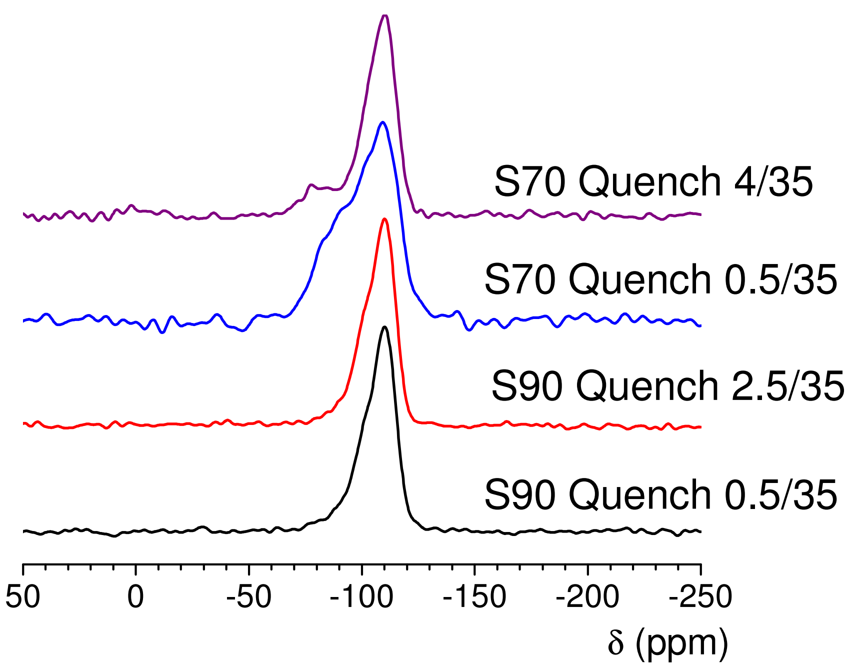
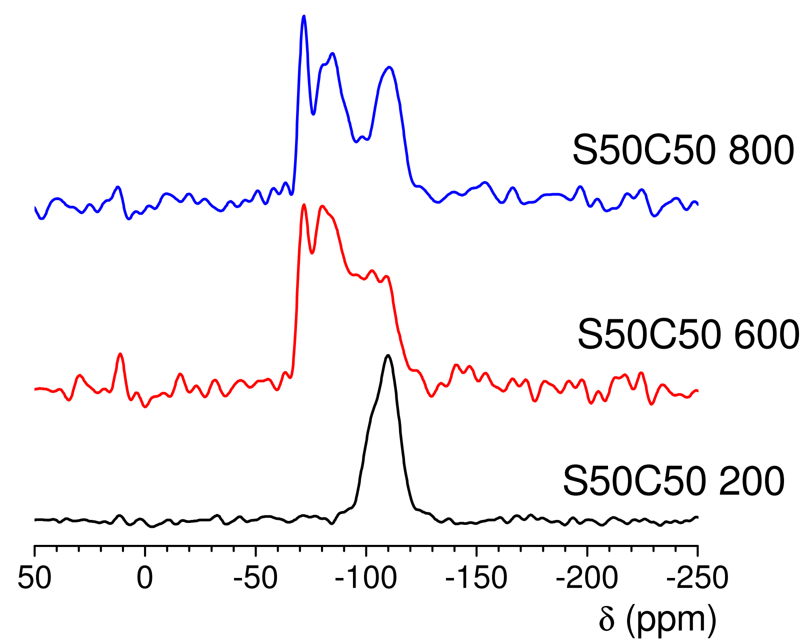
^{29}Si MAS NMR

SiO_2-CaO sol-gel samples:

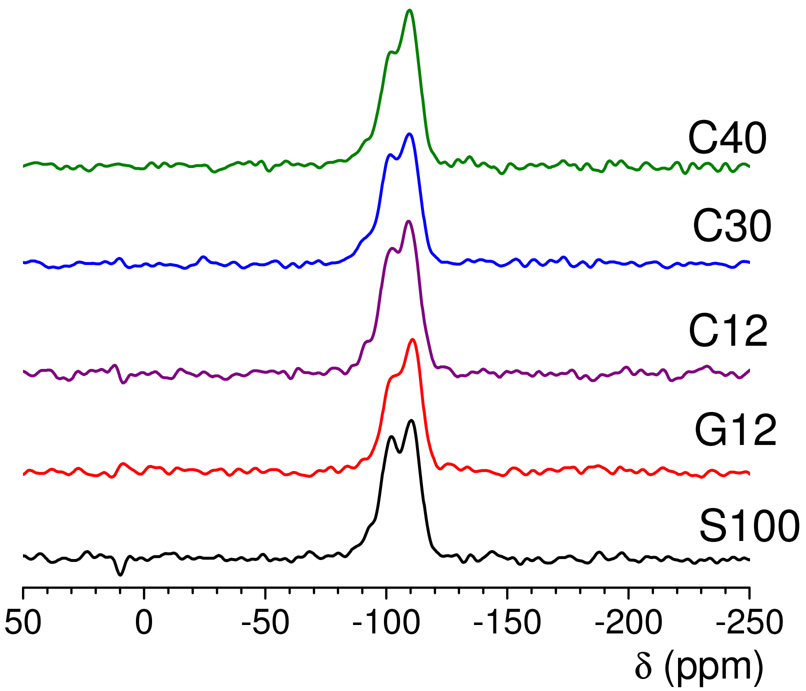
S50 – **50% SiO_2, 50% CaO**
S70 – **70% SiO_2, 30% CaO**
S90 – **90% SiO_2, 10% CaO**

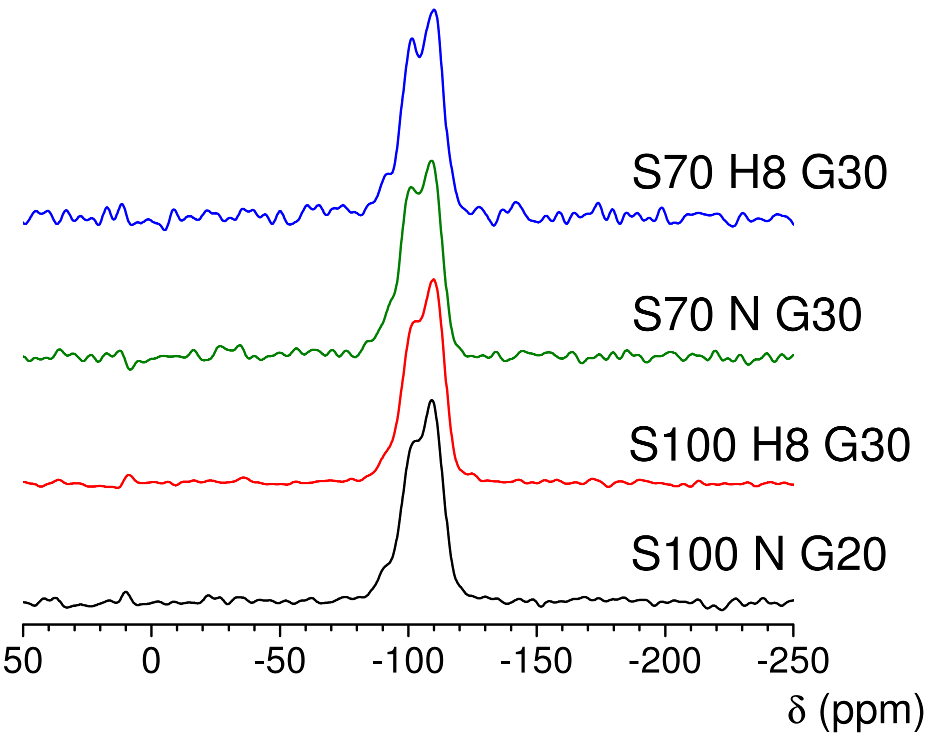




^{29}Si MAS NMR

Hybrids containing collagen (C) and gelatin (G)



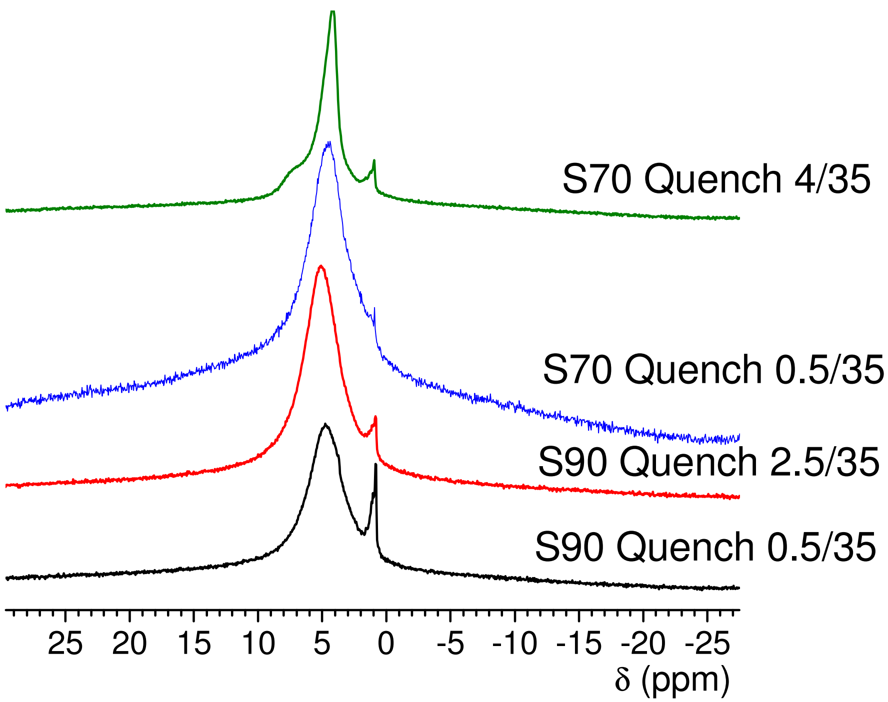


^{29}Si MAS NMR

Sample	Peak 5 (Q^0)			Peak 4 (Q^1)			Peak 3 (Q^2)			Peak 2 (Q^3)			Peak 1 (Q^4)		
	δ ppm	FWHM ppm	I %	δ ppm	FWHM ppm	I %	δ ppm	FWHM ppm	I %	δ ppm	FWHM ppm	I %	δ ppm	FWHM ppm	I %
S90 Quench 0.5/35	-	-	-	-81.1	6.02	2	-92.0	11.26	9	-100.6	9.16	21	-110.3	11.26	68
S90 Quench 2.5/35	-	-	-	-	-		-90.9	10.59	7	-100.8	9.76	27	-110.5	10.59	65
S70 Quench 0.5/35	-72.6	6.27	2	-81.0	9.02	10	-91.0	11.76	23	-100.4	9.41	16	-110.2	13.33	49
S70 Quench 4/35	-77.1	6.43	5	-83.9	8.03	5	-91.8	8.93	5	-101.7	10.71	26	-110.8	11.25	59
S50C50Et 200	-	-	-	-	-	-	-92.9	7.31	3	-101.2	7.65	21	-110.2	11.13	76
S50C50Et 600	-71.5	5.94	17	-78.7	7.58	17	-86.0	10.05	26	-102.6 -96.0	6.44 8.91	8 15	-109.6	9.48	17
S50C50Et 800	-71.9	5.59	19	-84.7 -79.2	6.52 5.59	16 12	-90.8	7.45	11	-97.8	5.78	4	-110.1	14.72	37
Organic-inorganic hybrids															
S100	-	-	-	-	-	-	-92.9	6.69	8	-101.3	7.86	40	-110.5	8.70	52
G12	-	-	-	-	-	-	-90.7	5.82	3	-101.9	9.22	41	-111.1	8.73	56
C12	-	-	-	-	-	-	-91.4	5.82	6	-100.9	8.81	41	-109.9	8.96	53
C30	-	-	-	-	-	-	-91.5	8.98	10	-100.7	7.83	34	-109.7	9.55	56
C40							-92.2	8.74	9	-100.7	7.46	30	-109.6	9.53	61
S100 N G20	-	-	-	-	-	-	-90.9	8.08	8	-101.0	8.85	39	-109.8	8.85	53
S100 H8 G30	-	-	-	-	-	-	-91.1	7.52	6	-101.0	9.20	40	-110.3	9.32	54
S70C30 N G30	-	-	-	-84.9	6.46	3	-92.0	6.64	8	-100.2	8.12	37	-109.2	9.23	52
S70C30 H8 G30	-	-	-	-	-	-	-91.2	7.10	8	-100.5	7.73	35	-109.9	9.62	57

Errors associated with measurements are—FWHM ± 50Hz, δ ±1.5 ppm and Integral ±2%.

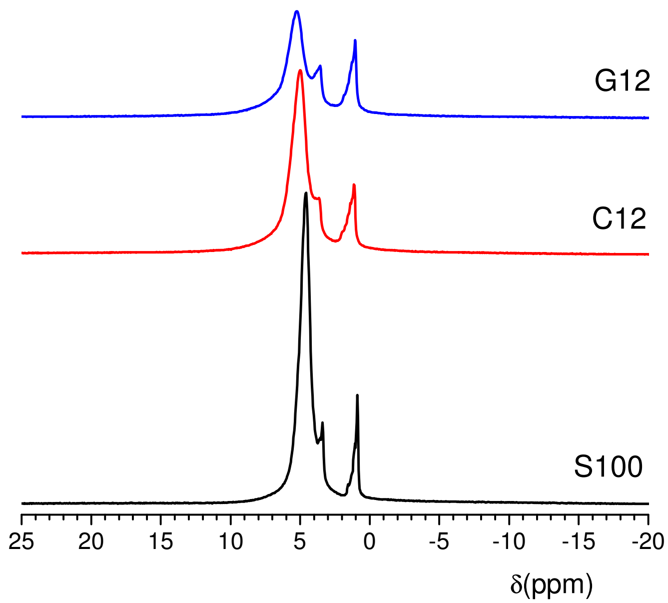
^{1}H MAS NMR

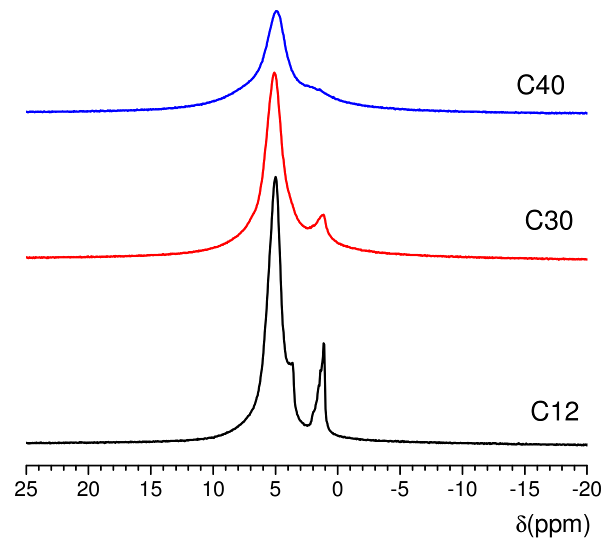


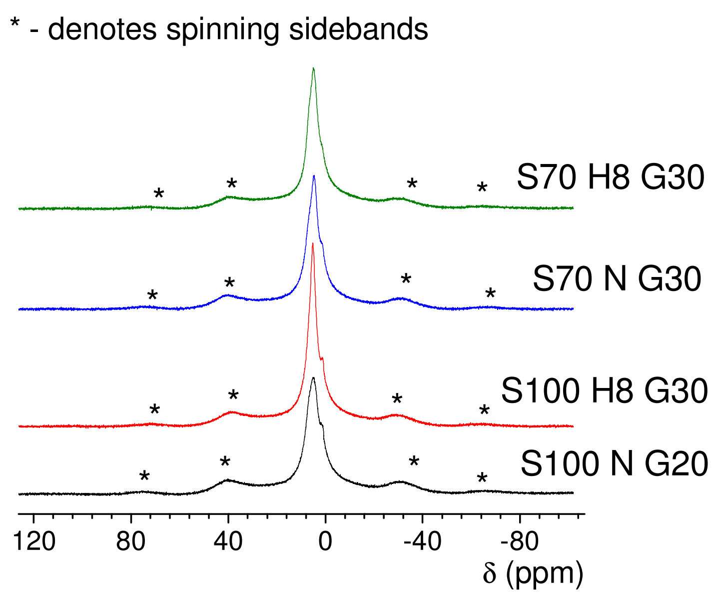
Sample	Hydrogen content (mol/g)
S90 Quench 0.5/35	4.14×10^{-3}
S90 Quench 2.5/35	5.42×10^{-3}
S70 Quench 0.5/35	3.19×10^{-3}
S70 Quench 4/35	3.66×10^{-3}

^{1}H MAS NMR

Organic-inorganic hybrids



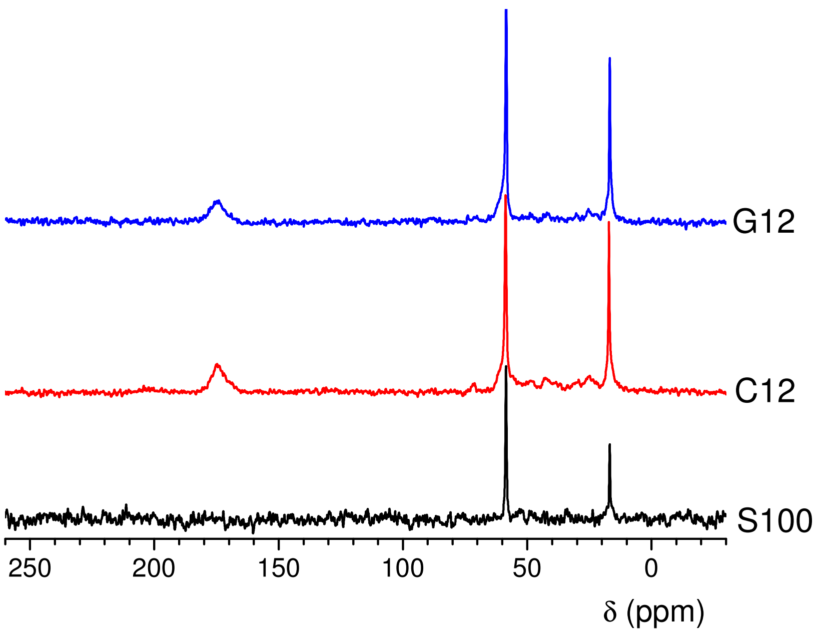




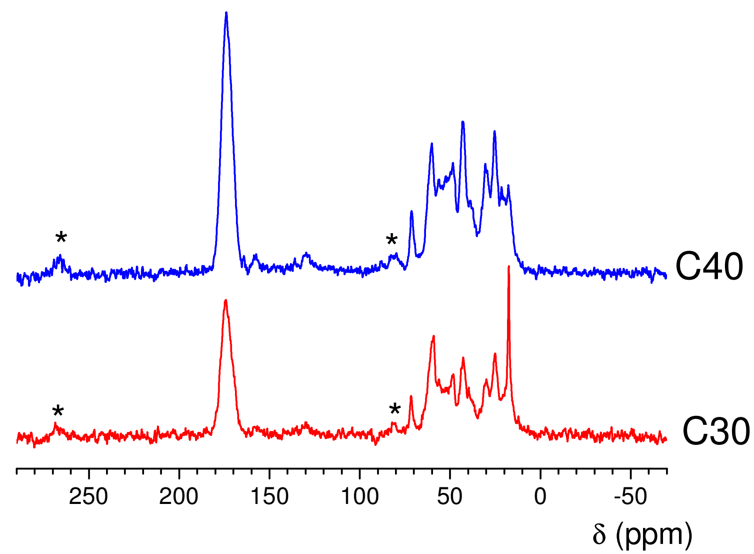
Sample	Hydrogen content (mol/g)
S100	1.21×10^{-2}
G12	1.16×10^{-2}
C12	1.08×10^{-2}
C30	1.28×10^{-2}
C40	1.20×10^{-2}
S100 N G20	1.85×10^{-2}
S100 H8 G30	1.83×10^{-2}
S70 N G30	2.12×10^{-2}
S70 H8 G30	2.24×10^{-2}

^{13}C CP MAS NMR

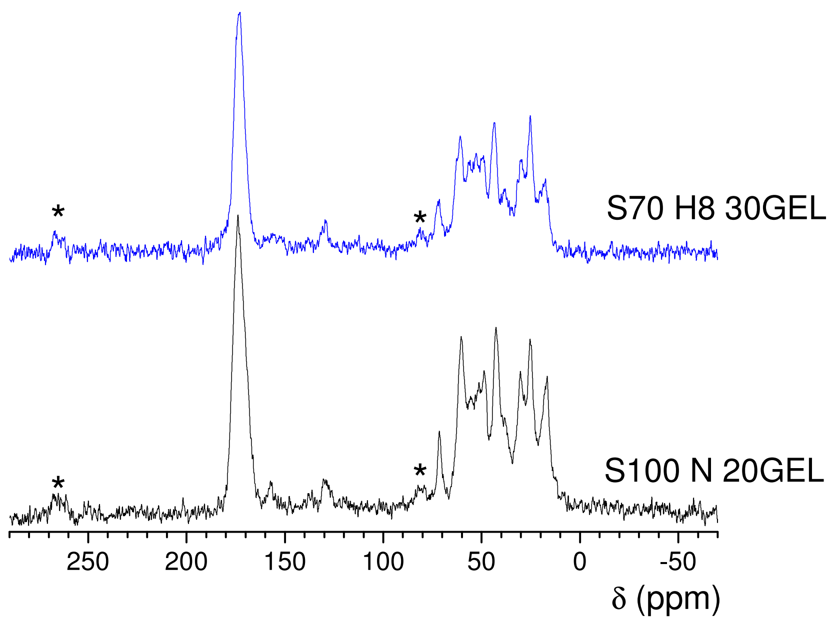
Hybrids containing collagen (C) and gelatin (G)



* denotes spinning sidebands

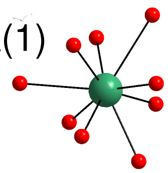


* denotes spinning sidebands

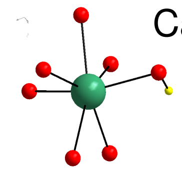


Probing the local environment of calcium in Mg-substituted apatites

Ca(1)

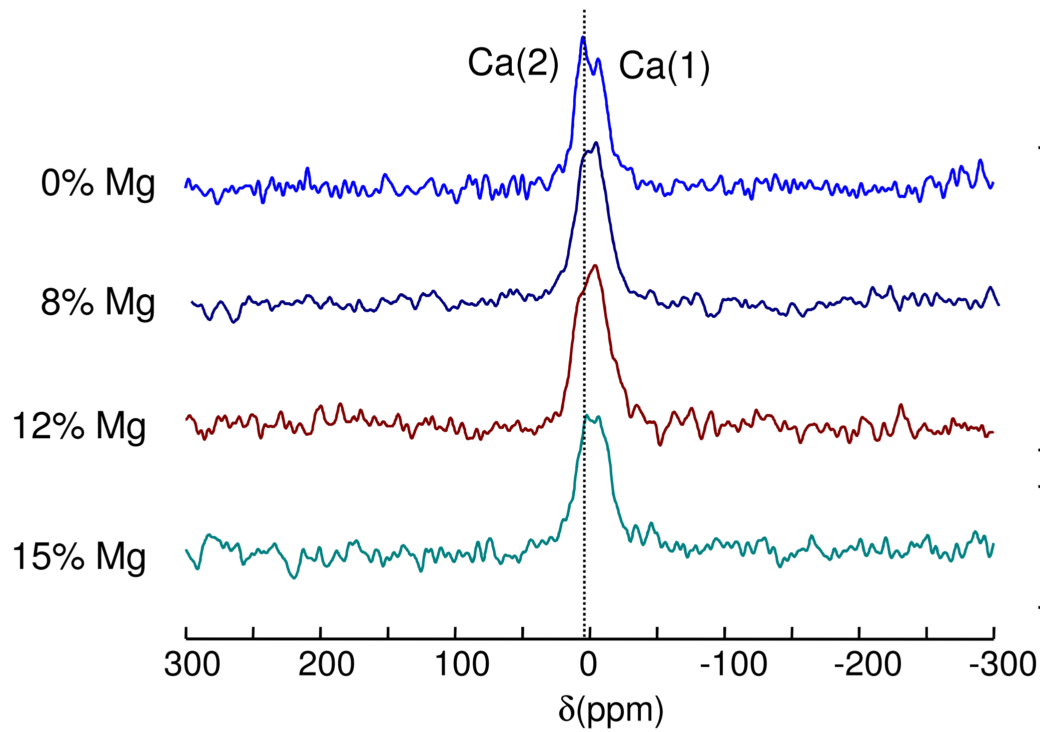


$Ca_{10-x}Mg_x(PO_4)_6(OH)_2$



Ca(2)

^{43}Ca MAS NMR spectra at 18.8 T



Decrease in relative intensity of Ca(2) signal

↓

Mg^{2+} enters the **Ca(2) site** at low Mg contents

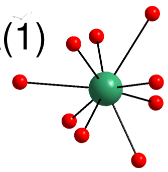
Mg^{2+} occupies Ca(1) **and** Ca(2) sites?

… but the interpretation of NMR data relies on the **hypothesis** that ^{43}Ca NMR parameters of the non-substituted apatite stay valid in the case of substituted apatites…

Is this actually true?

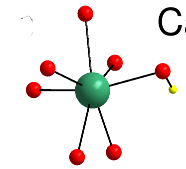
Probing the local environment of calcium in Mg-substituted apatites

Ca(1)

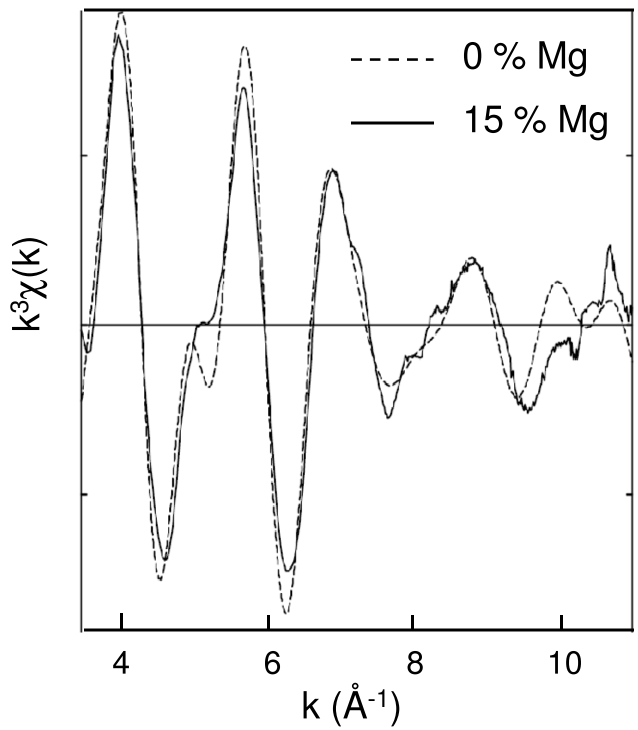


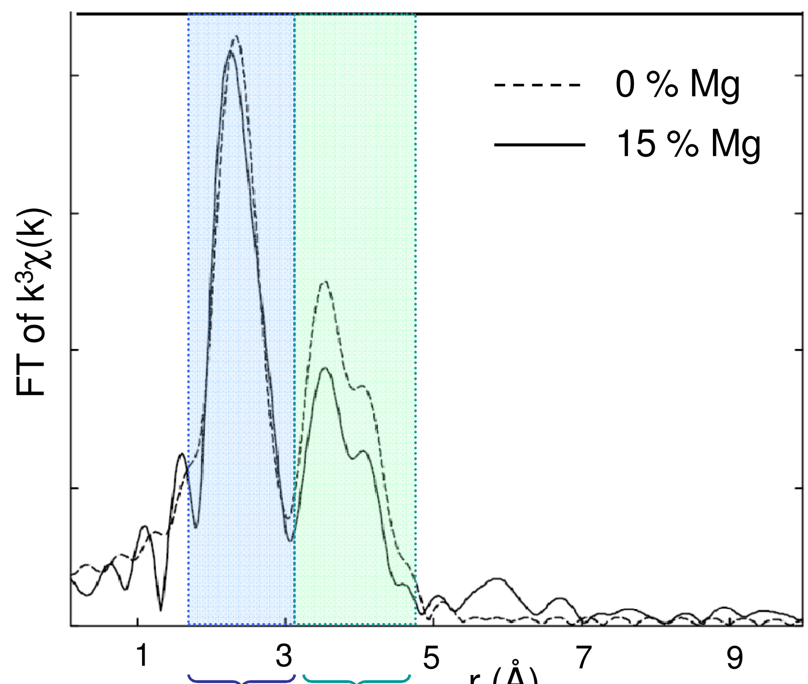
$Ca_{10-x}Mg_x(PO_4)_6(OH)_2$

Ca(2)



Ca K-edge EXAFS



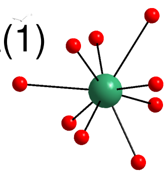


Ca…O shell:
very slight decrease of Ca…O distance in Mg-HA sample (consistent with XRD)

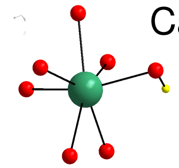
2nd shell (main contribution = Ca…Ca correlations):
Decrease in Mg-HA = proof that Mg enters the lattice

Probing the local environment of calcium in Mg-substituted apatites

Ca(1)

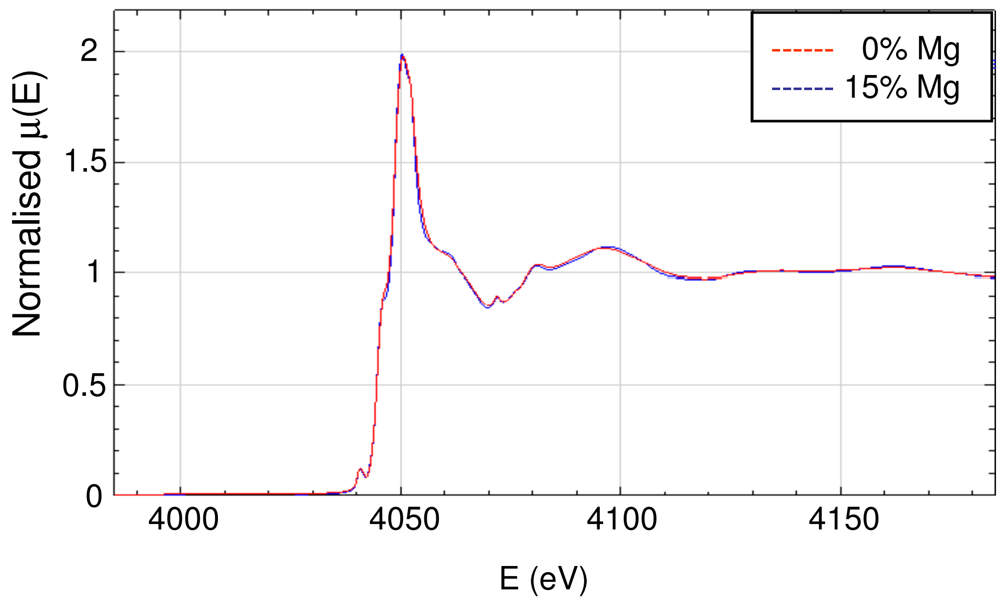


$Ca_{10-x}Mg_x(PO_4)_6(OH)_2$



Ca(2)

Ca K-edge XANES

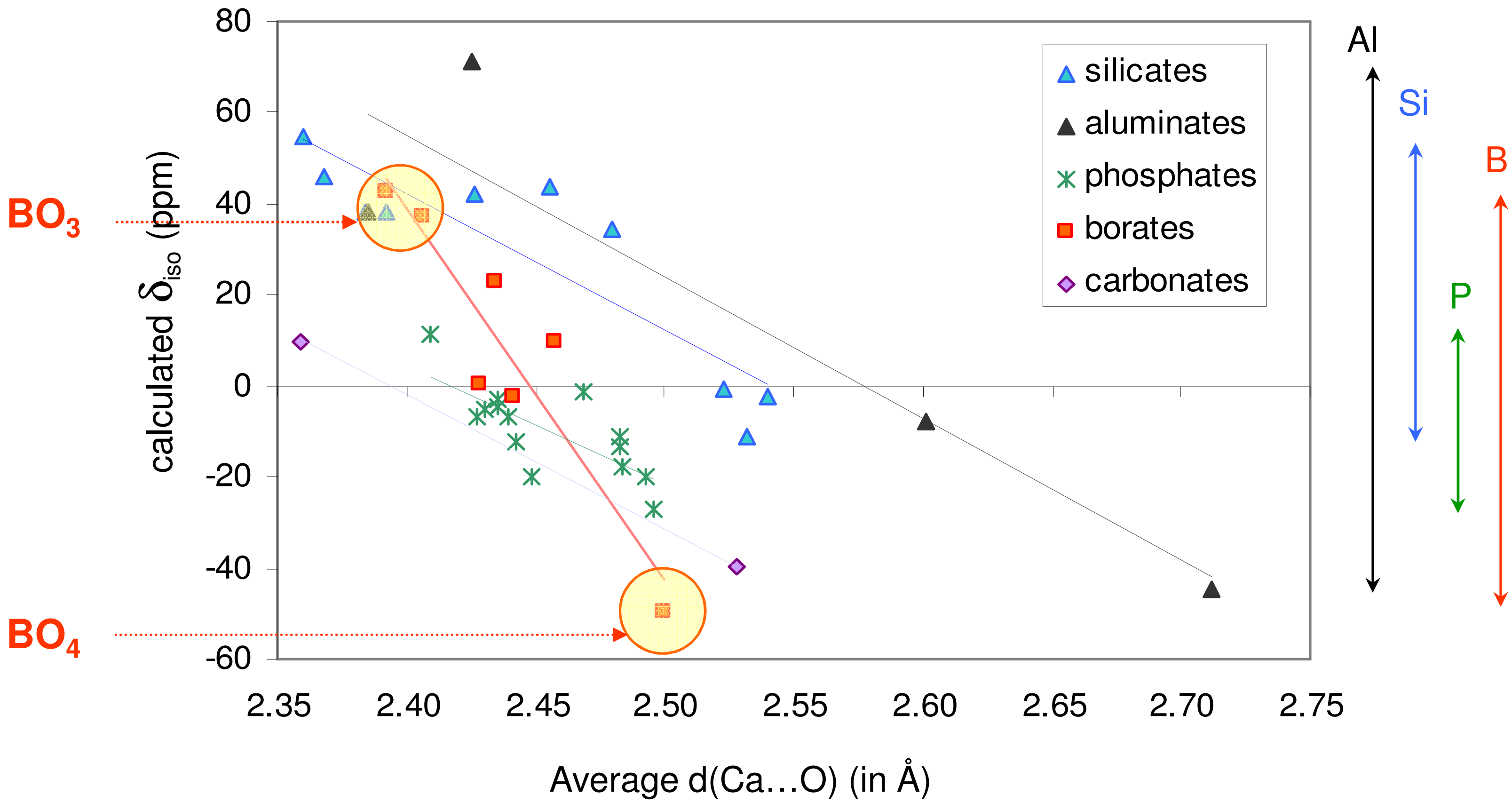


→ No difference between the 2 spectra :
The local geometry around the calcium is **hardly distorted**

The local environment around calcium is only **very slightly** modified due to Mg incorporation in the HA lattice (EXAFS + XANES).

The interpretation of ^{43}Ca NMR data is thus accurate:
Mg enters the Ca(2) site of HA at low levels of incorporation.

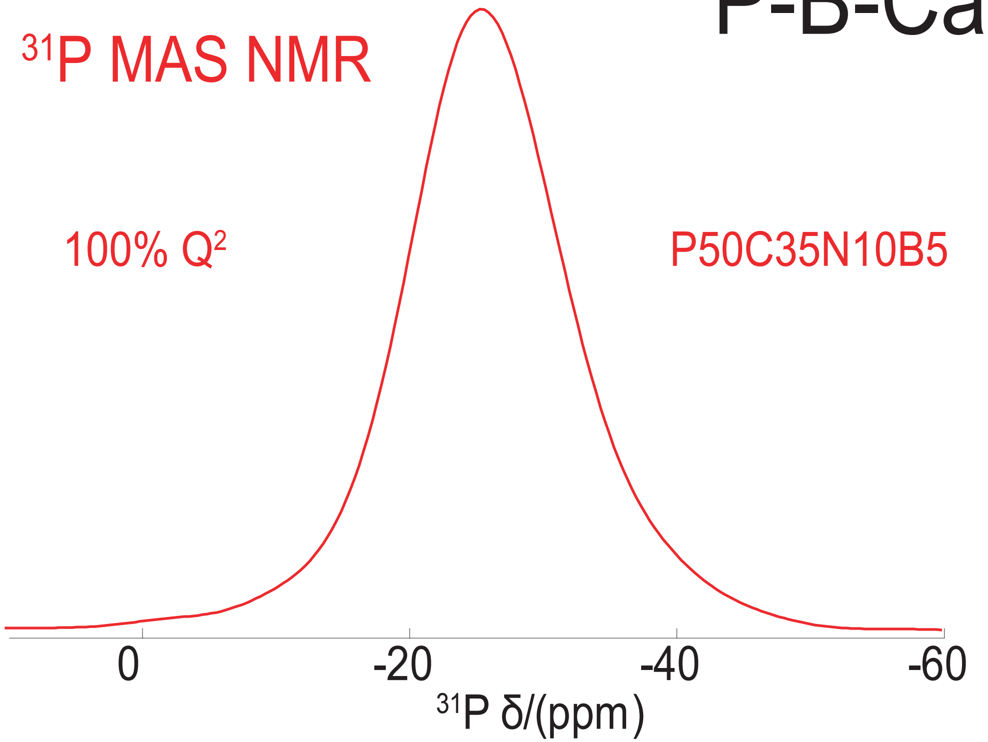
Probing the local environment of calcium in inorganic species: New perspectives from computational studies

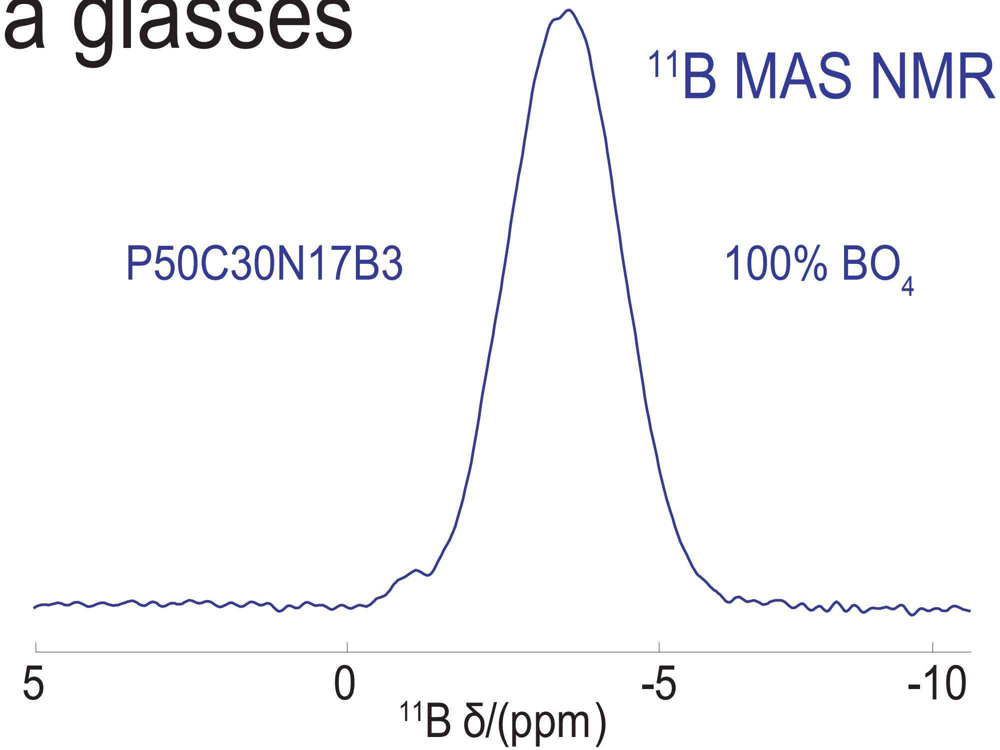


Strong dependance of δ_{iso} to the average Ca…O distance,
In particular in the case of **borates**

^{43}Ca NMR studies of calcium borates worth trying?

P-B-Ca-Na glasses





5 samples, varying [B], [C] and [N]

Small changes in chemical shift

Small changes in peak width

Same chemical shift and line width

100% of boron incorporated into phosphate network

P-B-Ca-Na glasses

^{31}P δ (ppm)	Sample	[C]/([B]+[N])	[B]/([C]+[N])
−24.8	P50C30N17B3	1.50	0.06
−25.1	P50C30N20	1.50	0.00
−25.1	P50C30N15B5	1.50	0.11
−25.5	P50C35N12B3	2.33	0.06
−25.8	P50C35N10B5	2.33	0.11

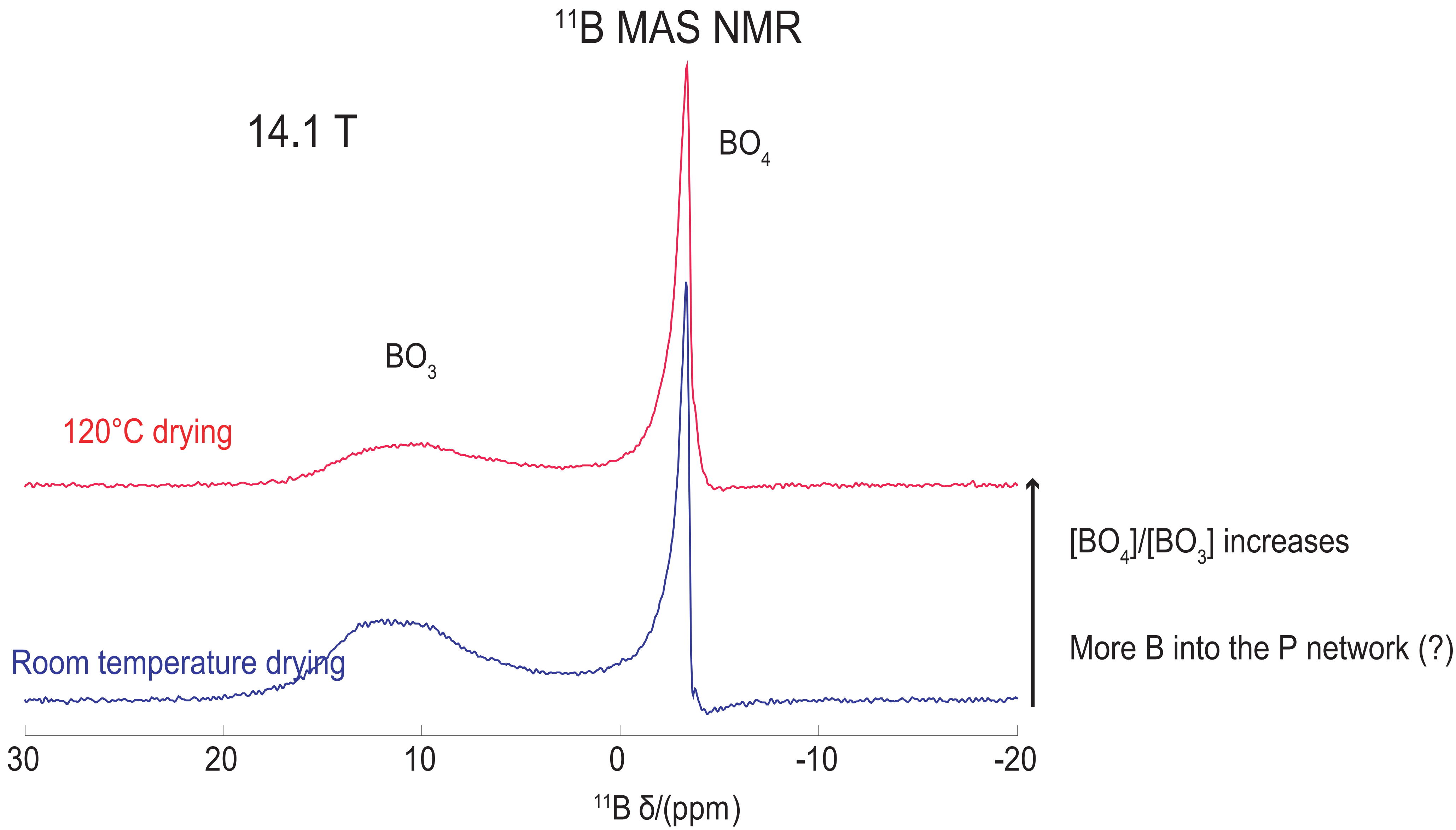
[C] has most effect on δ

Difference between [B] = 3 & [B] = 5

^{31}P width (ppm)	Sample	[C]/([B]+[N])	[B]/([C]+[N])
12.2	P50C30N17B3	1.50	0.06
12.9	P50C35N12B3	2.33	0.06
13.5	P50C30N20	1.50	0.00
13.6	P50C30N15B5	1.50	0.11
14.4	P50C35N10B5	2.33	0.11

[B] has most effect on width

P-B-Si gels

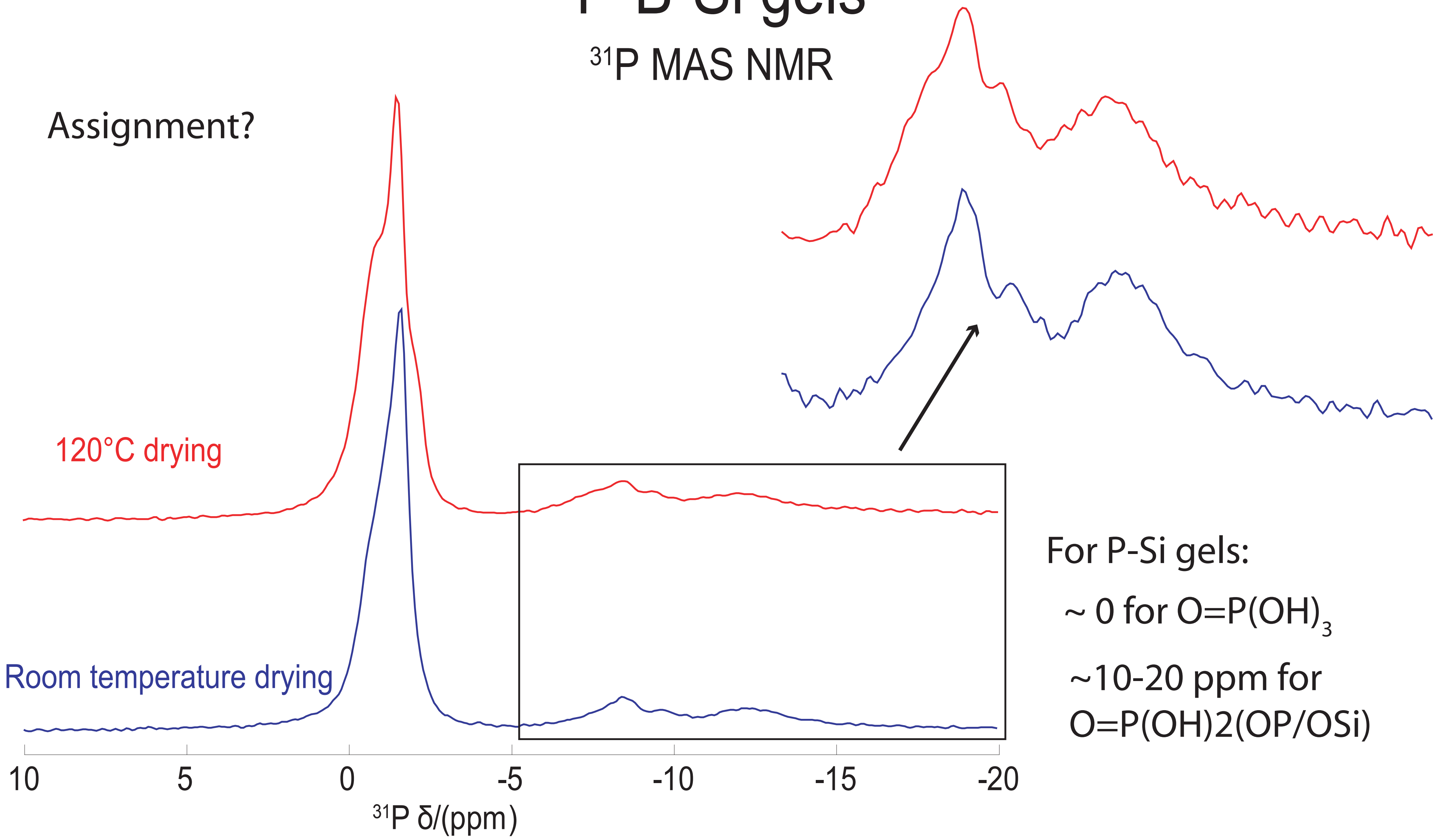


^{11}B MAS NMR
14.1 T
BO$_4$
BO$_3$
120°C drying
Room temperature drying
[BO$_4$]/[BO$_3$] increases
More B into the P network (?)
30
20
10
0
-10
-20
^{11}B δ/(ppm)

P-B-Si gels

^{31}P MAS NMR

Assignment?



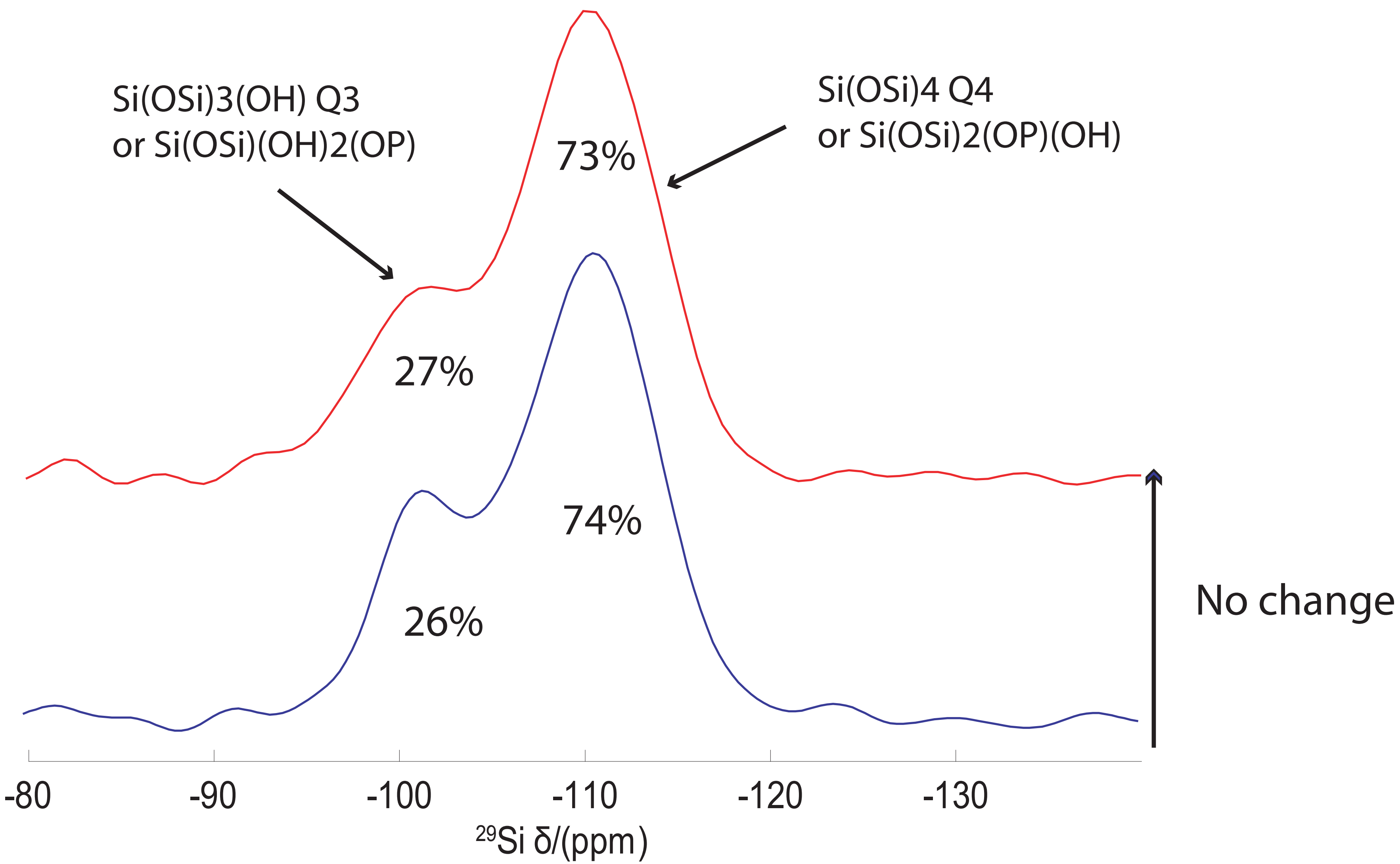
For P-Si gels:

~ 0 for $O{=}P(OH)_3$

~10-20 ppm for O=P(OH)2(OP/OSi)

P-B-Si gels

^{29}Si MAS NMR



Publications in Progress

- *Abou Neel E. A., Chrzanowski W., Pickup D. M., O'Dell L A, Newport R.J., Smith M. E., Knowles J C. Structural properties of strontium doped phosphate based glasses. Journal of the Royal Society Interface: Submitted.*

- *Abou Neel E.A., Sabeel P. V., Knowles J.C. Phosphate based glasses: A perspective. (In Process for Submission).*

- *Abou Neel E. A., Chrzanowski W., Valappil S. P., O'Dell L. A., Pickup D. M., Smith M. E., Newport R. J., Knowles J. C. Synergetic effect of calcium oxide and titanium dioxides on the properties of meta-phosphate based glasses. (In Process for Submission).*

- *In Vivo work on Titanium and Zinc titanium glasses.*

- *In vitro biocompatibility of Titanium with high calcium content glasses.*

Previous study :

(50mol%)P_2O_5 (30)CaO (20-x)Na_2O (x)TiO_2
{x=0,5,10,15}

This study :

(45mol%)P_2O_5 (30)CaO (25-x)Na_2O (x)TiO_2
{x=0,1,3,5,10,15}

(55mol%)P_2O_5 (30)CaO (15-x)Na_2O (x)TiO_2
{x=0,1,3,5}

Bulk glass characterization

- ✓ Density measurements
- ✓ Degradation studies
- ✓ Differential thermal analysis
- ✓ Ion release measurements using IC
- ✓ Ti release using ICP mass
- ✓ X-ray powder diffraction (XRD)

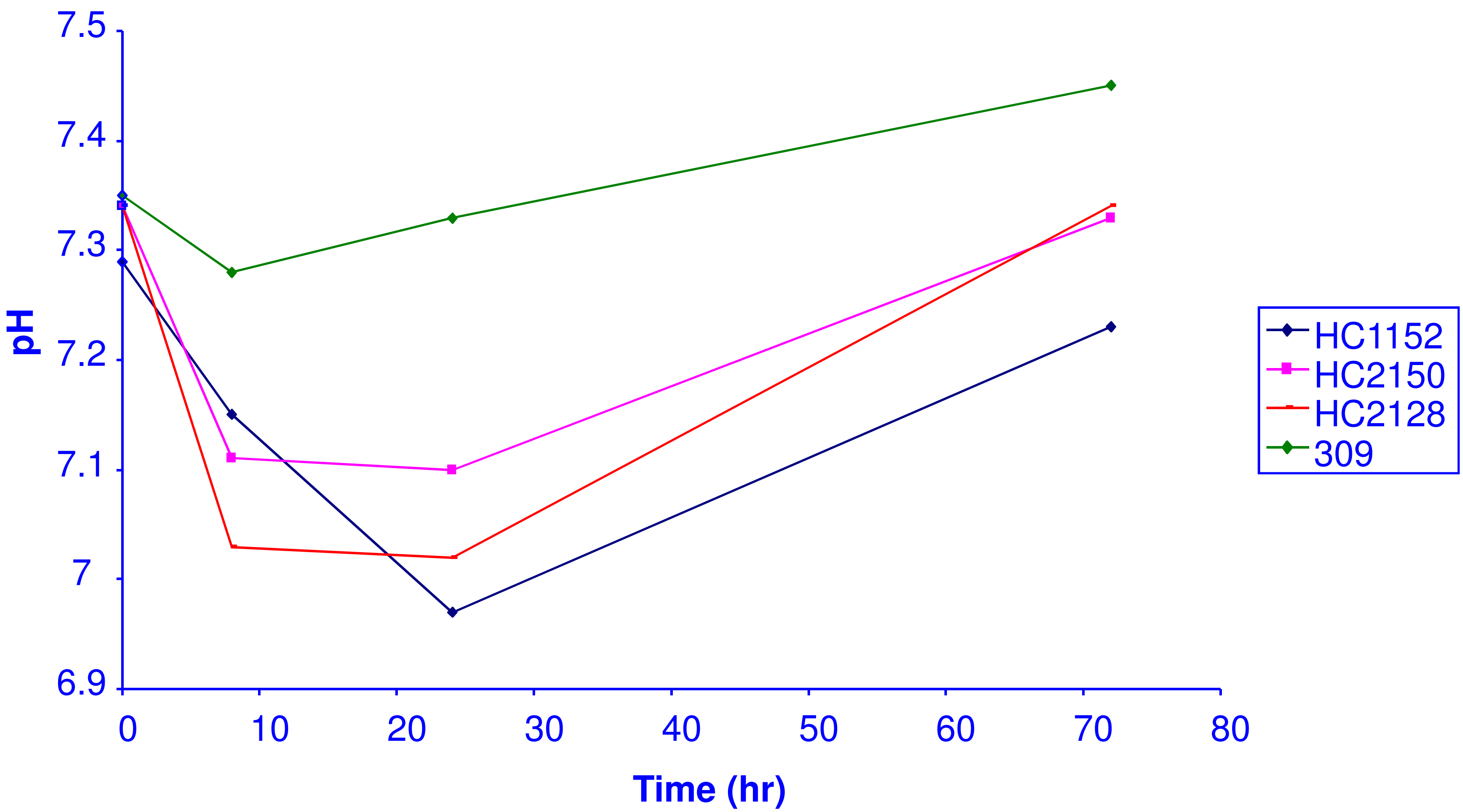
Looking at Glass Ceramics

investigating the crystallisation kinetics of conversion to glass ceramic via:

- Differential thermal analysis
- High Temperature XRD

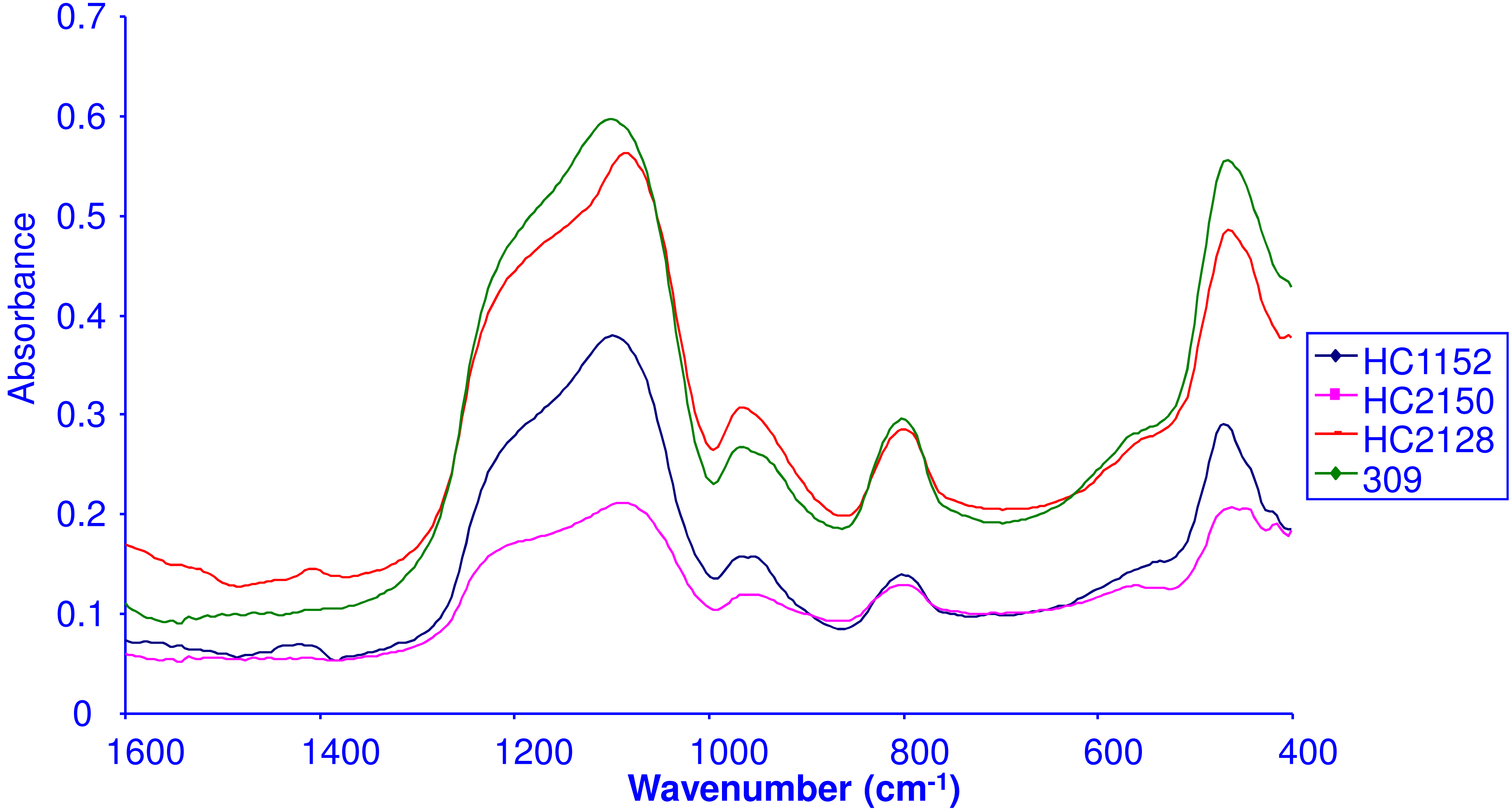
SBF – pH

pH changes of SBF with nanocomposite monoliths



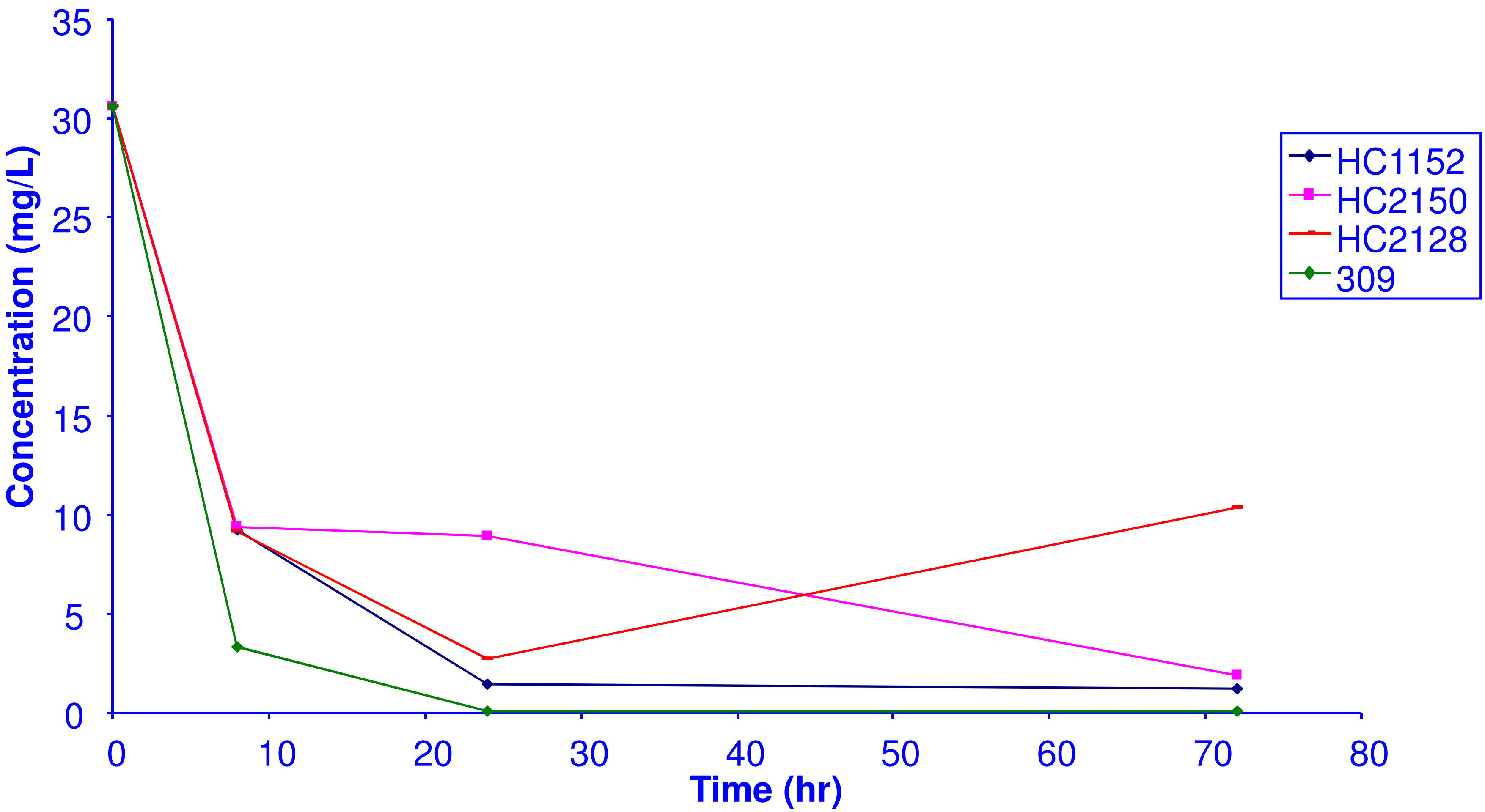
FTIR of SBF samples

Samples reacted for 3days.



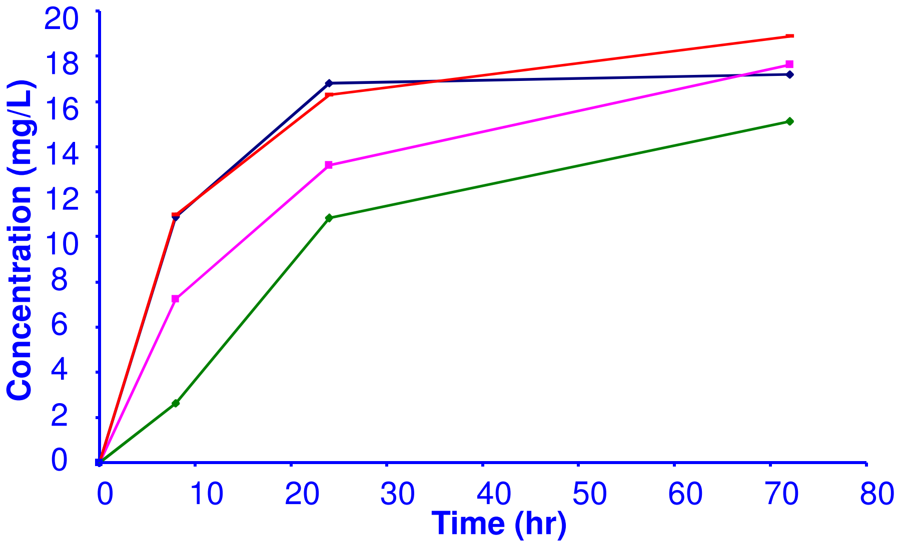
ICP Results

SBF P ion concentration

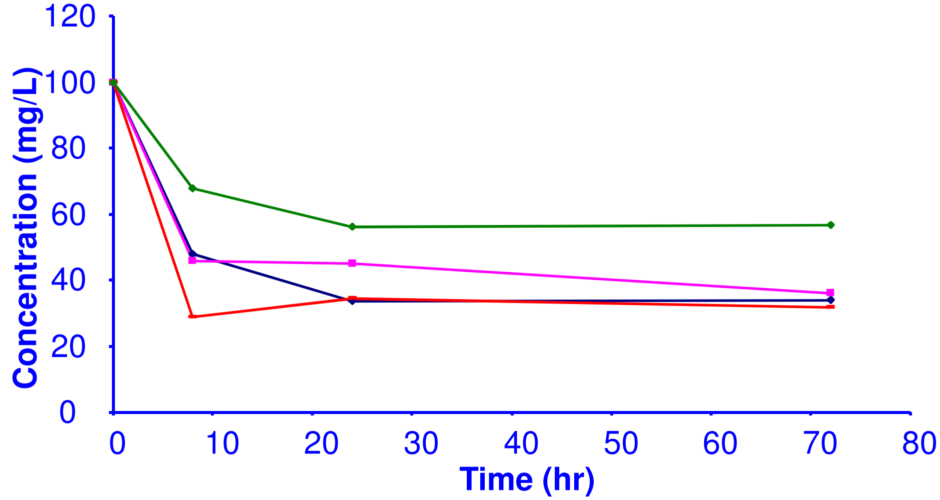


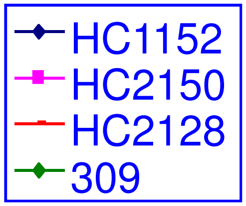
ICP Results 3

SBF Si Ion concentration



SBF Ca Ion concentration





To do

- Samples for toxicity and cell culture
- Mechanical (3-point bending and compression)
- ^{29}Si NMR

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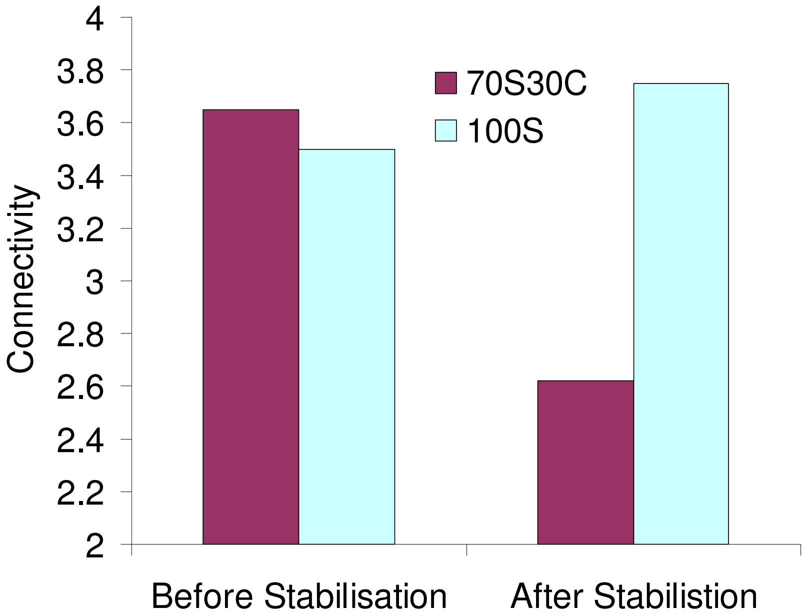
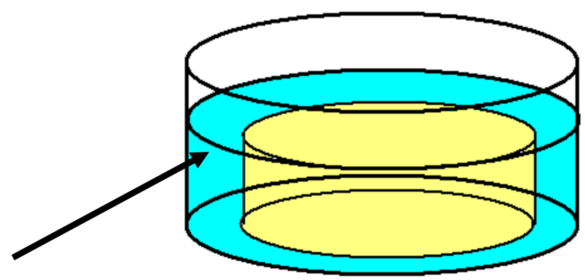
Previously, NMR

- Connectivity Reduced
- Ca not incorporated
- **Quantified by ICP**
- Expelled Liquor after Aging
- [Ca] 1.1 mol/L
- Almost 100% Ca Dissolved!
- This can explain why…





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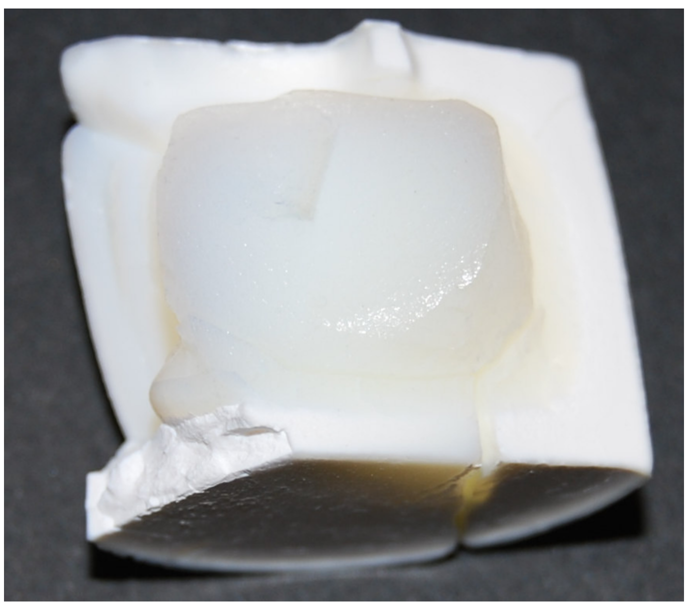
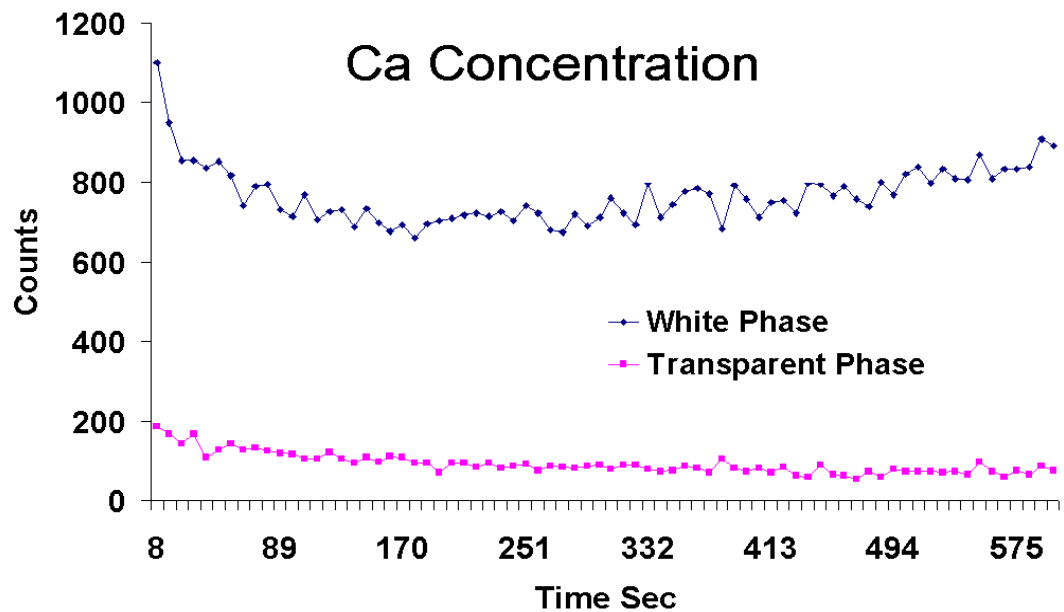
Phase Separation

- During Drying, heterogeneous deposition
- Capillary effects, expelled liquor first
- 25% Ca deposited outside, diffusion difficulty
- **Confirmed by SIMS**
- This can explain why…





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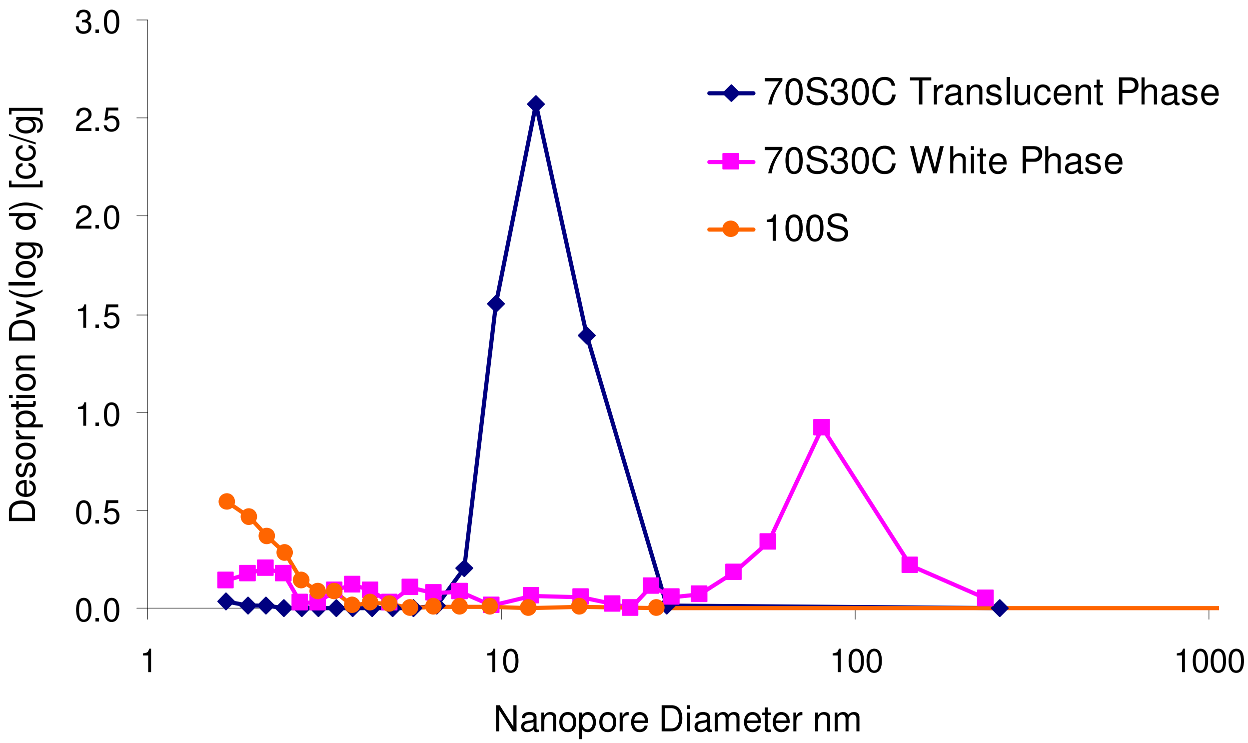
Broad Pore Size Range

- Due to Ca distribution
- Higher [Ca], larger pores!
- Larger pores, lower transparency!



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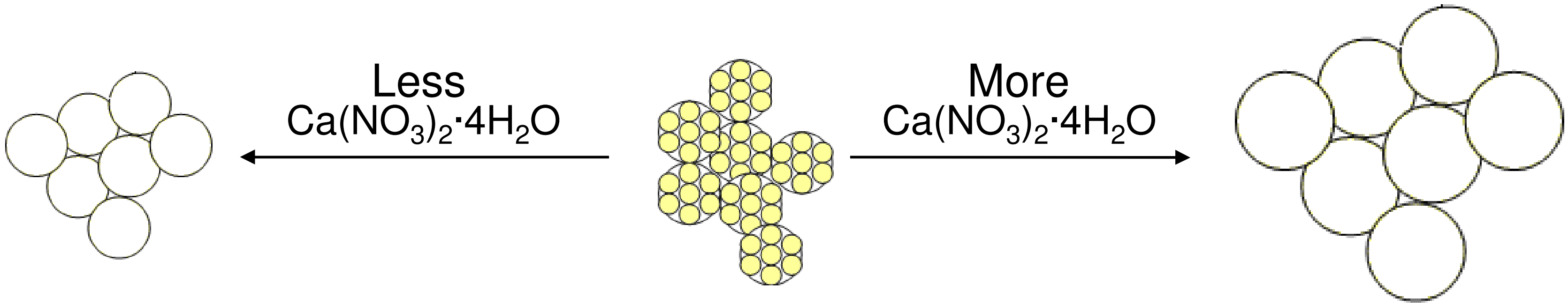
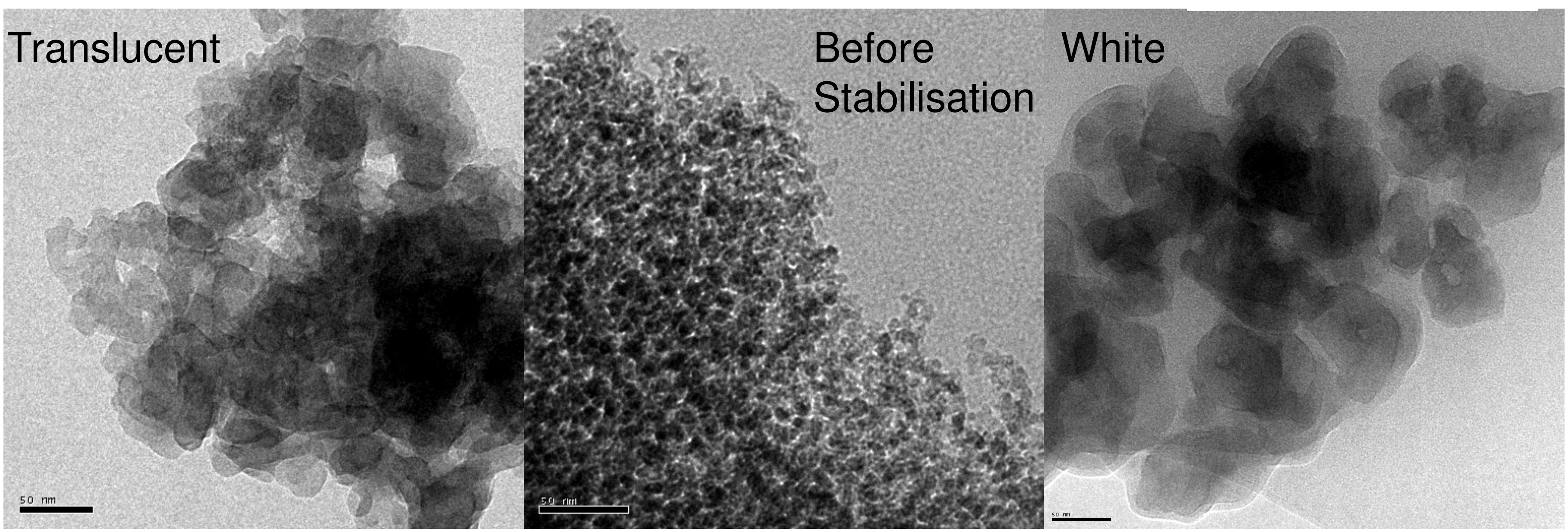
New Role of Calcium

- Not only a “Modifier”, but also a “Fuser”





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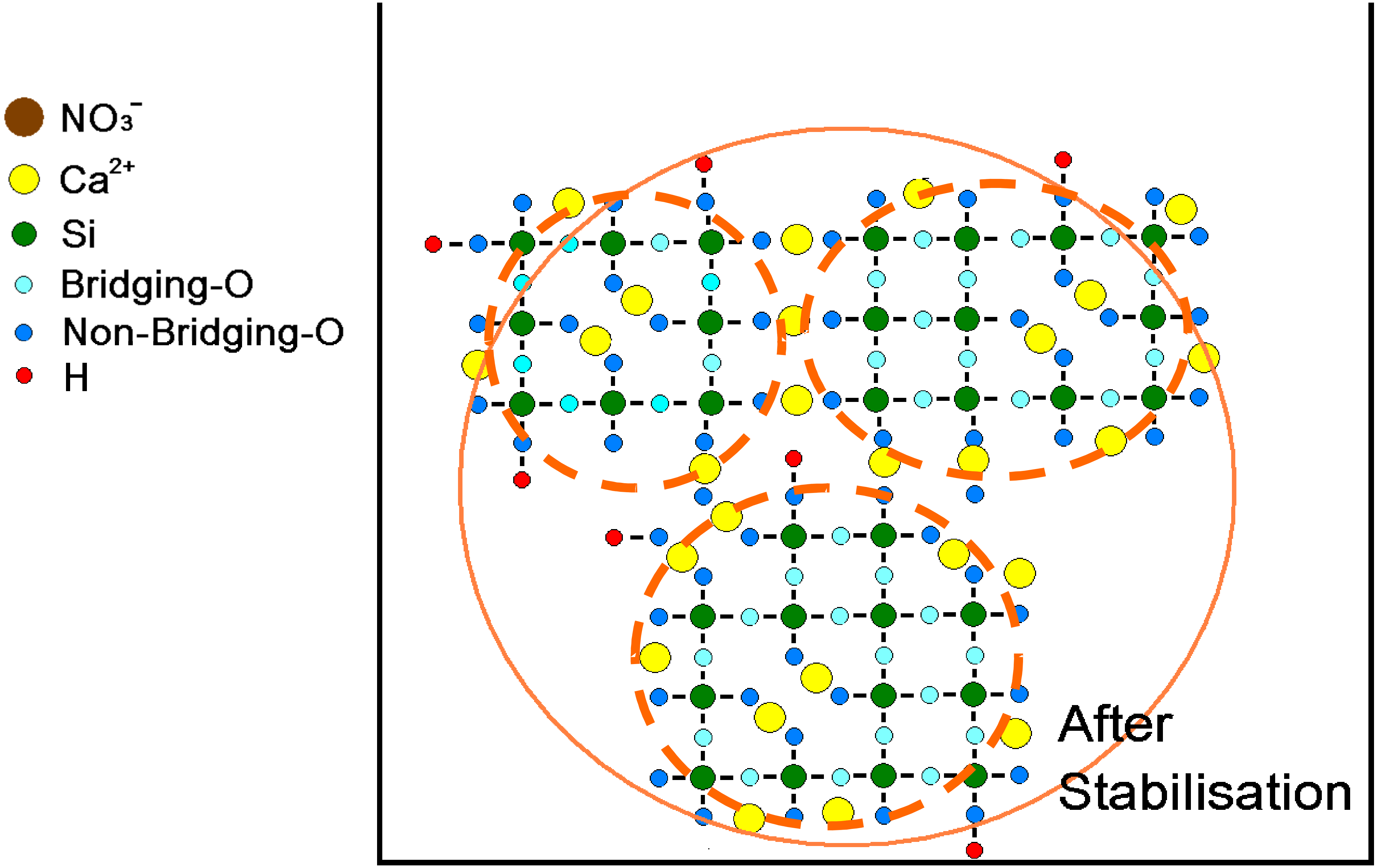
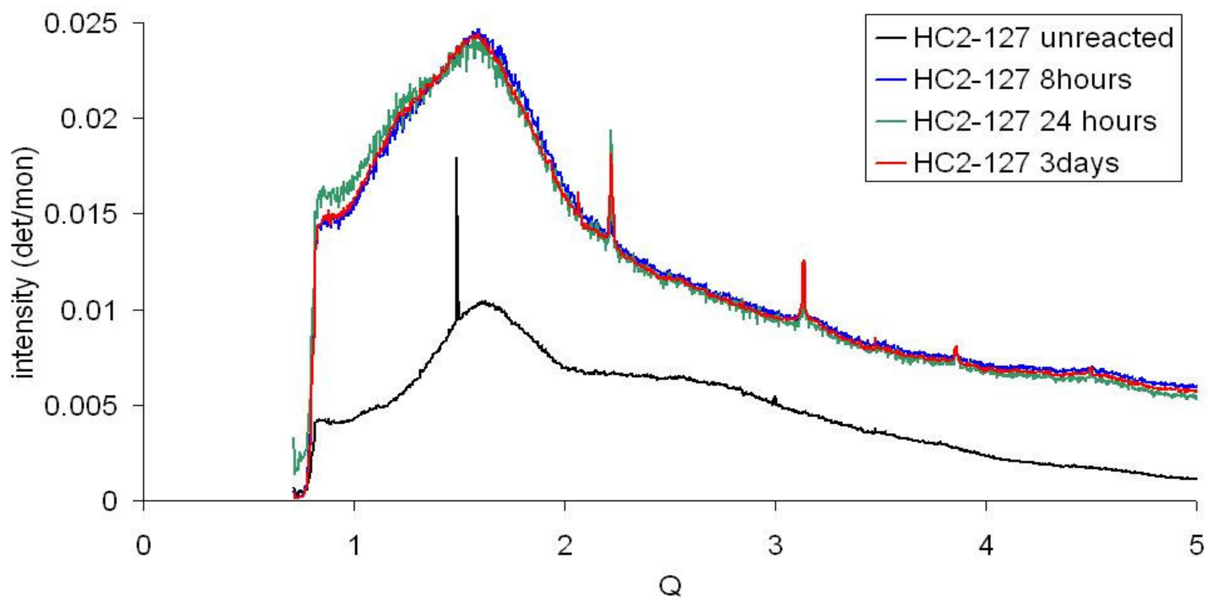
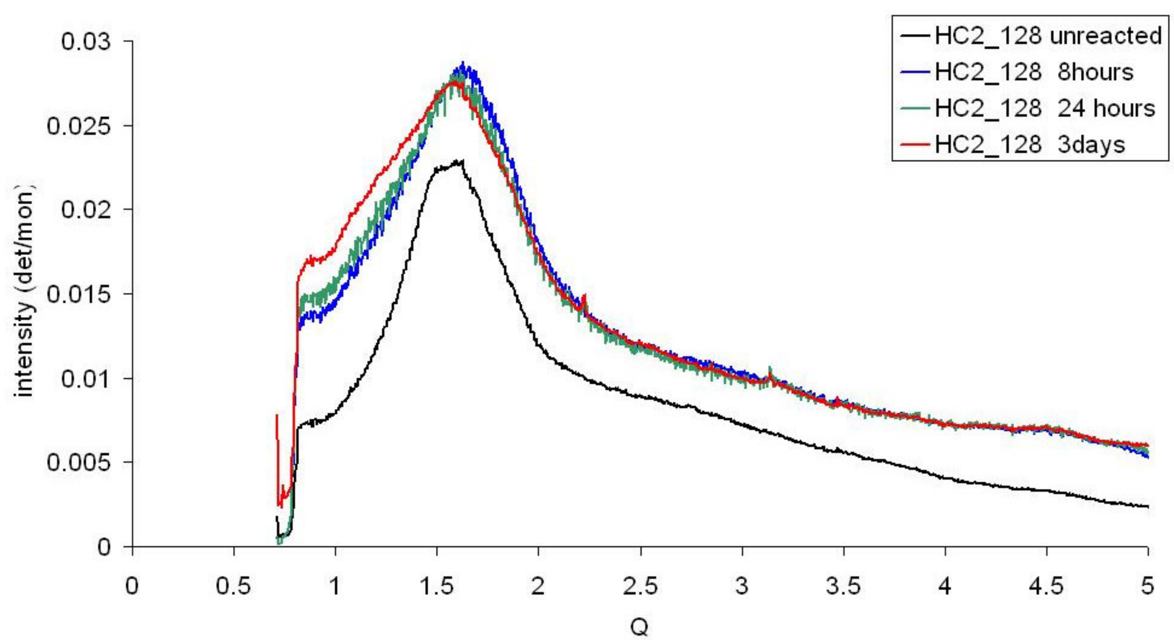
Mechanism

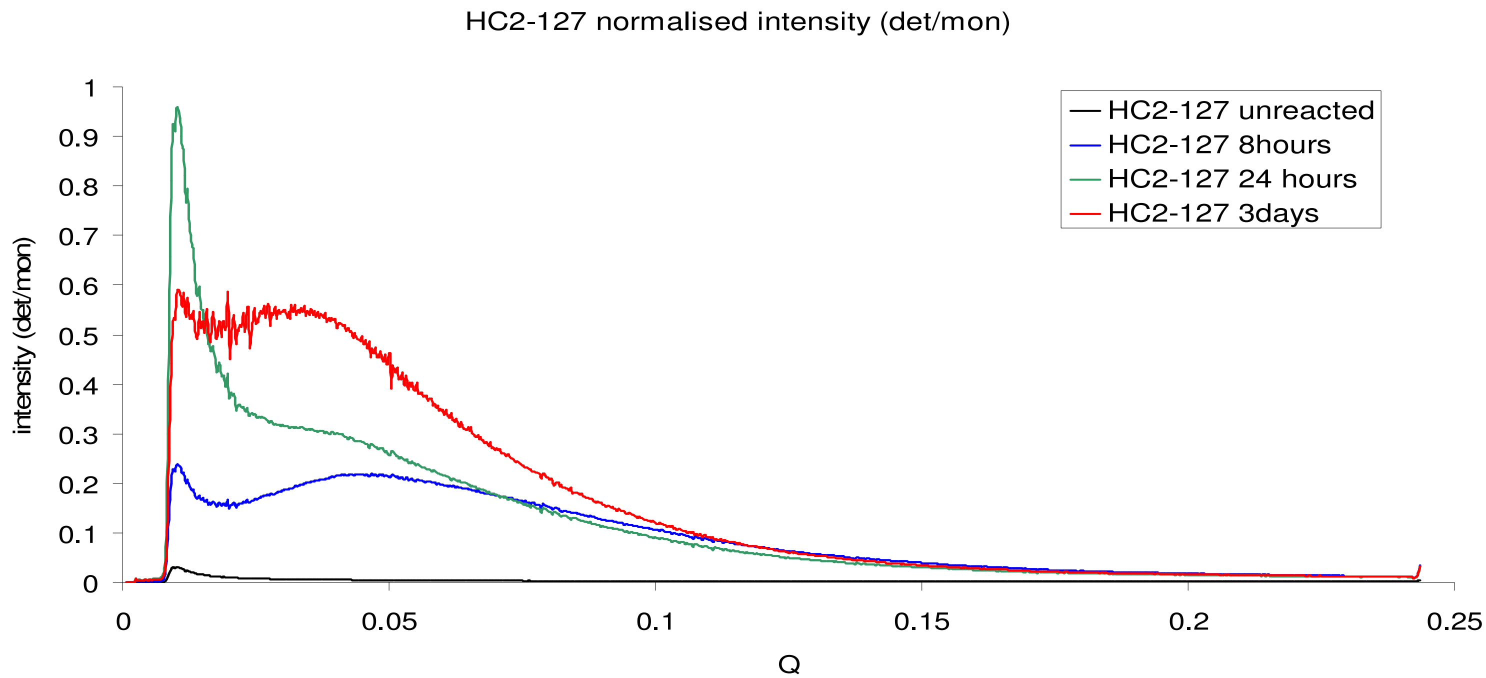


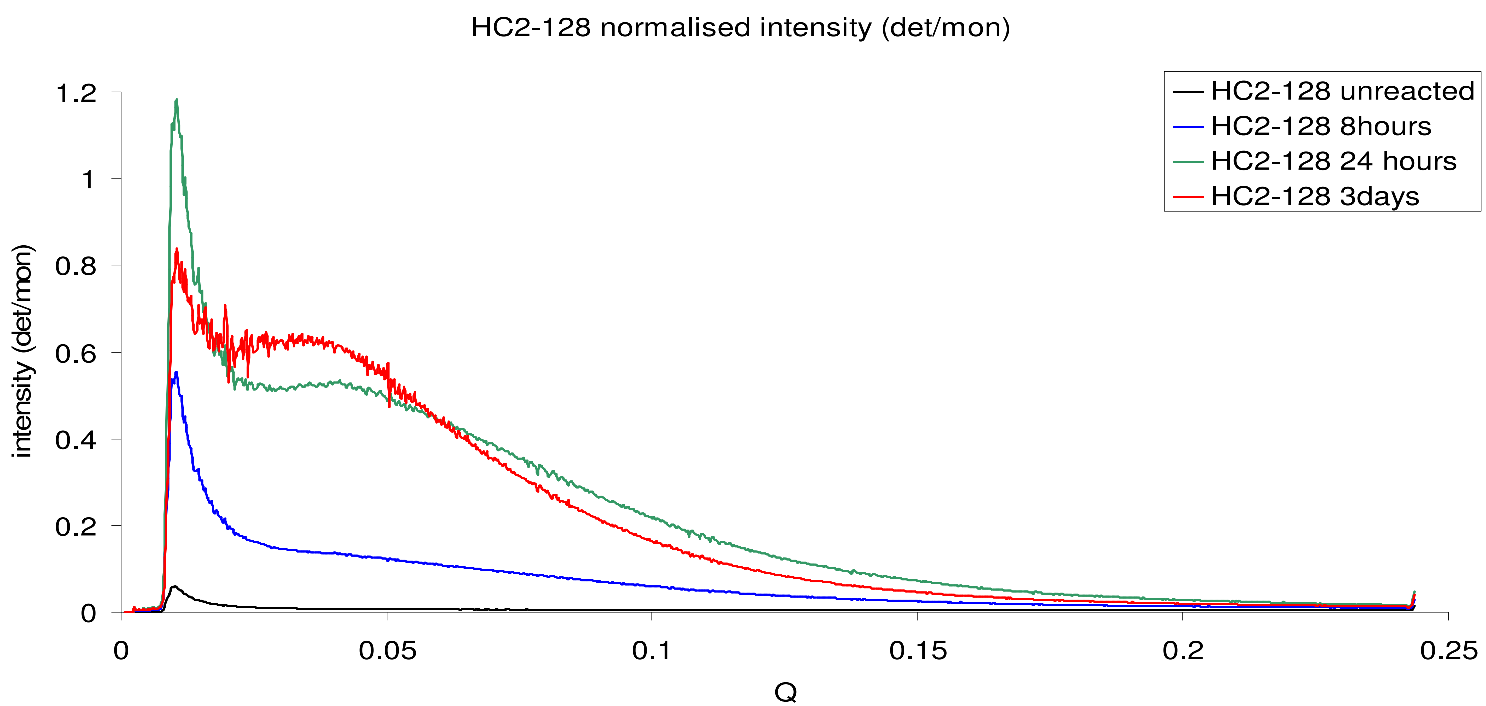
HC2-127 normalised intensity (det/mon)



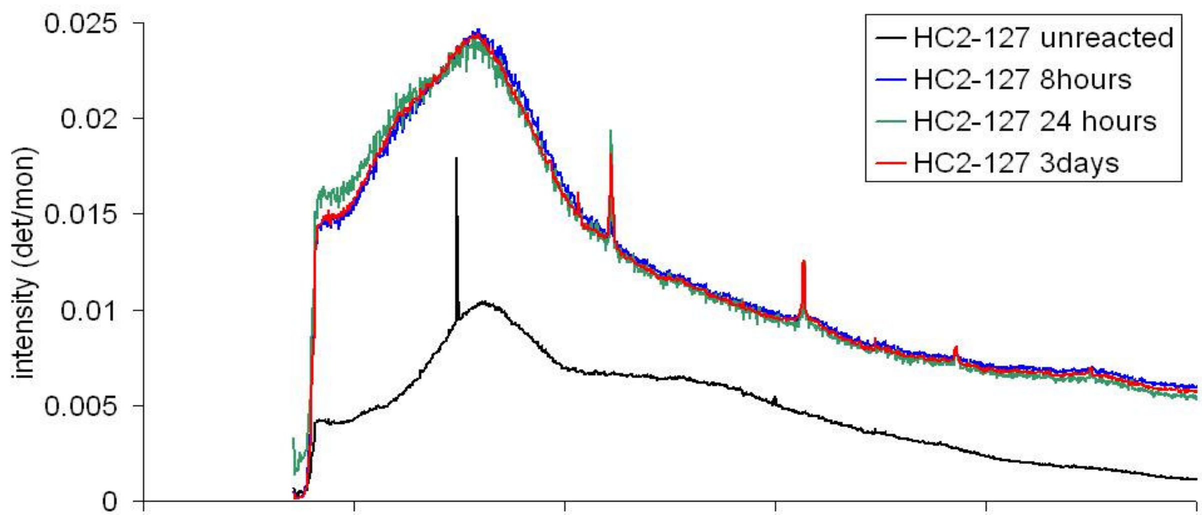
HC2-128 normalised intensity (det/mon)



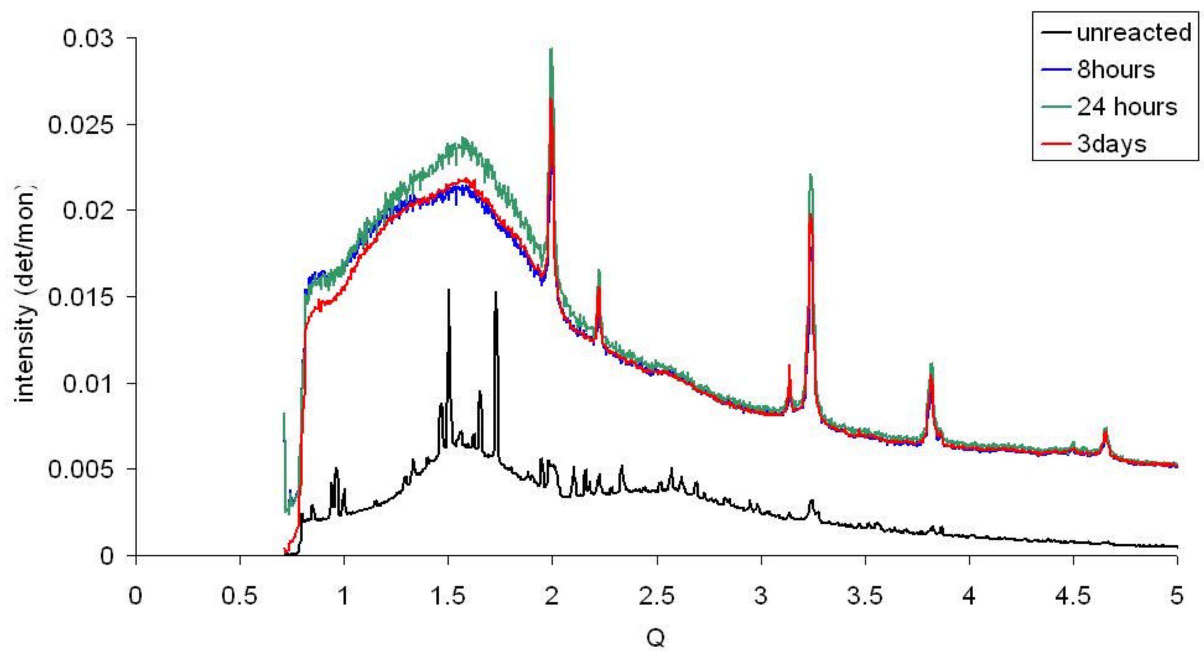

HC2-127 normalised intensity (det/mon)
intensity (det/mon)
Q
HC2-127 unreacted
HC2-127 8hours
HC2-127 24 hours
HC2-127 3days
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0.05
0.15
0.25

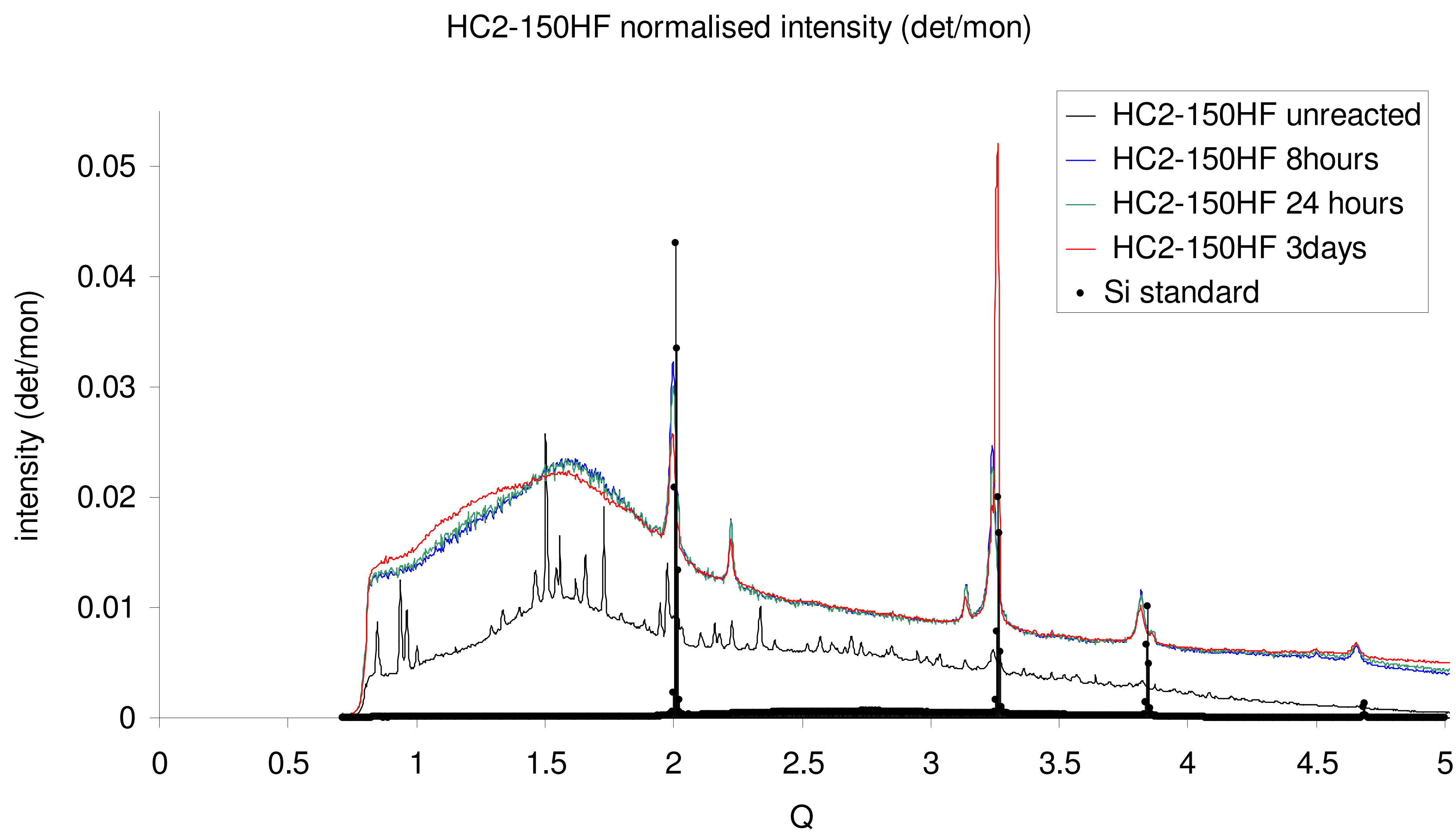

HC2-128 normalised intensity (det/mon)
intensity (det/mon)
Q
HC2-128 unreacted
HC2-128 8hours
HC2-128 24 hours
HC2-128 3days
0
0.2
0.4
0.6
0.8
1
1.2
0.05
0.1
0.15
0.25

HC2-127 normalised intensity (det/mon)

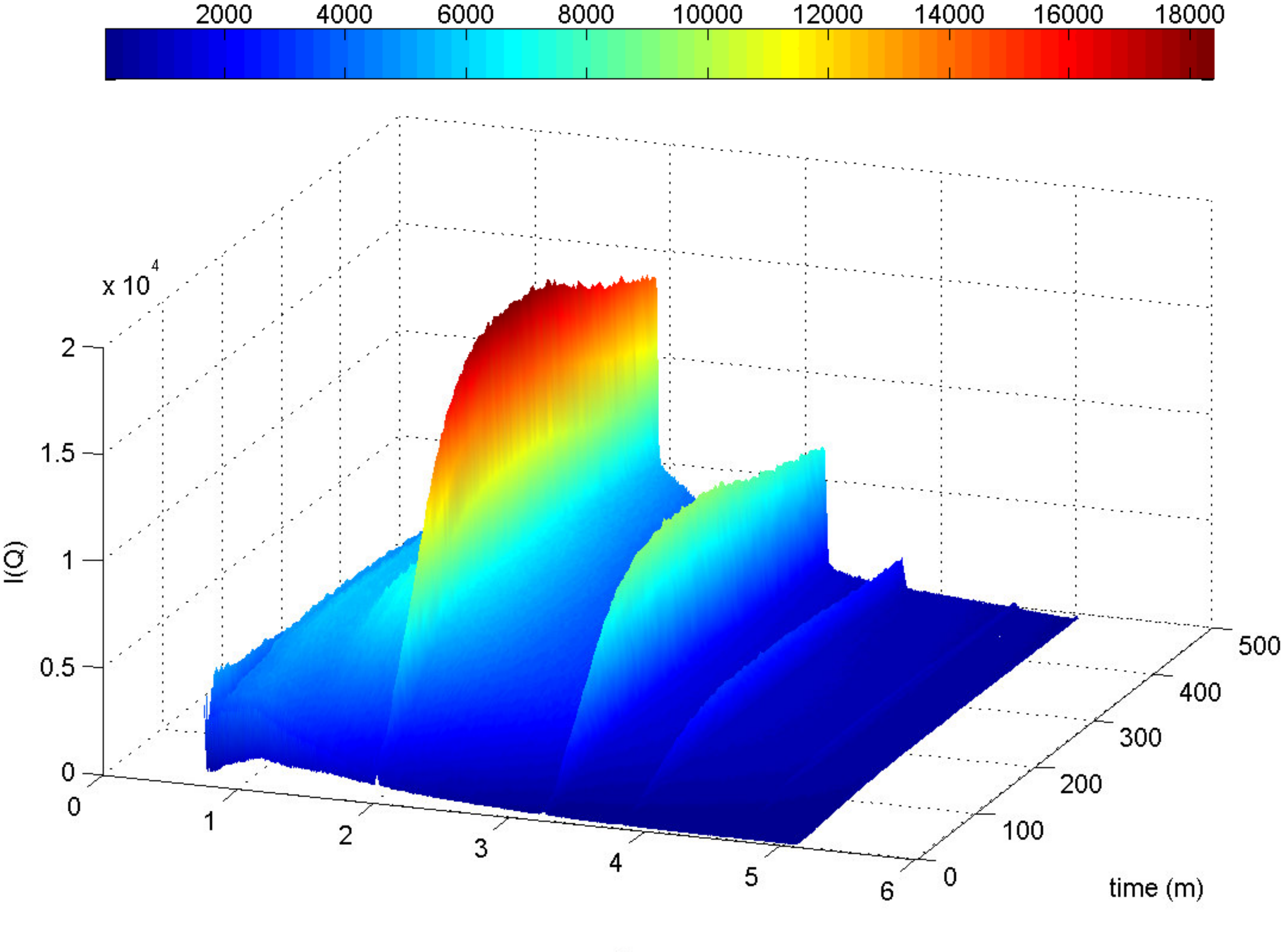


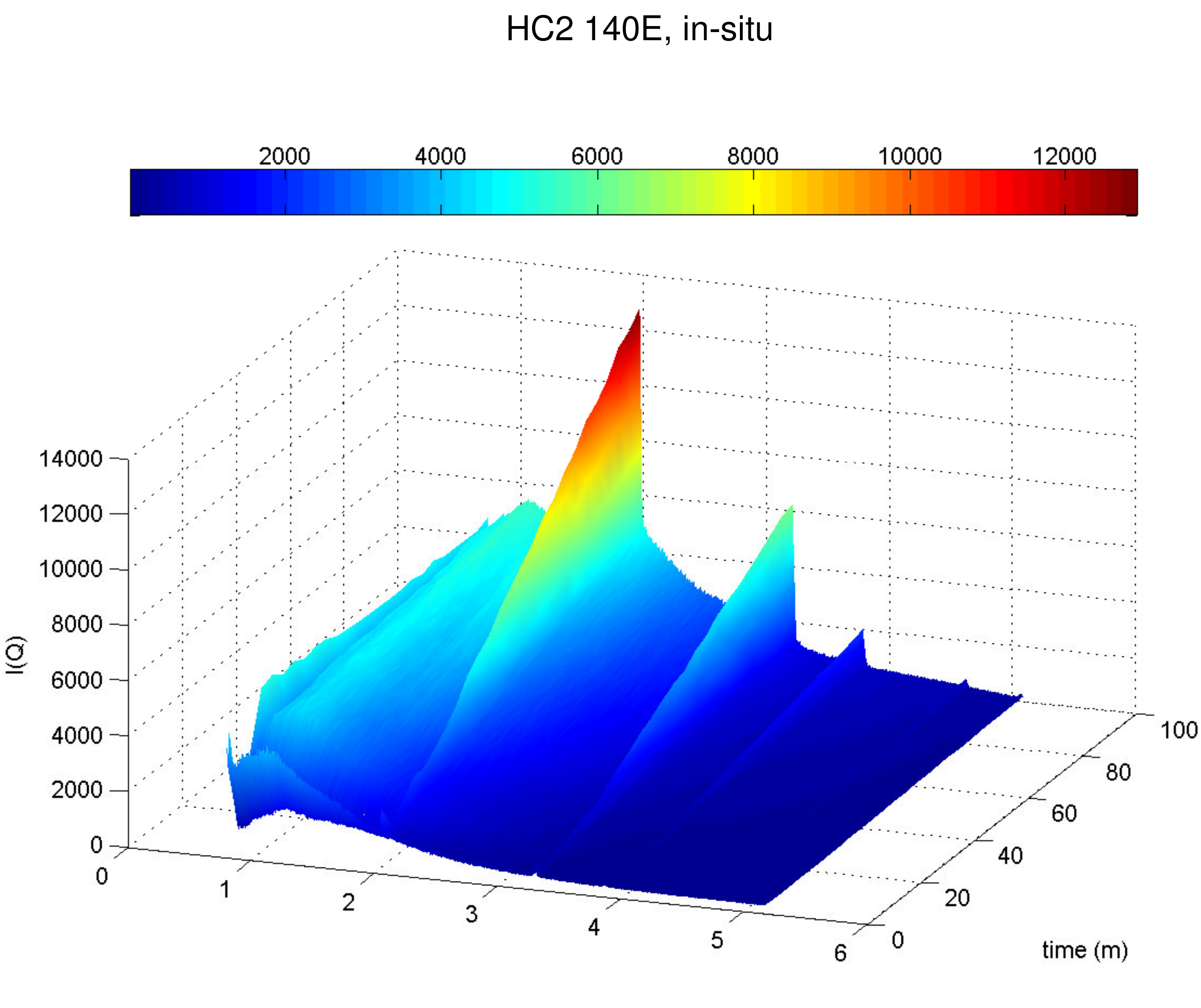
HC2-166 normalised intensity (det/mon)

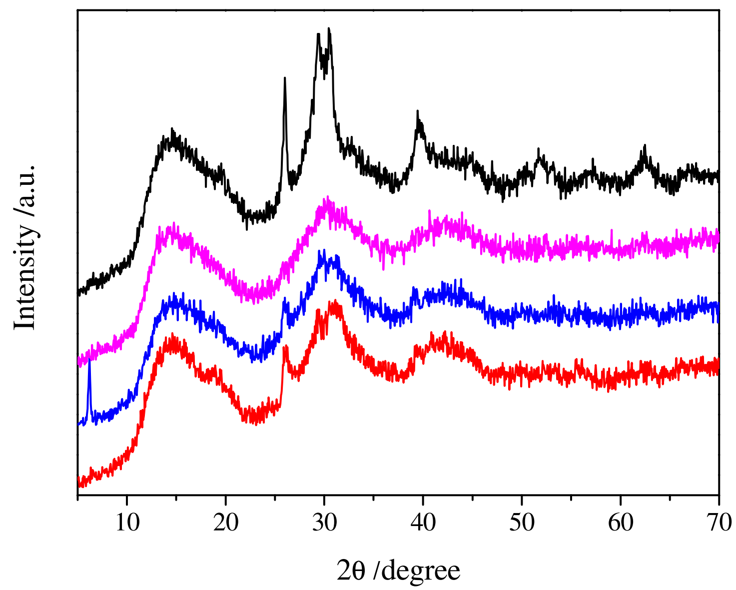



HC2-150HF normalised intensity (det/mon)
intensity (det/mon)
Q
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
HC2-150HF unreacted
HC2-150HF 8hours
HC2-150HF 24 hours
HC2-150HF 3days
Si standard

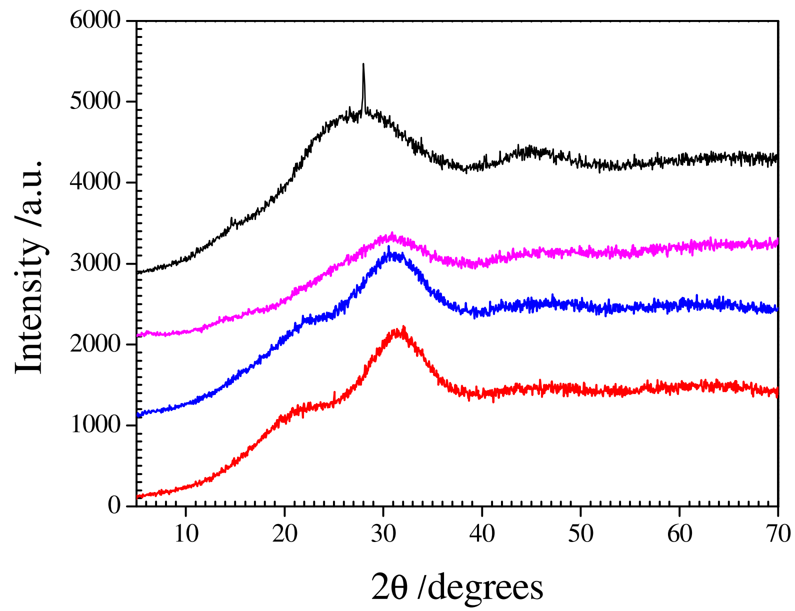
HC2 140E, in-situ



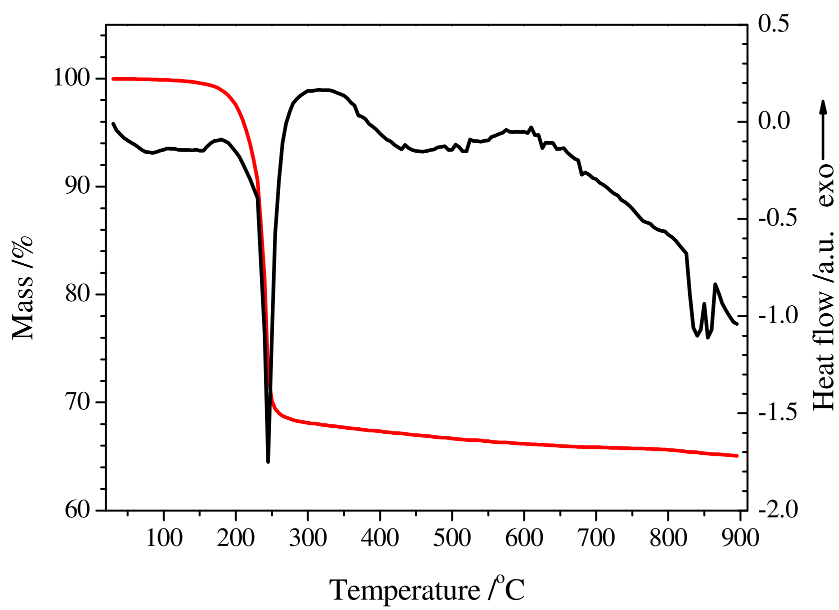

HC2 140E, in-situ
2000
4000
6000
8000
10000
12000
14000
I(Q)
0
1
2
3
4
5
6
20
40
60
80
100
time (m)
-



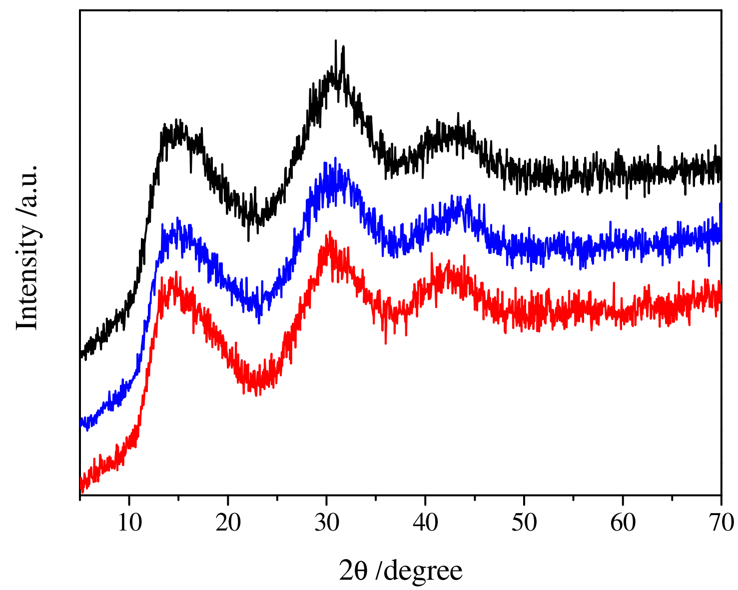
Conventional XRD spectra for sol-gel sodium borophosphate heat treated at 120 °C (From bottom to top: $P_{40}B_{10}Na_{40}$, $P_{40}B_{15}Na_{35}$, $P_{40}B_{20}Na_{40}$, $P_{40}B_{30}Na_{20}$



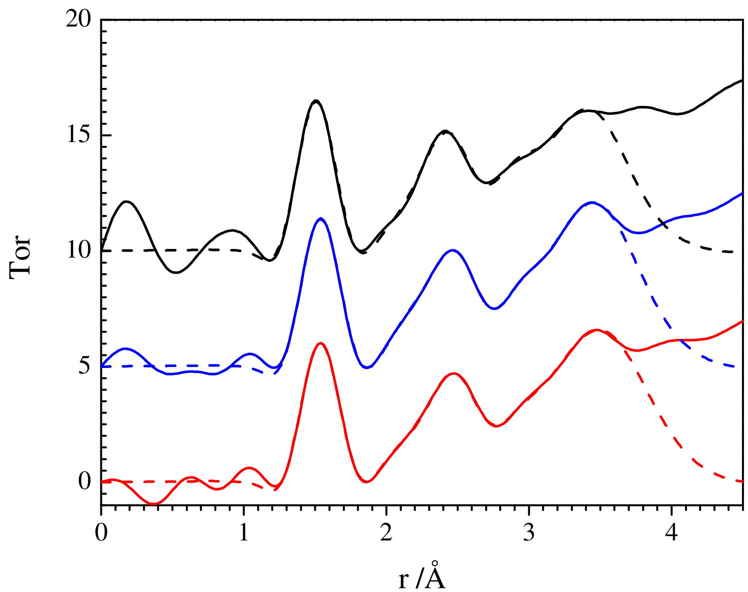
Conventional XRD spectra for melt-quenched sodium borophosphate heat treated at 120 °C (From bottom to top: $P_{40}B_{10}Na_{40}$, $P_{40}B_{15}Na_{35}$, $P_{40}B_{20}Na_{40}$, $P_{40}B_{30}Na_{20}$



TGA/DTA traces for sol-gel sodium borophosphate $P_{40}B_{20}Na_{40}$ heat treated at 120 °C



Conventional XRD spectra for sol-gel borophosphate $P_{40}B_{20}Na_{40}$ heat treated at 120 (bottom), 200 (middle) and 350 (top) °C



Total correlation function for sol-gel sodium borophosphate $P_{40}B_{20}Na_{40}$ heat treated at 200 (bottom), 350 (middle) °C and melt-quenched P40B20Na40 (top)

		$P\text{-}O_T$	$P\text{-}O_B$	Na-O	O···O	B···B	P···B	P···P	Na···Na
	r /Å	1.51	1.55	2.27	2.50	2.67	2.76	2.90	3.12
SG_200 °C	CN	1.1	2.8	3.9	5.5	1.7	0.8	0.8	7.4
	σ	0.03	0.05	0.15	0.09	0.07	0.01	0.12	0.24
	r /Å	1.48	1.57	2.29	2.51	2.67	2.75	2.91	3.10
SG_350 °C	CN	1.4	2.9	5.3	4.8	1.1	0.9	1.2	4.9
	σ	0.04	0.05	0.12	0.07	0.07	0.01	0.11	0.24
	r /Å	1.46	1.55	2.31	2.47	2.68	2.75	2.91	3.13
MQ	CN	1.7	2.4	5.4	4.5	0.3	1.8	2.1	6.2
	σ	0.02	0.04	0.13	0.08	0.06	0.01	0.13	0.27