMR Spectrometer

## NMR Spectra

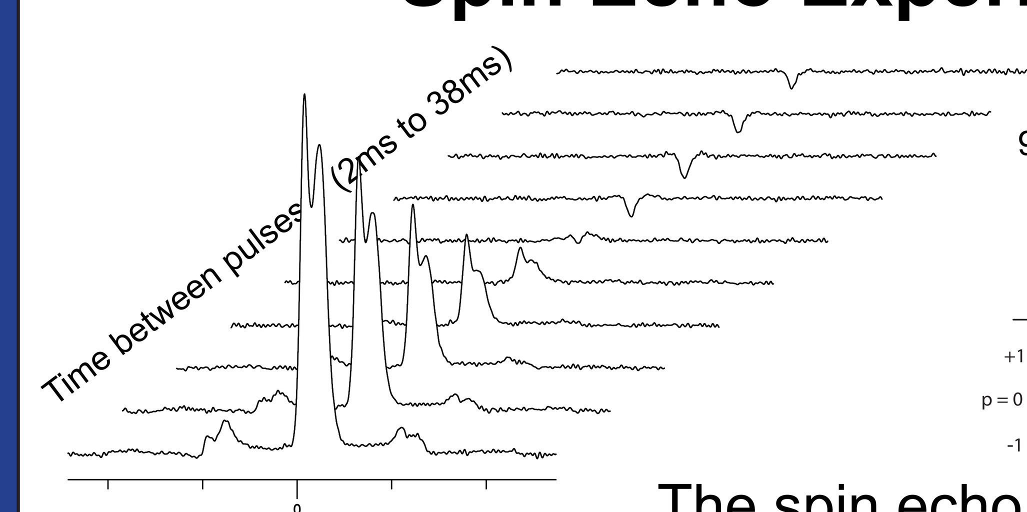


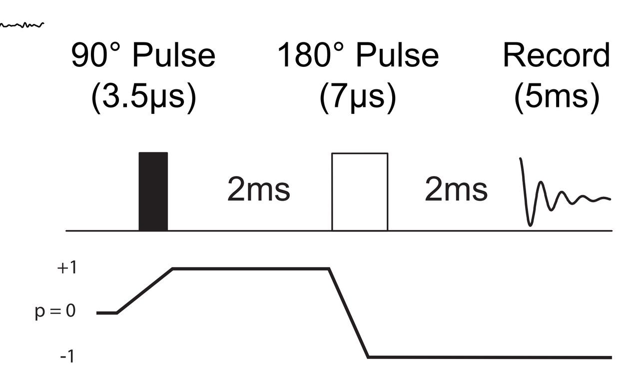

These spectra show how different durations the glass spent at 1100°C affected the structure of the glass. $Q_1$ is the $P(OP)O_3^{2-}$ site, $Q_2$ is the $P(OP)_2O_2^{1-}$ site.




The three peaks of the $^{27}Al$ spectrum represent the three coordination sites that alumina can exist in the glass. The alumina dissolved into the glass from the furnace crucibles.

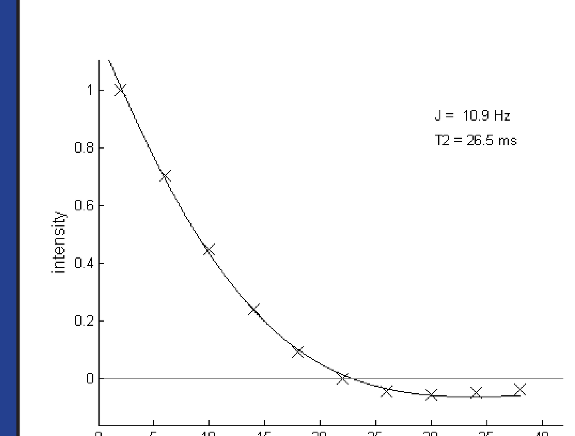
## Spin Echo Experiment




Above: Spin echo experiment with varying time between pulses

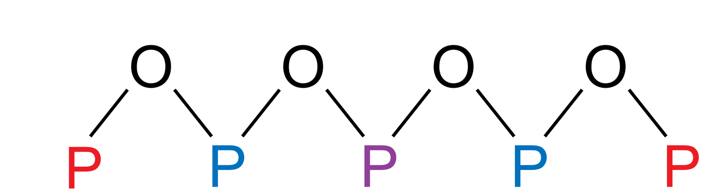
Below: Plot of peak heights against time between pulses

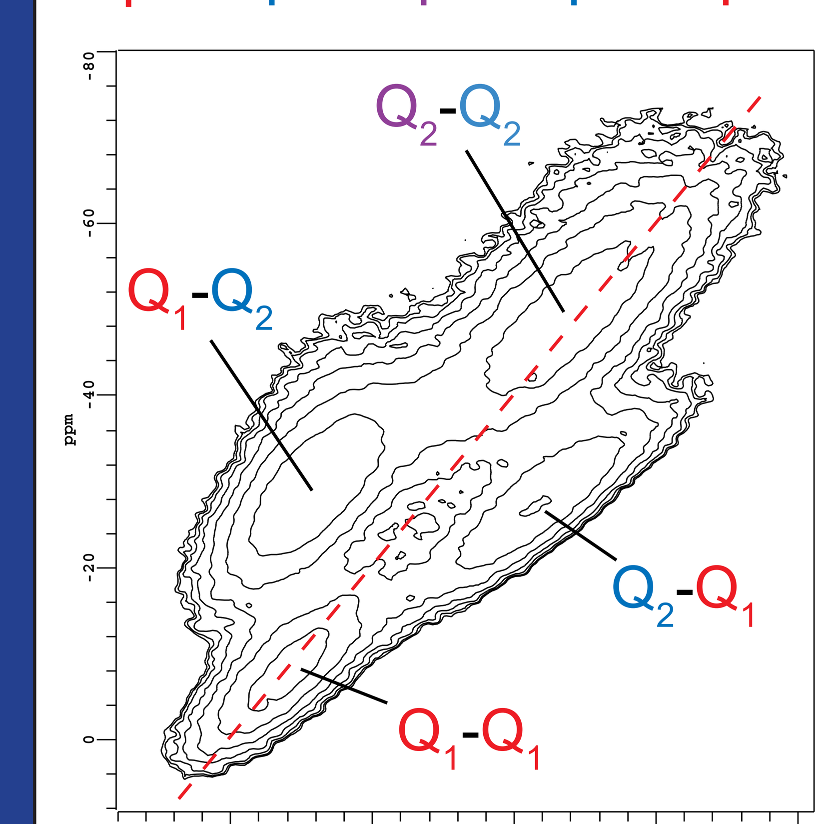


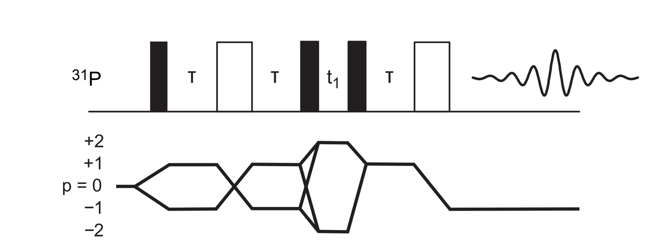

The spin echo removes broadening due to the inherent disorder in the glass. Hence we can measure the basic through bond connectivities of the P-O-P chain. It is also a potential source of structural information such as bond angles. By fitting the decay to $cos(2\pi J\tau)exp(-2\tau/T_2)$ we can find the through bond J-Coupling value of two Phosphorus nuclei. (See graph on left)

## Two-Dimensional Spectroscopy

The ironically named INADEQUATE pulse sequence, which stands for Incredible Natural Abundance DoublE QUAntum Transfer Experiment, produces 2D spectra that are more informative than 1D spectra in that they reveal which atoms are bonded together.





The refocussed INADEQUATE pulse sequence

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