Leibniz Universität Hannover

Institut für Mineralogie

Claus Rüscher

Geopolymer:

- handling/hosting hydrides for storing Hydrogen
- As green binder

1. Project “Jirasit/Thailand”
2. Project “Temuujin/Mongolia”
3. Project “Tchakoute/Cameroon”
4. Project “Debnath/Bangladesh”

Mineralogy since 1831 in Hannover

Georg Chritian Hunäus

28.9.1843 bis 1873

2nd chair: first oil drilling in 1858 in Wietze close to Hannover

2015: Visit at Salzgitter AG (steel fabrication)

Thanks to AvH/DAAD/“Lower saxonia“/DFG

Bonjour Prof. Rüscher,
I am preparing the program for our present Geopolymer Camp (July 9-11) and I finished reading the various recent papers (2017-2018) dedicated to Phosphate-based Geopolymer. My intention is to focus on this chemistry in the First session on Tuesday, July 10, morning (at 11:00) titled “Acid-based geopolymers (phosphate/MK-based): chemistry and terminology”. Would you be available and make a presentation on the recent works of your team?
…
Thank you in advance for your input.
Mit freundlichen Grüssen,
JD

Thanks to JD!!

1. Mechanical and microstructural properties of metakaolin-based geopolymer cements from sodium waterglass and phosphoric acid solution as hardeners: A comparative study. **Tchakouté, H. K.,** Rüscher, C. H., Applied Clay Science 140 (2017) 81-87**.**

2. Influence of the molar concentration of phosphoric acid solution on the properties of metakaolin-phosphate-based geopolymer cements. **Tchakoute, H. K.,** Rüscher, C.H., Kamseu, E., Andreola, F., Leonelli, C., Appl. Clay Science 147 (2017) 184-194**.**

3. The influence of gibbsite in kaolin and the formation of berlinite on the properties of metakaolin-phosphate-based geopolymer cements. **Tchakoute, H.K.,** Rüscher, C.H., Kamseu, E., Djobo, J.N.Y., Leonelli, C., Mat. Chem. Phys. 199 (2017) 280-288**.**

4. Influence of gibbsite and quartz in kaolin on the properties of metakaolin-based geopolymer cements. **Tchakoute, H. K.,** Rüscher, C. H., Djobo, J. N. Y., Kenne, B. B. D., Njopwouo, D., Applied Clay Science 107 (2015) 188–194**.**

⇒ Use of natural raw material, kaolin! => compare „activation“ with phosphoric acid versus NWG (sodium silicate solution) => effect of X M H_3PO_4 => compare again (main characterisations: XRD/IR/TG/CS)

3. The influence of gibbsite in kaolin and the formation of berlinite on the properties of metakaolin-phosphate-based geopolymer cements. **Tchakoute, H.K., et al.**, 2017**:**
Kaolins from Cameroon K2, K3

4. Tchakoute, H. K., et al., 2015**:** Influence of gibbsite and quartz in kaolin on the properties of metakaolin-based geopolymer cements. **Tchakoute, H. K., et al.,** 2015**:**
Kaolins from Cameroon: K1, K2, K3

Chemical composition of the kaolins (K_1, K_2 and K_3) in mass percent.

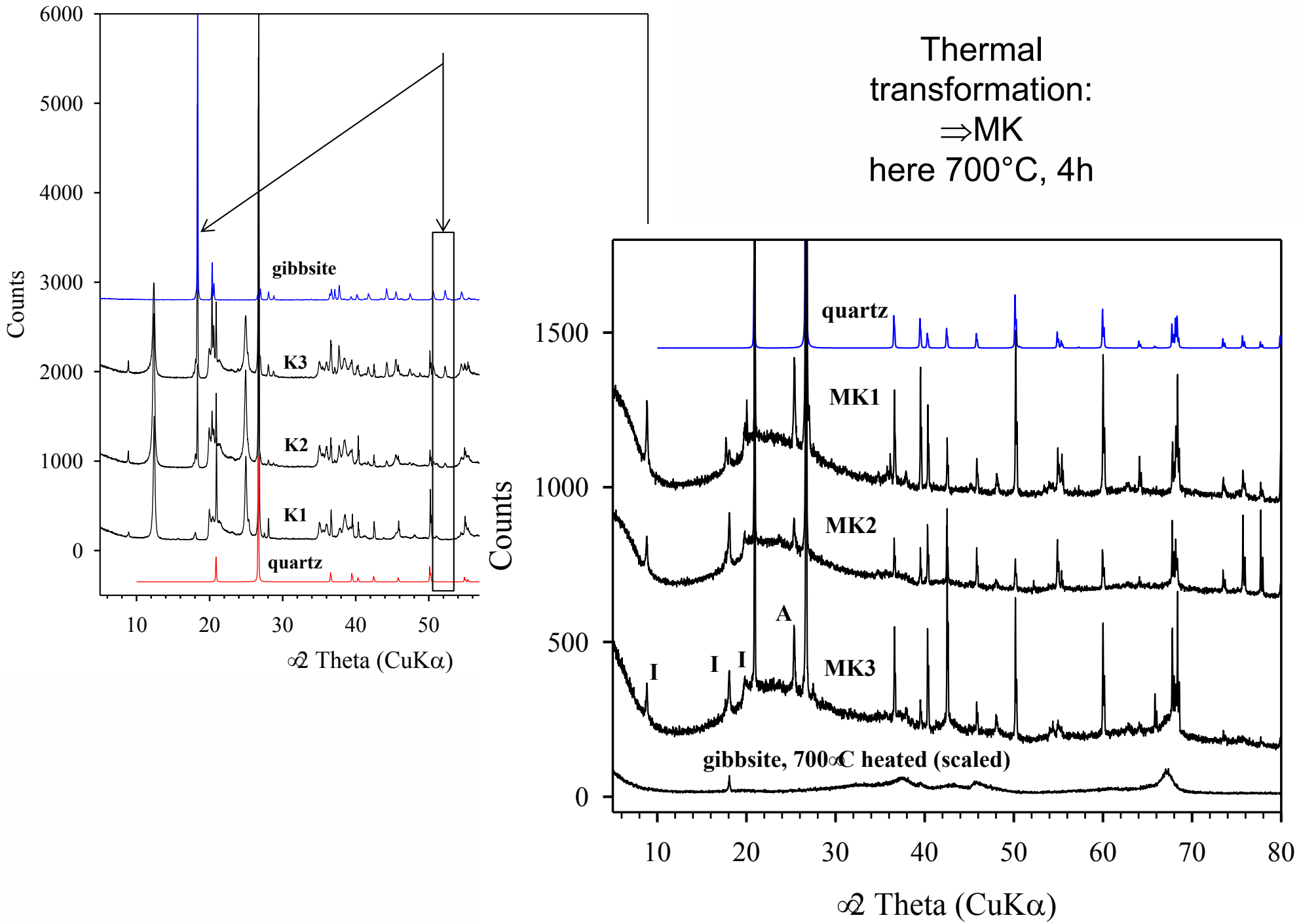
Oxide	K_1	K_2	K_3
SiO_2	44.10	47.2	39.09
Al_2O_3	33.90	35.1	39.44
Fe_2O_3	0.99	0.46	0.74
K_2O	0.42	0.46	0.30
TiO_2	0.83	0.49	1.14
MgO	0.20	0.19	0.13
Na_2O	0.20	<0.1	/
CaO	0.21	<0.1	/
SO_3	<0.02	< 0.01	/
P_2O_5	0.03	/	0.06
Cr_2O_3	0.02	/	/
MnO	0.01	/	/
LOI	14.75	14.94	18.48

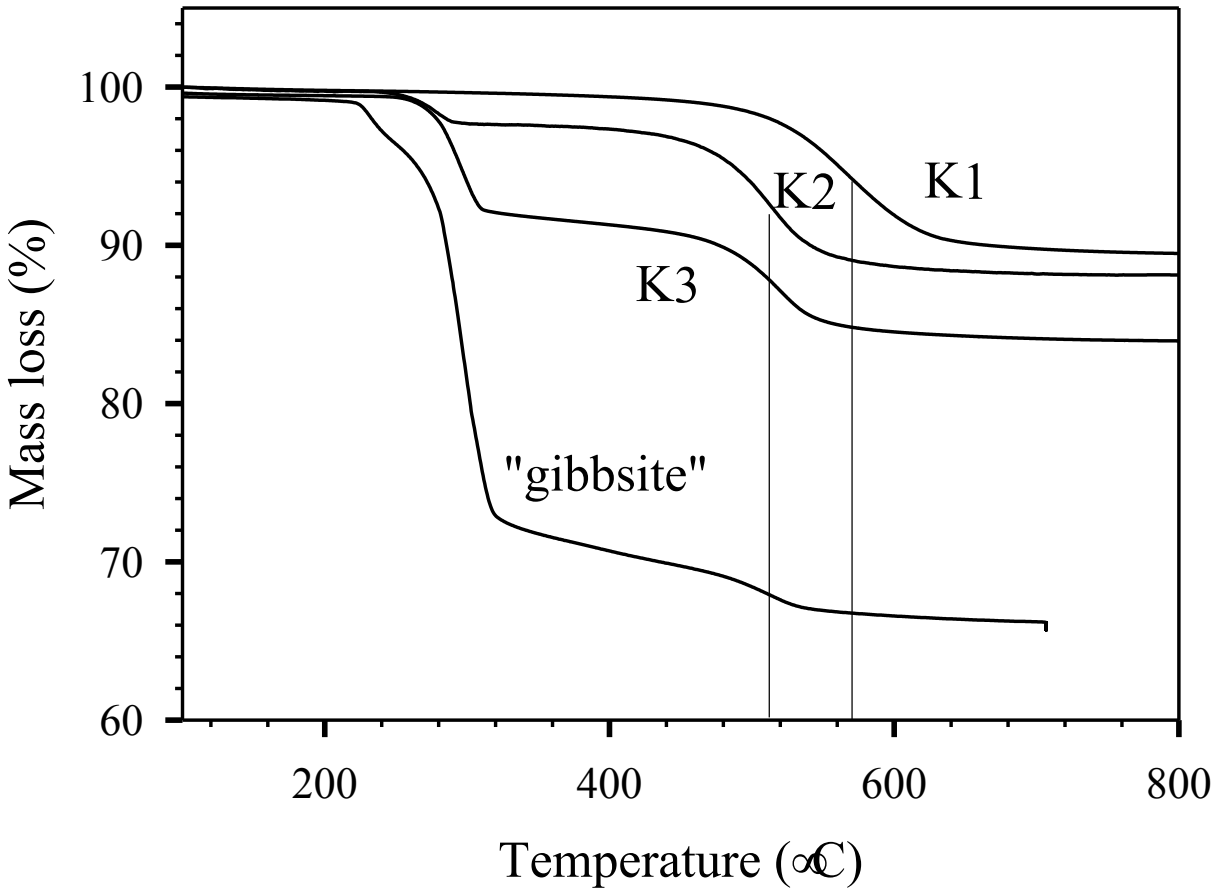
LOI: loss on ignition at 1000 °C.

K_4 (Cameroon)

SiO_2	41.46
Al_2O_3	31.47
Fe_2O_3	7.65
K_2O	0.51
MgO	1.50
Na_2O	0.65
CaO	0.69
SO_3	0.15
P_2O_5	0.09
MnO	0.06
LOI	15.76

What sense makes the bulk chemical composition?

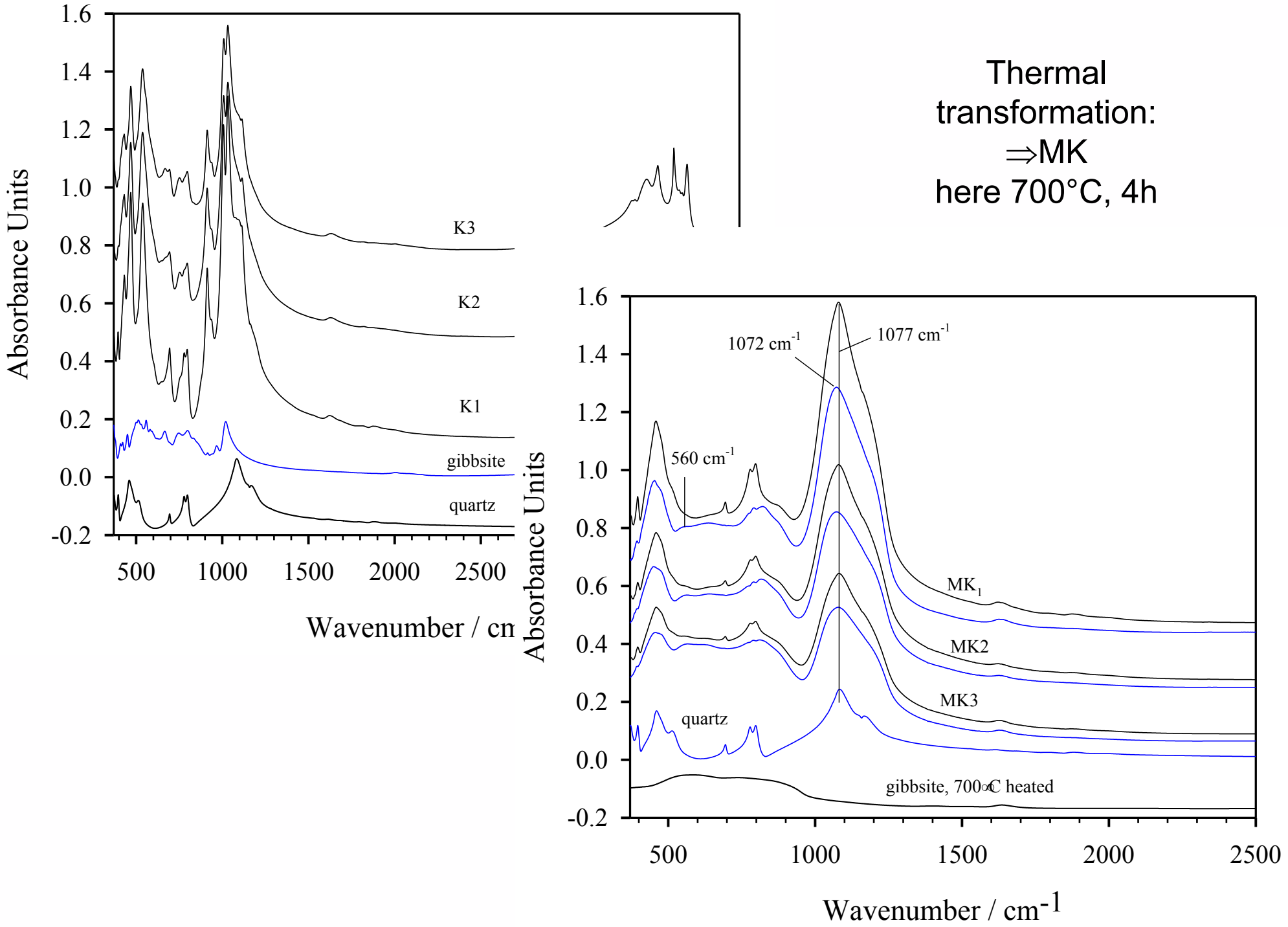

Thermal
transformation:
⇒MK
here 700°C, 4h
Counts
2 Theta (CuKα)
gibbsite
K3
K2
K1
quartz
MK1
MK2
MK3
A
I
gibbsite, 700°C heated (scaled)

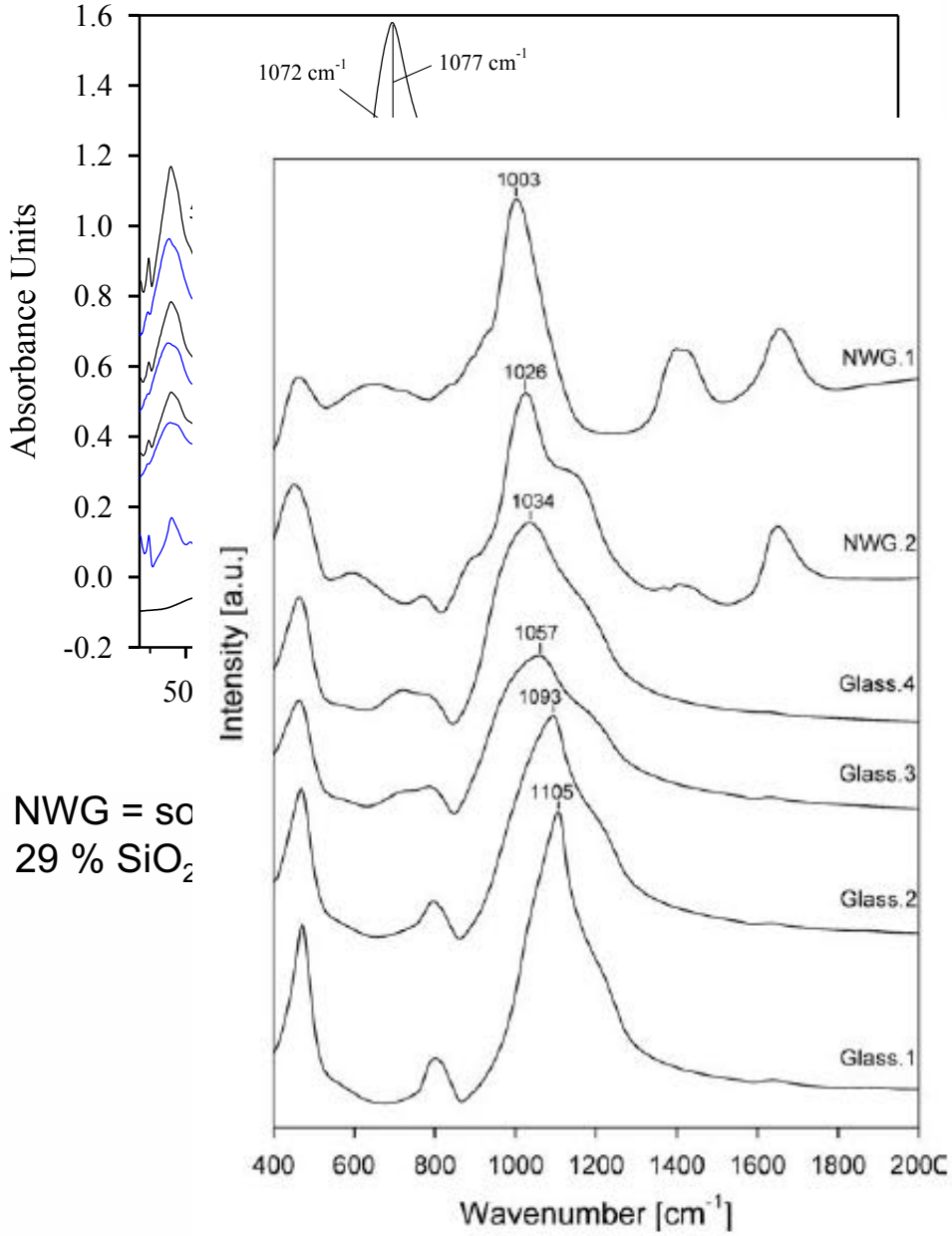


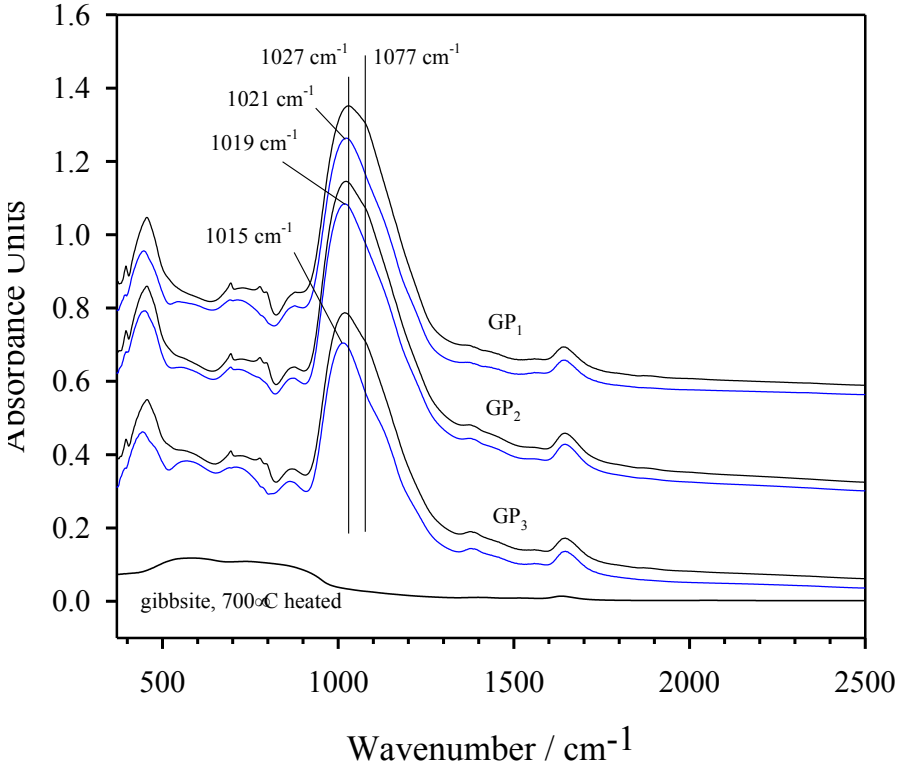
Kaolinite „ideally“:

$Al_2Si_2O_5(OH)_4 \Rightarrow [Al_2O_3{*}Si_2O_4] + 2\ H_2O$

-13.9 wt% expected!

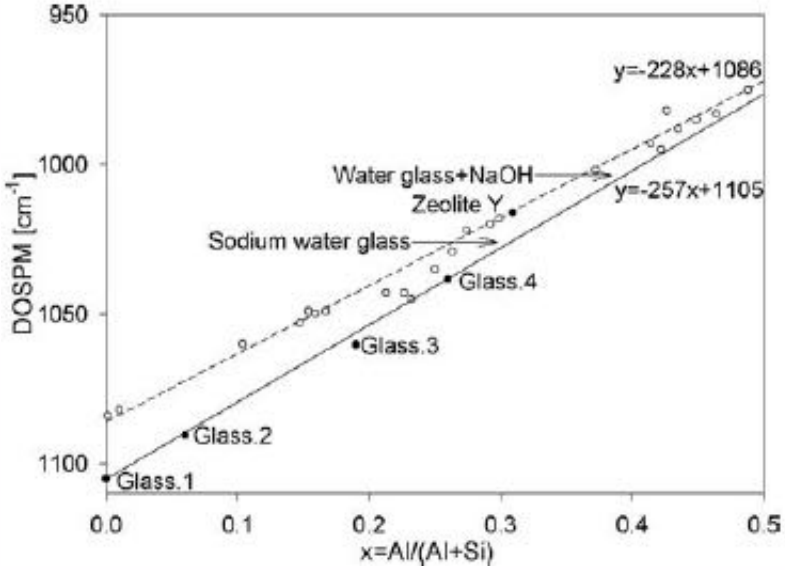

Thermal transformation:
⇒MK
here 700°C, 4h
Absorbance Units
Wavenumber / cm
K3
K2
K1
gibbsite
quartz
1072 cm-1
1077 cm-1
560 cm-1
MK1
MK2
MK3
quartz
gibbsite, 700°C heated
Absorbance Units
Wavenumber / cm-1



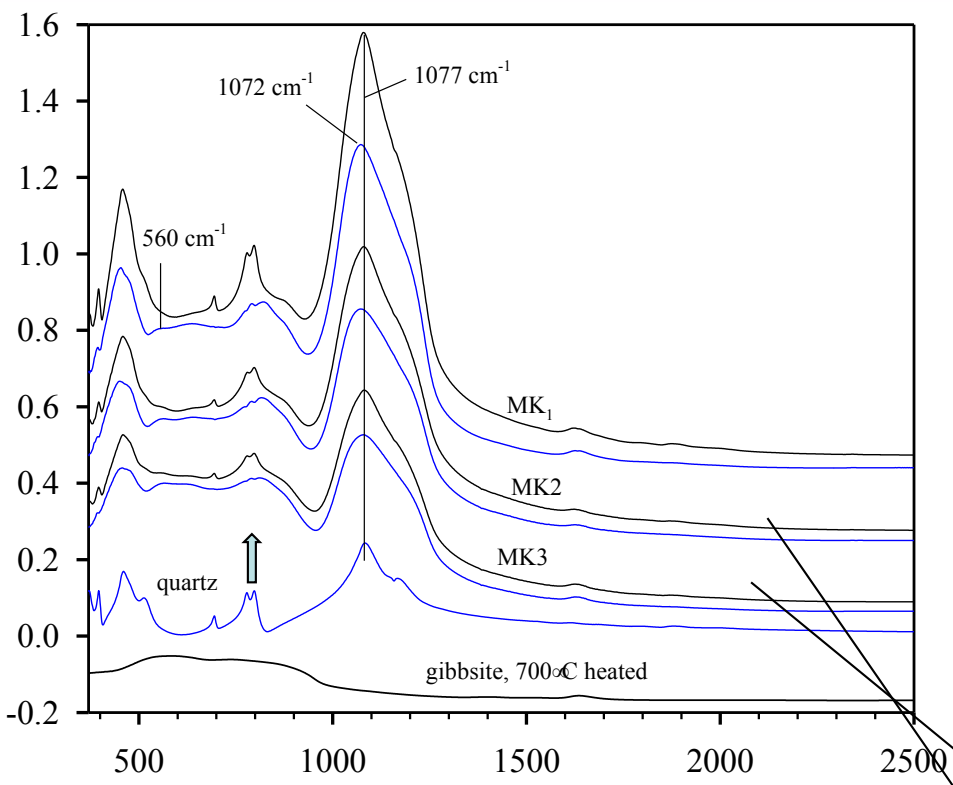


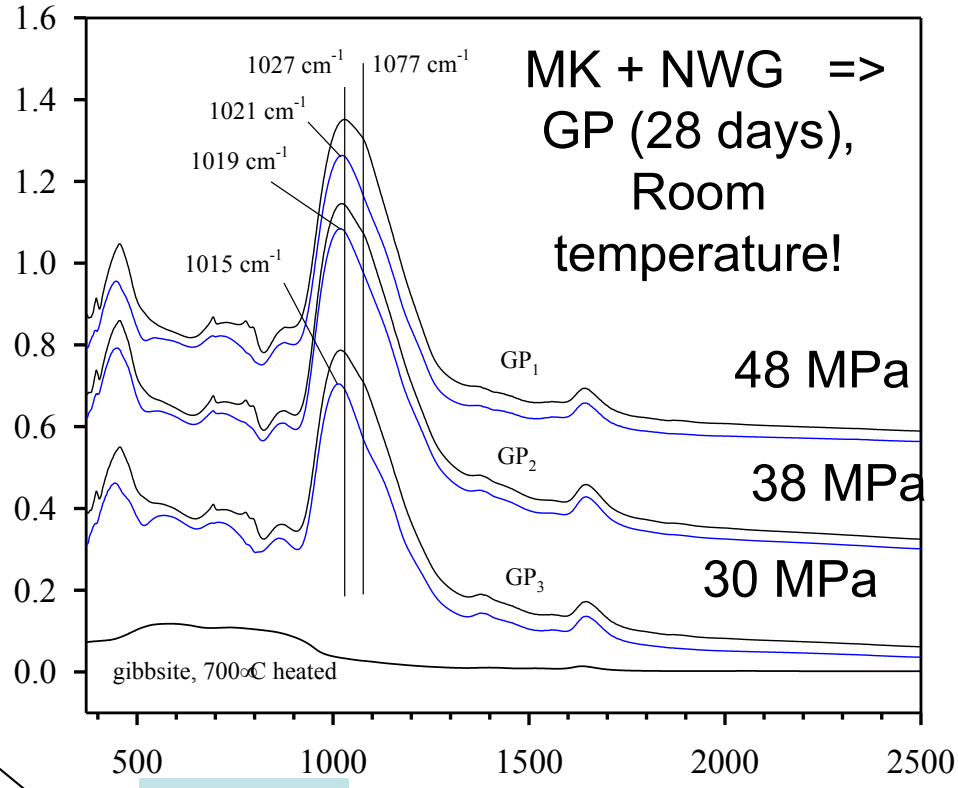
NWG = so
29 % SiO_2

=> GP (28 days), liq/sol = 0.87



DOSPM? Eur. J. Mineral, 2010: Silicate-, aluminosilicate and calciumsilicate gels for building materials…



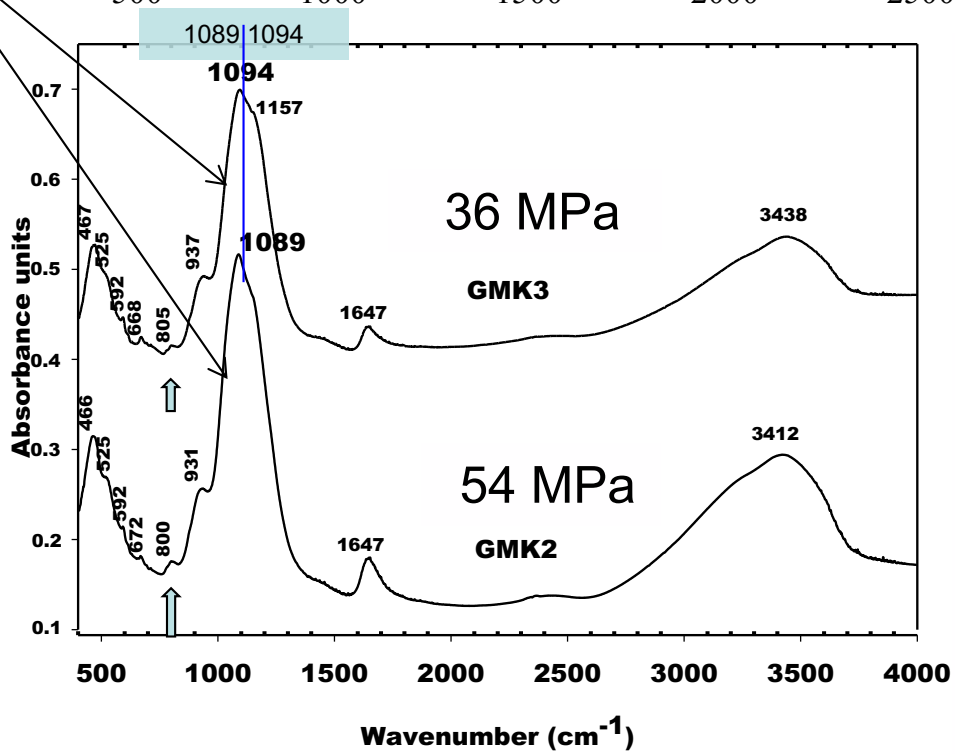


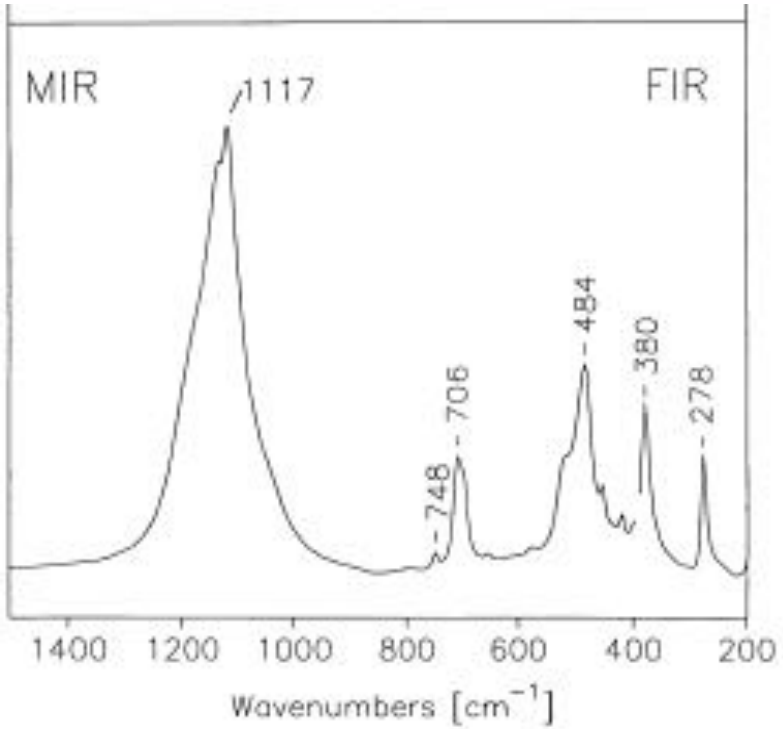
MK + 10 M phosporic acid => XX,
liq/sol = 0.95, 60°C for 24 h (28 days)

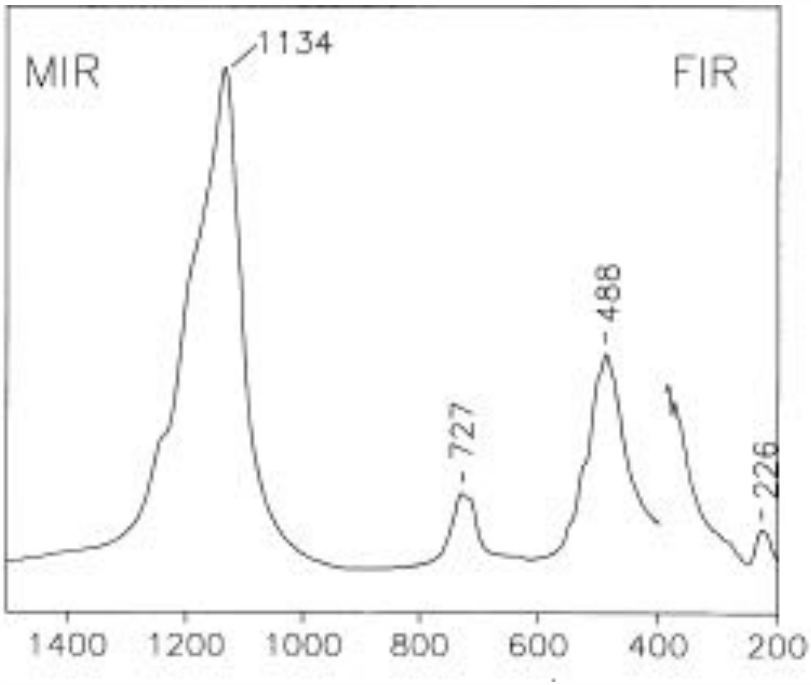
Consider DOSPM!	$[PO_4]$	NWG
MK_1 (22%Qz)		1021
MK_2 (10%Qz 11%Al_2O_3):	1089	1019
MK_3 (8% Qz 28%$A_{l2}O_3$):	1094	1015

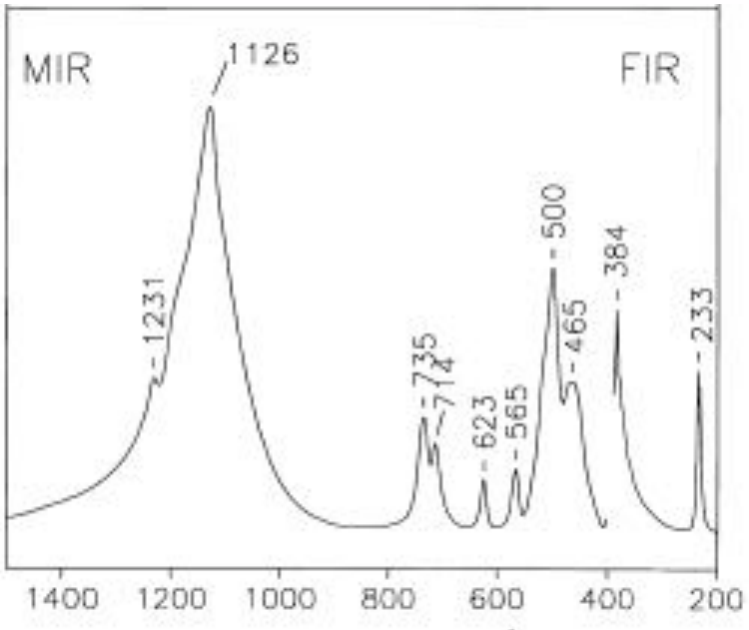
	$[PO_4]$	NWG
MK_1 (22%Qz)		48 MPa
MK_2 (10%Qz 11%Al_2O_3):	54 MPa	38 MPa
MK_3 (8% Qz 28%$A_{l2}O_3$):	36 MPa	54 MPa

Here: γ-, χ-Al_2O_3 has obviously negative effect on strength, Quartz positive!









IR spectra of $AlPO_4$ polymorphs ($SiSiO_4$)

Journal of Molecular Structure 555 (2000) 351–356

The $AlPO_4$ polymorphs structure in the light of Raman and IR spectroscopy studies

M. Rokita*, M. Handke, W. Mozgawa

University of Mining and Metallurgy (AGH), Department of Materials Science and Ceramics, al Mickiewicza 30, 30-059 Kraków, Poland

MK + 10 M phosporic acid => XX,
liq/sol = 0.95, 60°C for 24 h (28 days)

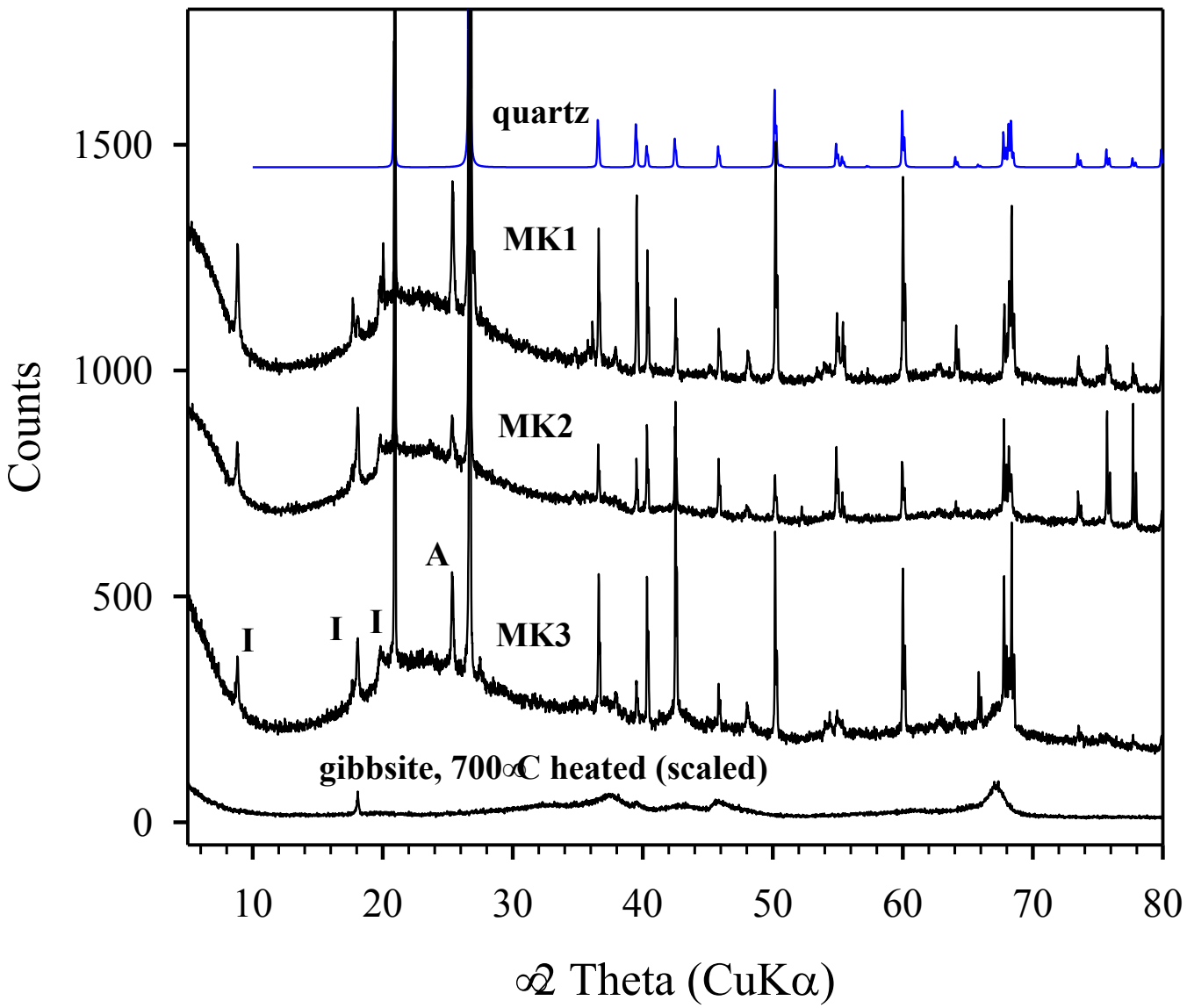
MK + NWG => GP (28 days),
liq/sol = 0.87

NWG = sodium silicate solution:
29 % SiO_2, 9% Na_2O, 62% H_2O
(wt%)

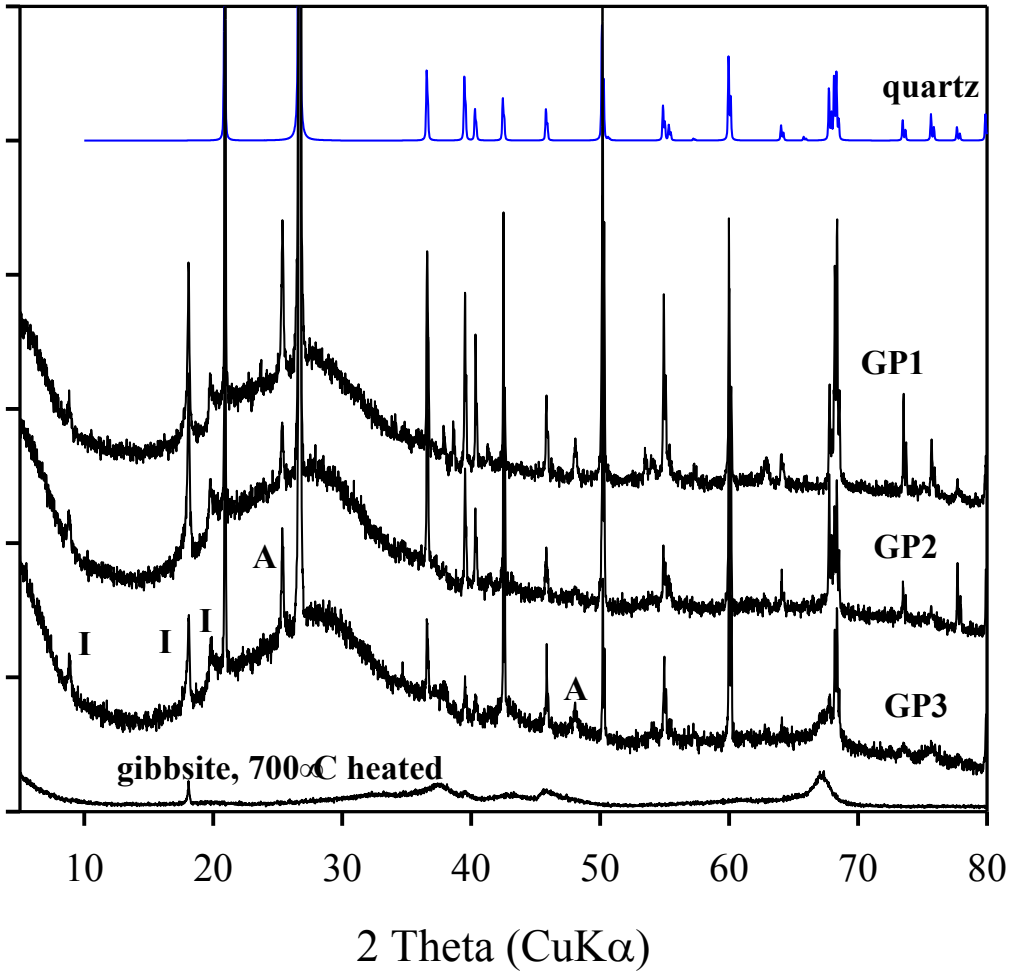
Now, many things could be investigated:

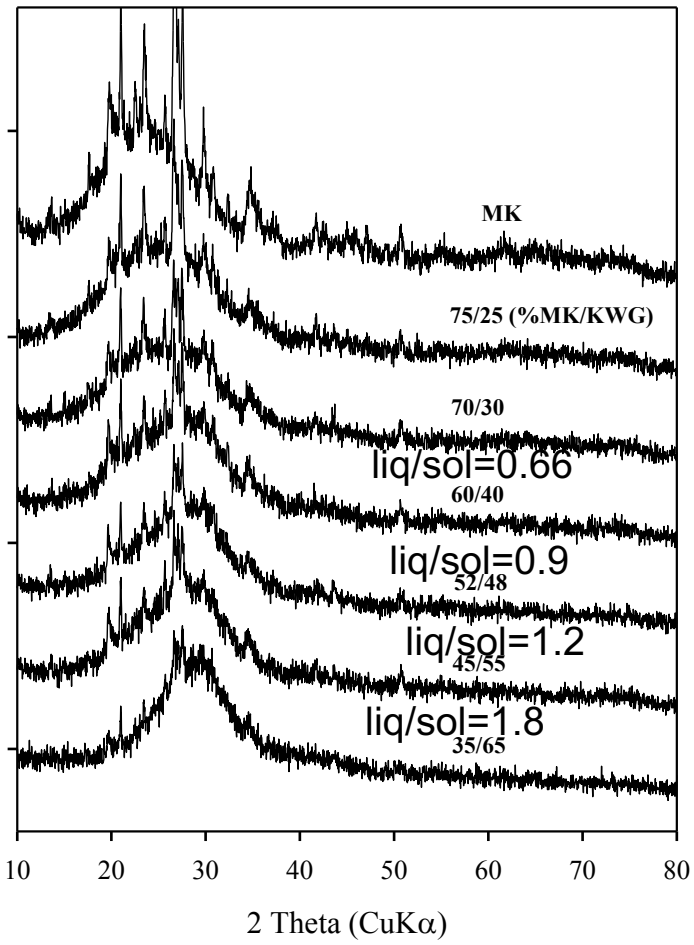
How much Geopolymer is inside and what type of Geopolymer and how intra- and inter-connected, i.e. with the additions?

1st: Consider γ-, χ-Al_2O_3, Quartz and unreacted MK

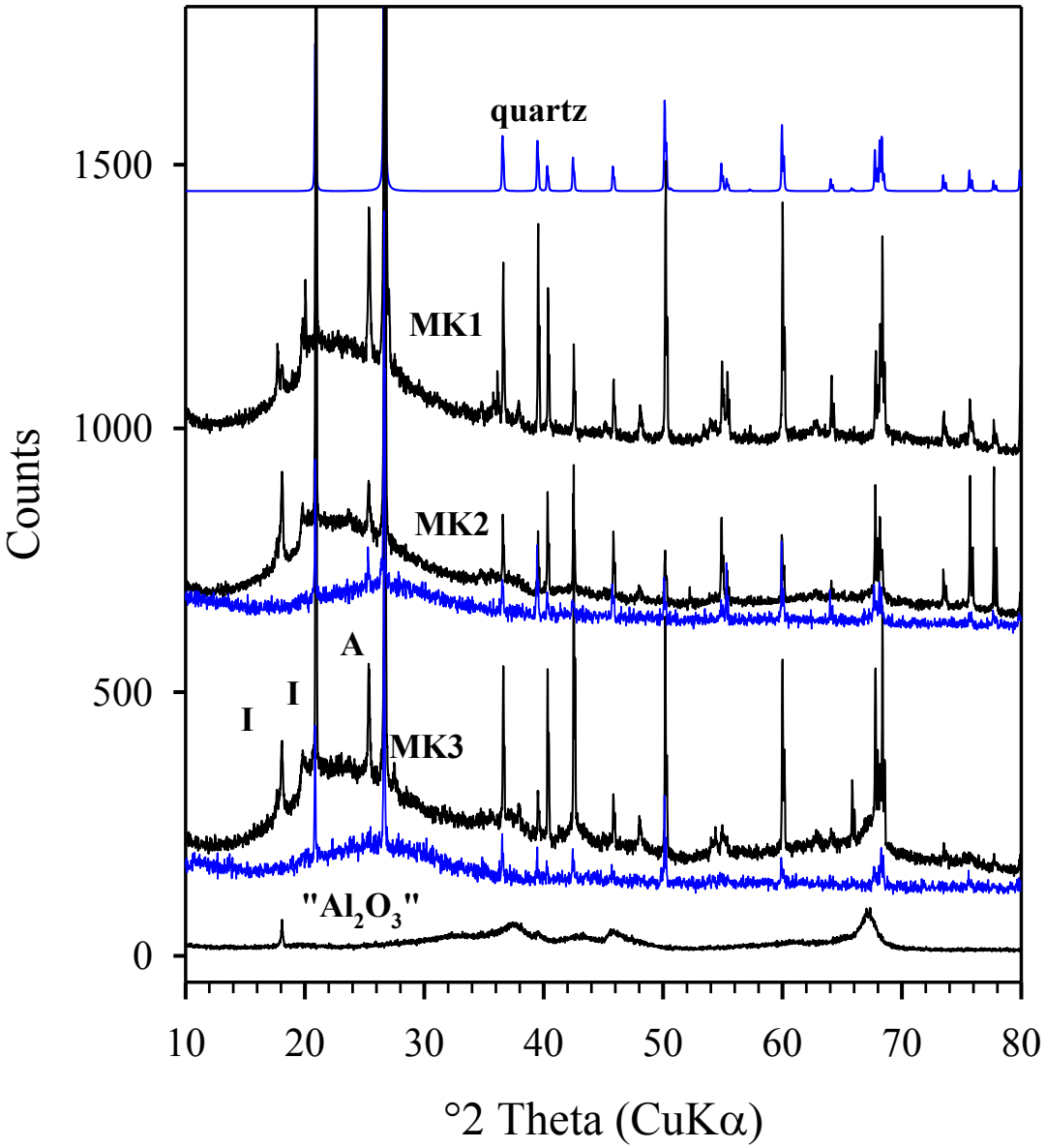


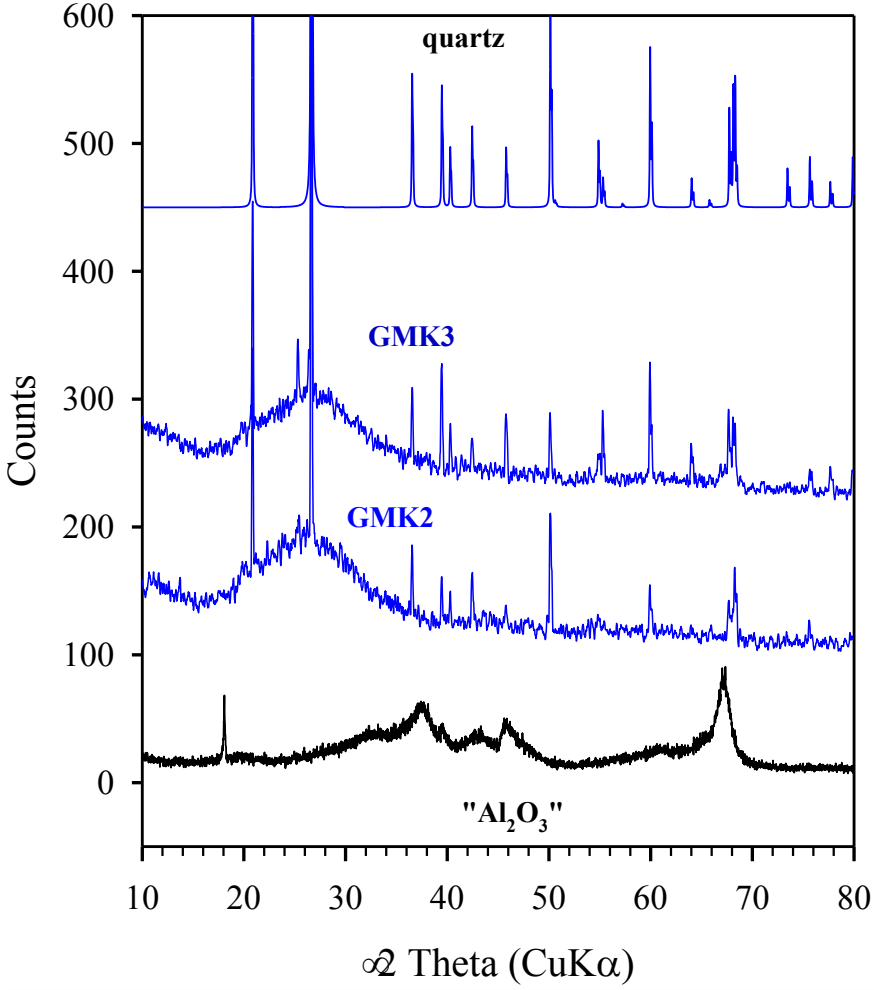
MK + NWG => GP (28 days), liq/sol = 0.87, unreacted MK?

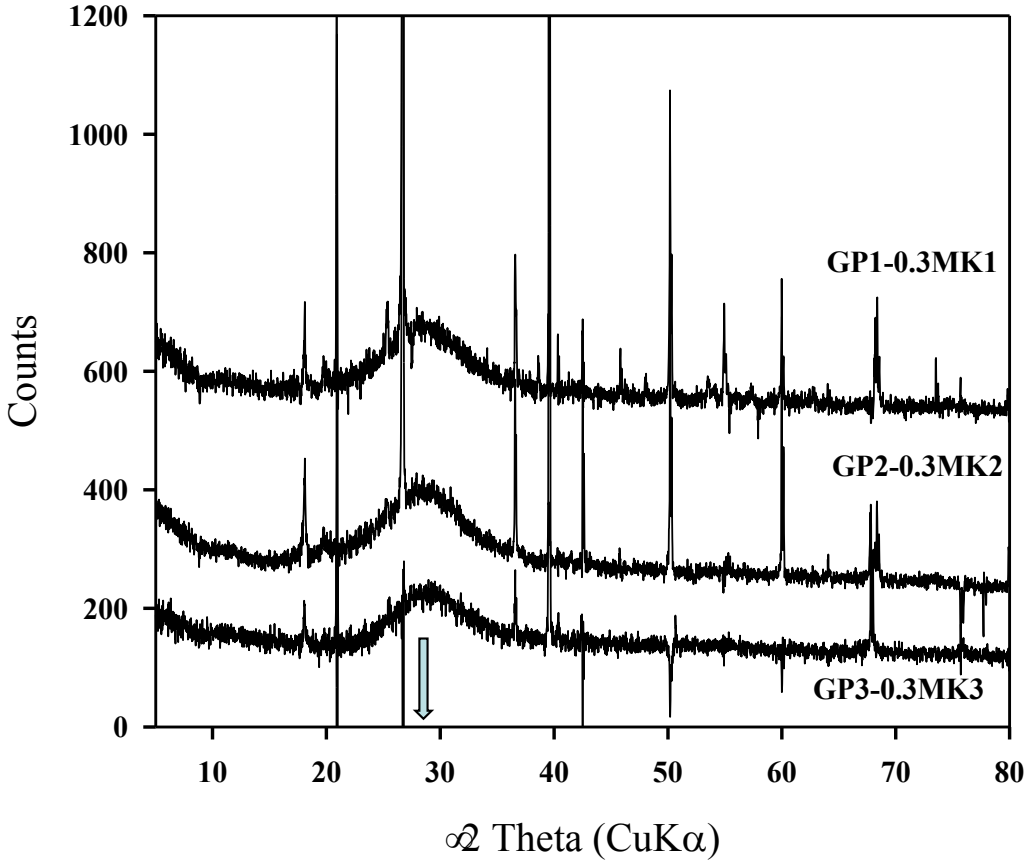


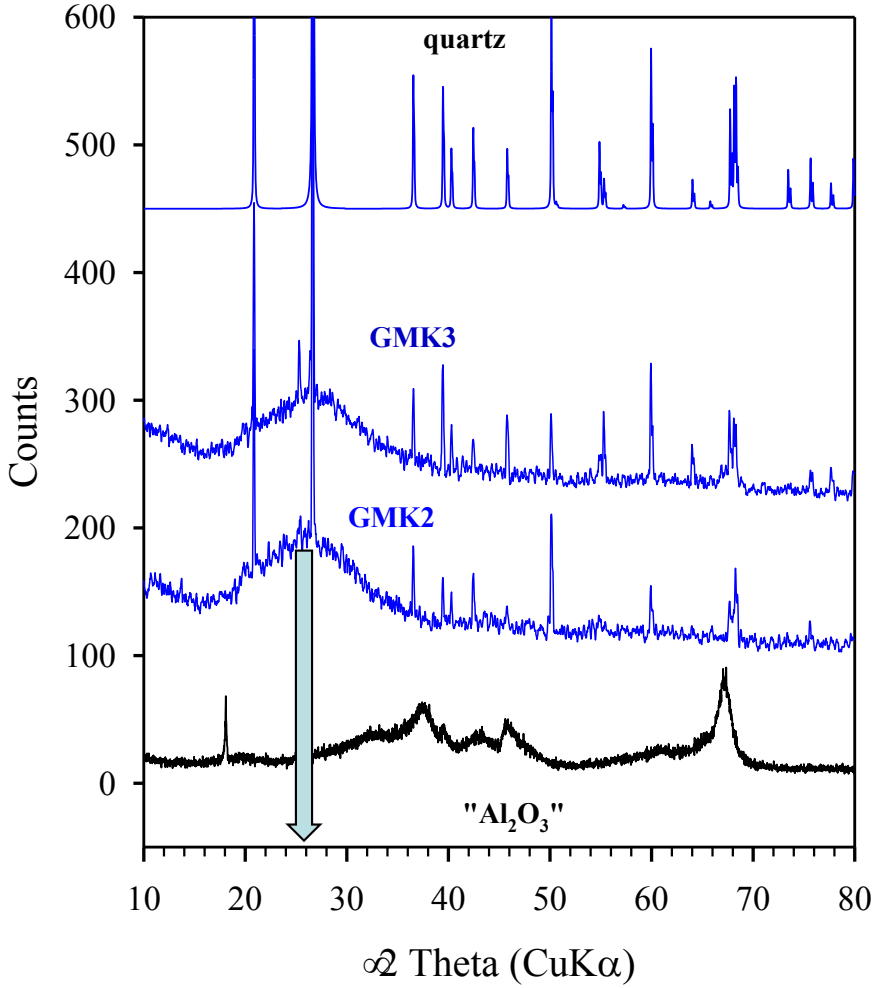


MK + 10 M phosporic acid => XX,
liq/sol = 0.95, 60°C for 24 h (28 days)



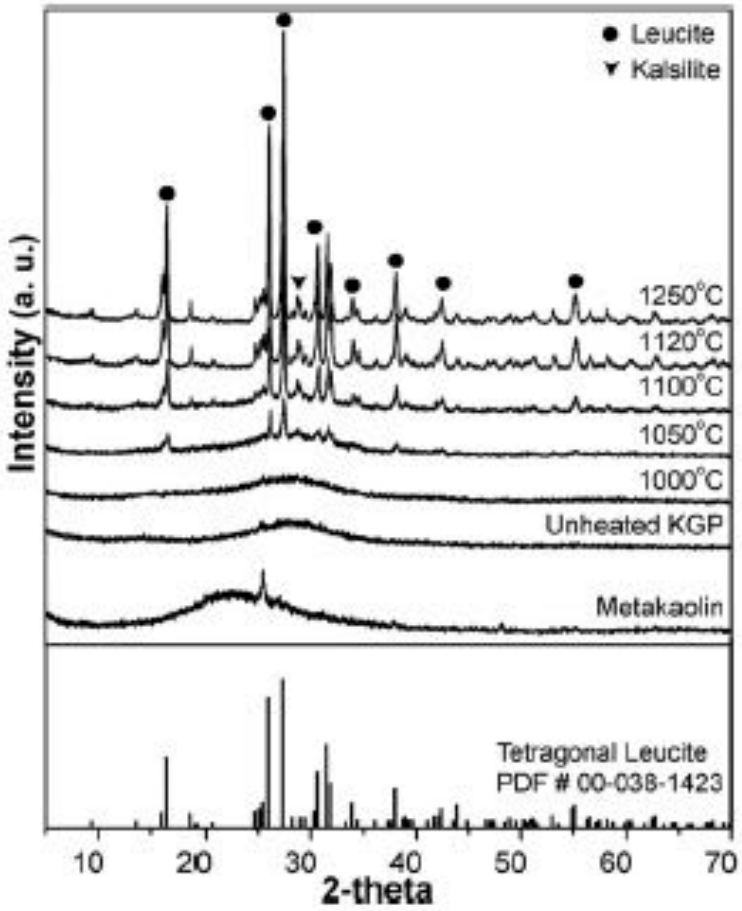


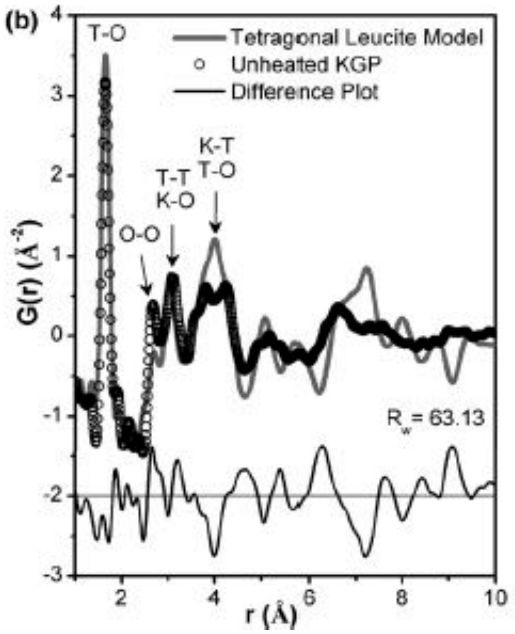


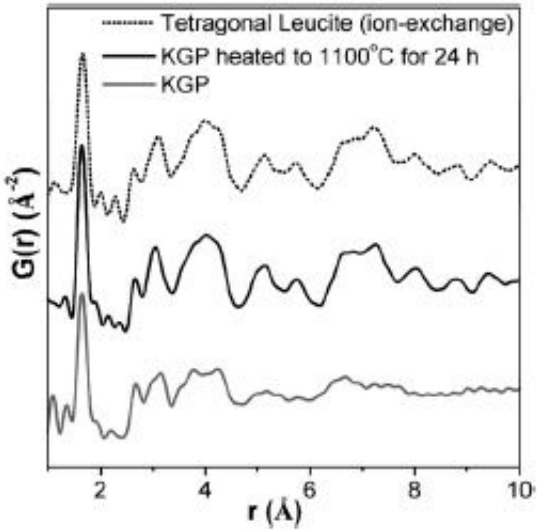


Unreacted MK subtracted
=>Observe: „Main structural unit)

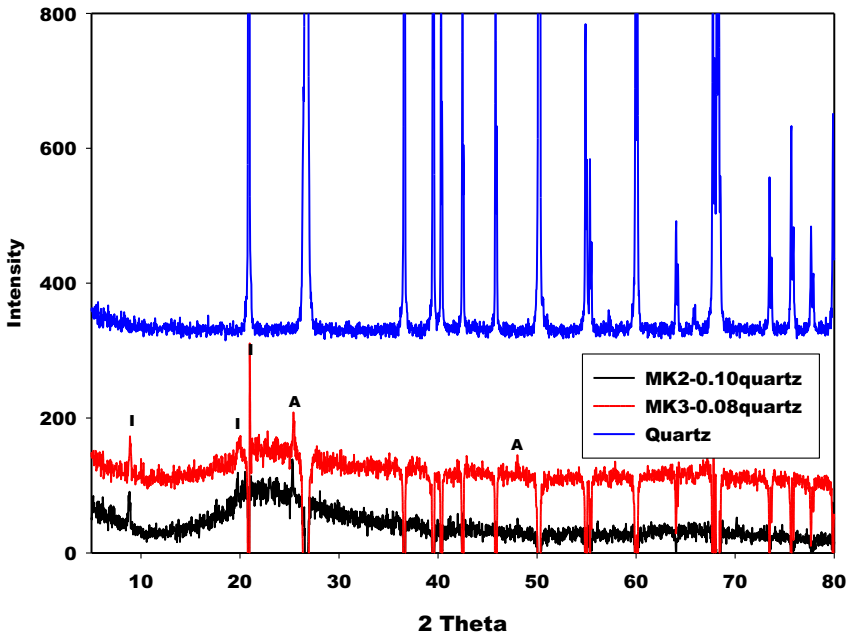
		NWG	$[PO_4]$
MK_1 (22%Qz)	: GP1	48 Mpa	
MK_2 (10%Qz 11%Al_2O_3):	GP2	38 MPa	GMK2 / 54 MPa
MK_3 (8% Qz 28%$A_{l2}O_3$):	GP3	36 MPa	GMK3 / 36 MPa



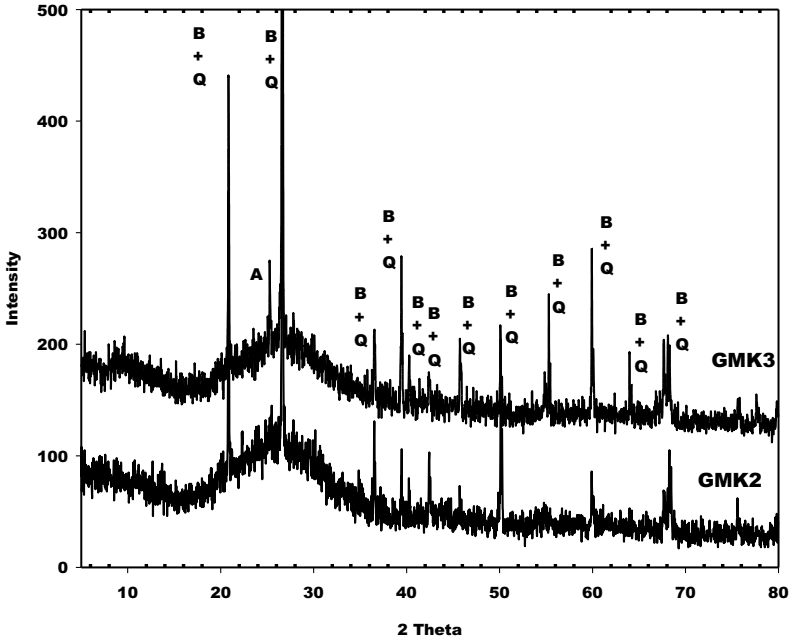


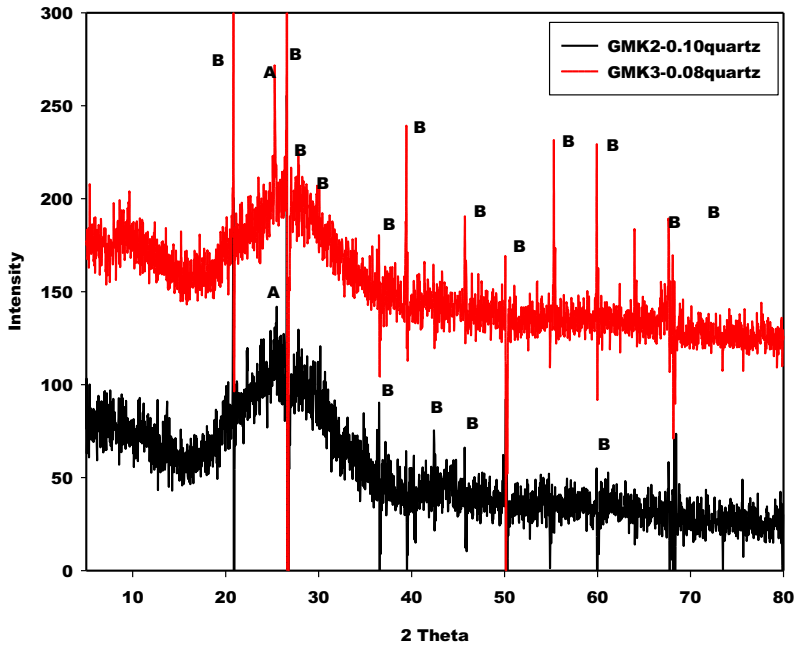


Bell ….Kriven, J. Mater. Chem. 18 (2008) 5974: X-Ray pair distribution analysis …(of „total scattering“ synchrotron data)!



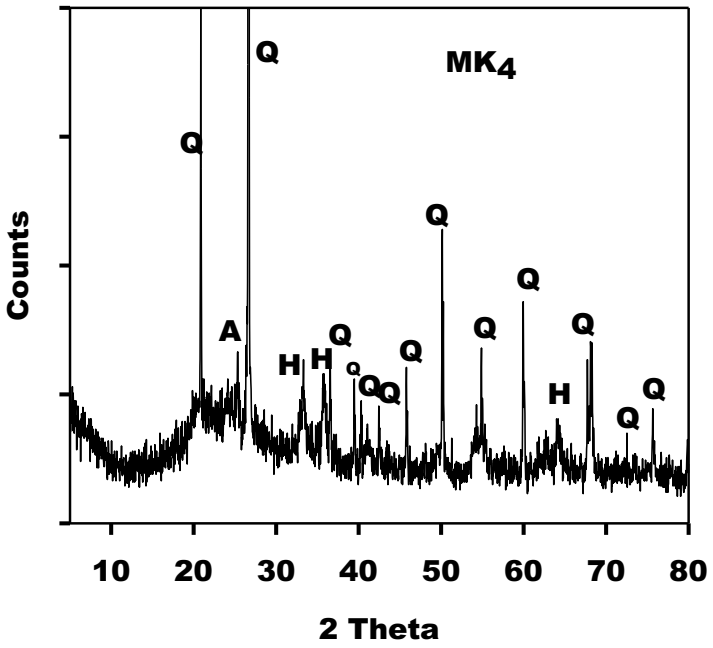
MK + 10 M phosporic acid => XX,
liq/sol = 0.95, 60°C for 24 h (28 days)

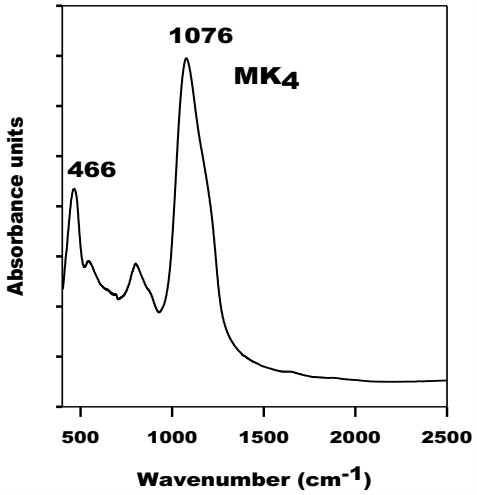


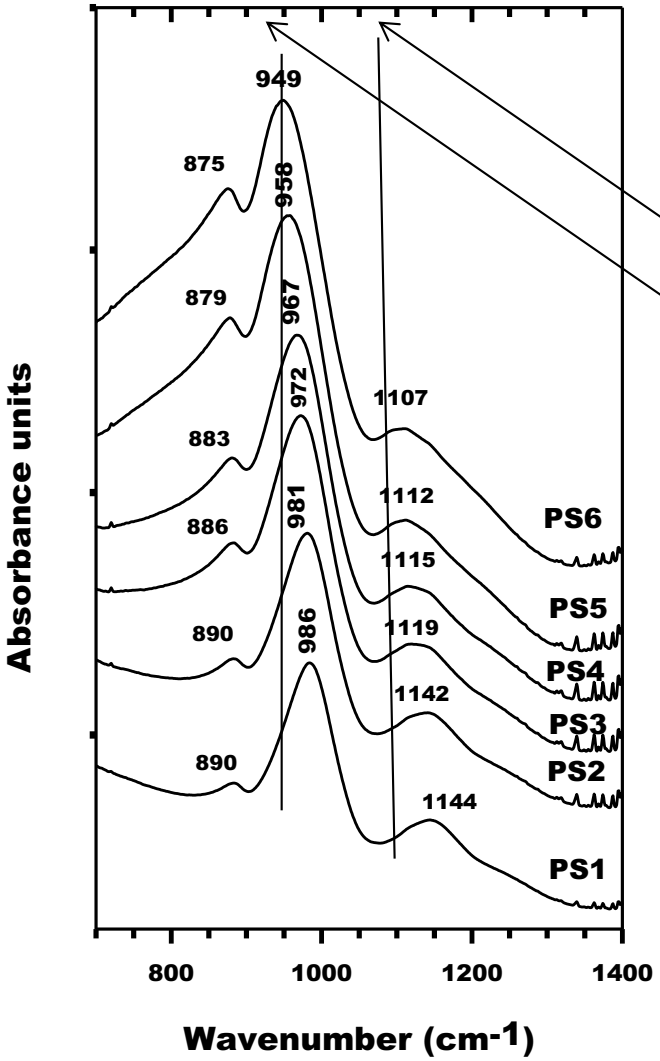


2nd : Consider the effect of $[PO_4]^{3-}$ concentration

MK_4 + X M phosporic acid, liq/sol = 0.80, 60°C for 24 h (28 days)

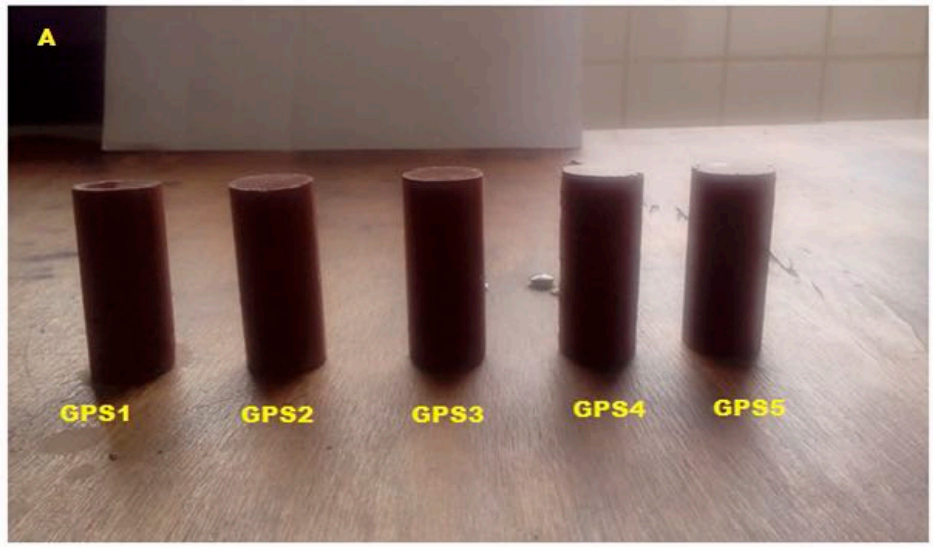


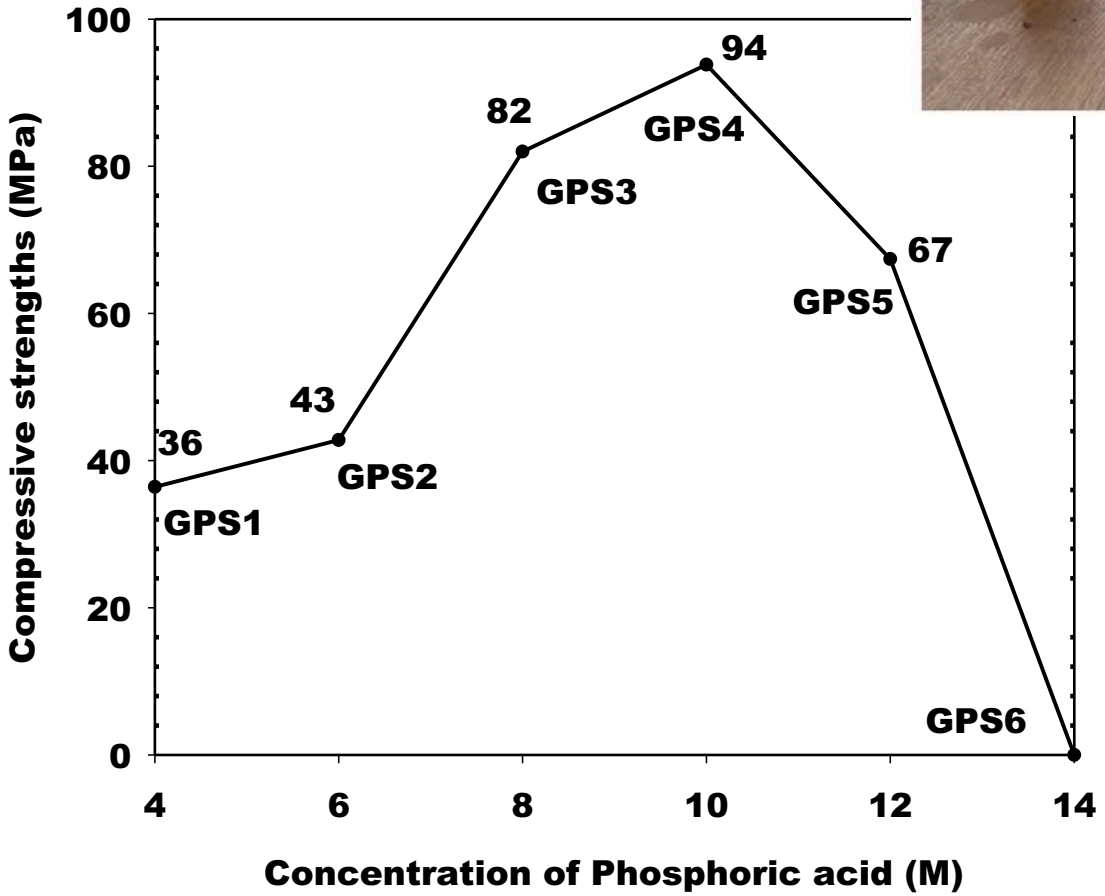


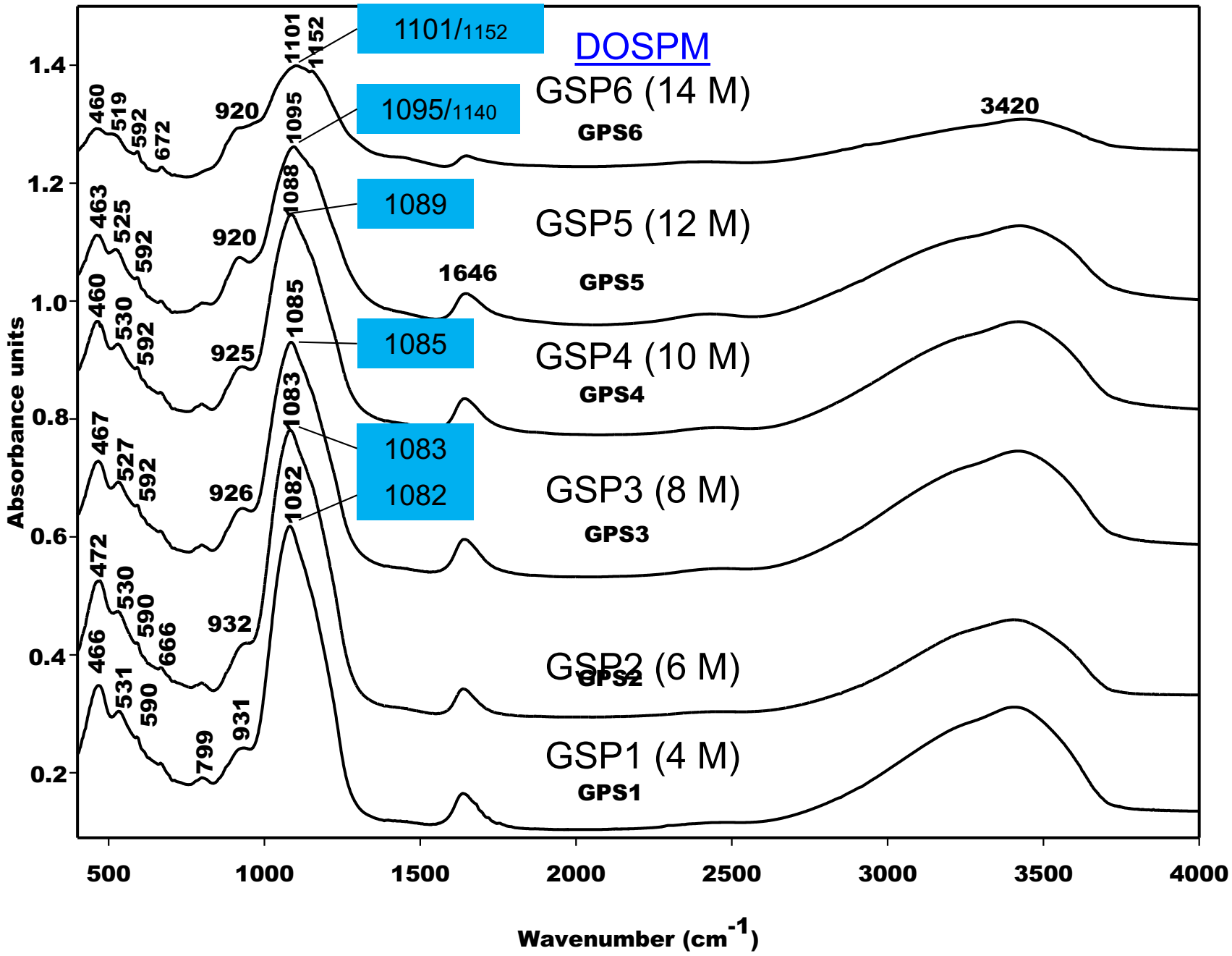


K_4 (Cameroon)	
SiO_2	41.46
Al_2O_3	31.47
Fe_2O_3	7.65
K_2O	0.51
MgO	1.50
Na_2O	0.65
CaO	0.69
SO_3	0.15
P_2O_5	0.09
MnO	0.06
LOI	15.76

M14: 875 949 1107 (PS6)
M12: 879 967 1112 (PS5)
M10: 883 967 1115 (PS4)
M08: 886 972 1119 (PS3)
M06: 890 961 1142 (PS2)
M04: 890 986 1144 (PS1)

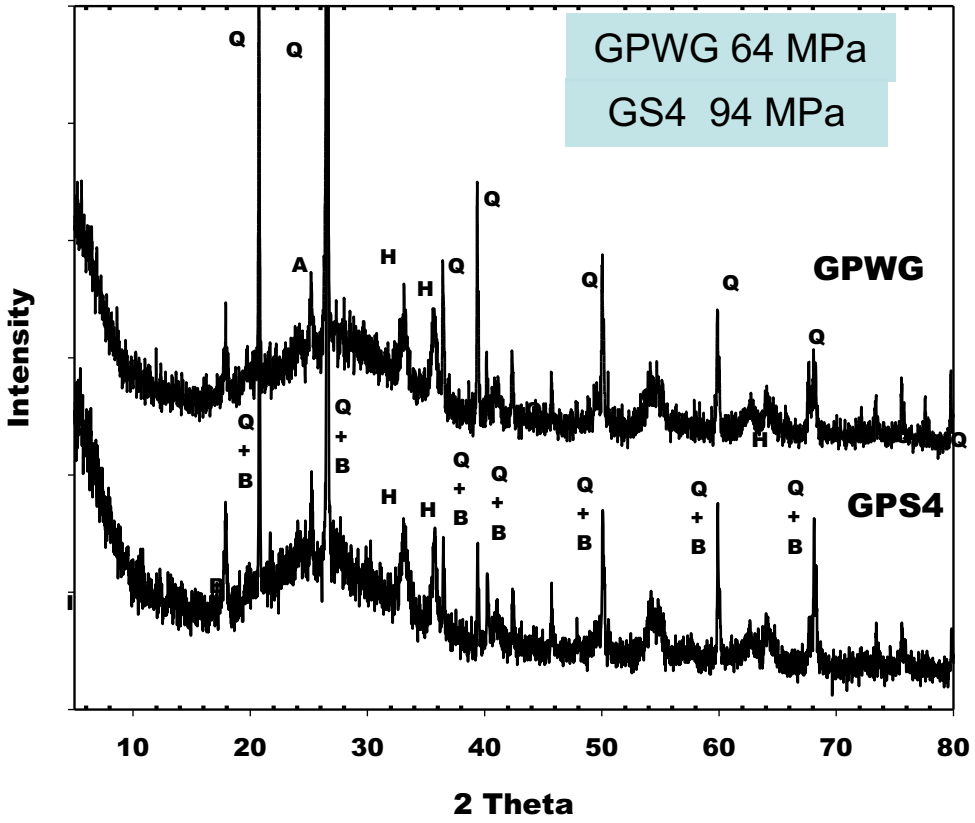

A
GPS1
GPS2
GPS3
GPS4
GPS5

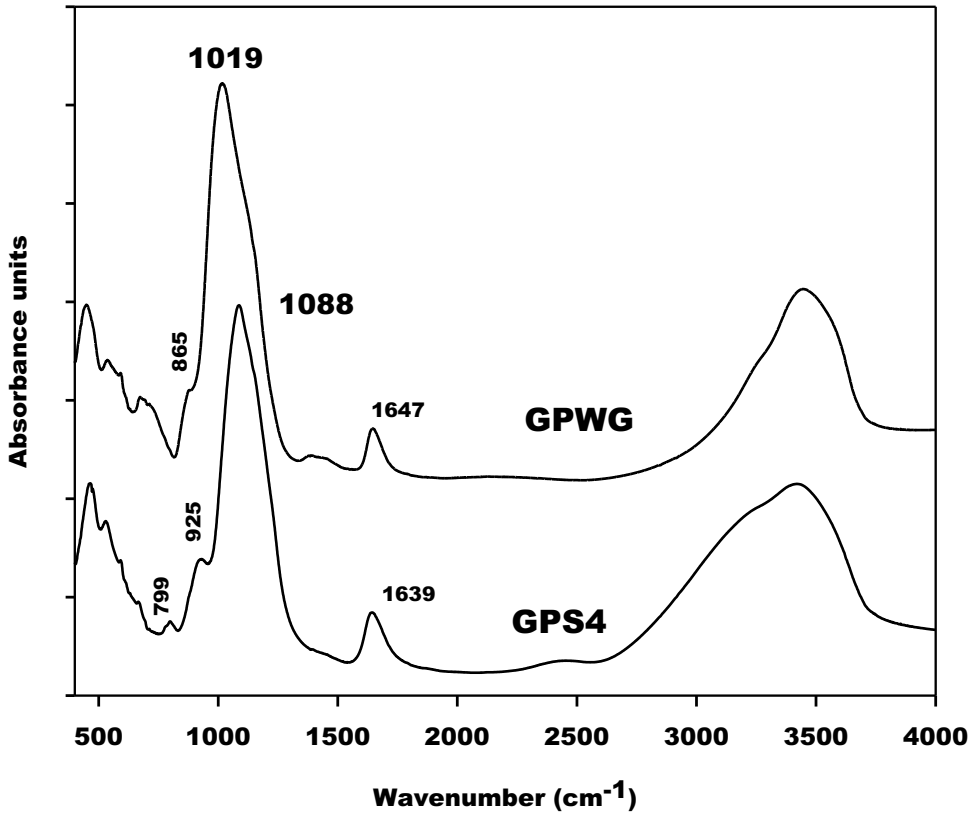

Compressive strengths (MPa)
100
80
60
40
20
0
4
6
8
10
12
14
Concentration of Phosphoric acid (M)
36
GPS1
43
GPS2
82
GPS3
94
GPS4
67
GPS5
GPS6


DOSPM
1101/1152
1095/1140
1089
1085
1083
1082
GSP6 (14 M)
GPS6
GSP5 (12 M)
GPS5
GSP4 (10 M)
GPS4
GSP3 (8 M)
GPS3
GSP2 (6 M)
GPS2
GSP1 (4 M)
GPS1
1101
1152
1095
1088
1085
1083
1082
920
925
926
932
931
1646
3420
460
519
592
672
463
525
530
467
527
472
590
666
531
799
Absorbance units
Wavenumber (cm-1)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
500
1000
1500
2000
2500
3000
3500
4000

GPWG: MK_4 + NWG, liq/sol = 0.80, (28 days)

GPS4: MK_4 + 10 M phosporic acid, liq/sol = 0.80, 60°C for 24 h (28 days)





Here: Not convinced on Q + B, instead the contribution of B is small!

⇒Use of natural raw material, kaolin!

⇒compare „activation“ with phosphoric acid versus NWG (sodium silicate solution)

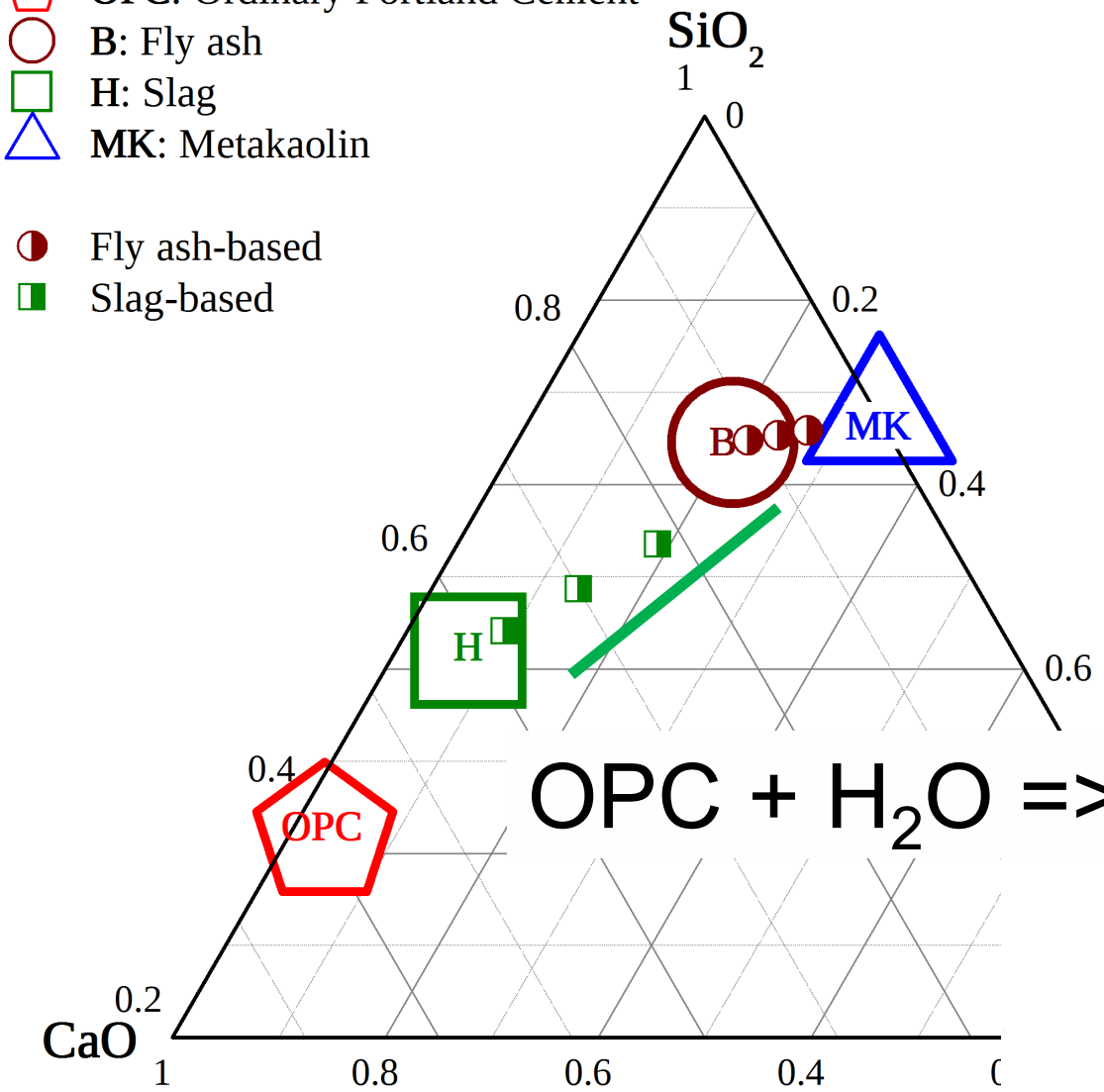
⇒ effect of X M H_3PO_4

If time: Compare Geopolymers based on

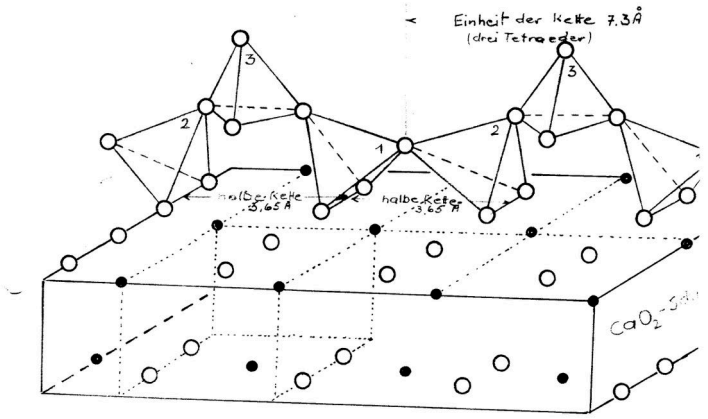
- Polysiloxo-polyphosphate
- Polysiloxo
- Polysiloxo-sialate

OPC: Ordinary Portland Cement
B: Fly ash
H: Slag
MK: Metakaolin

Fly ash-based
Slag-based

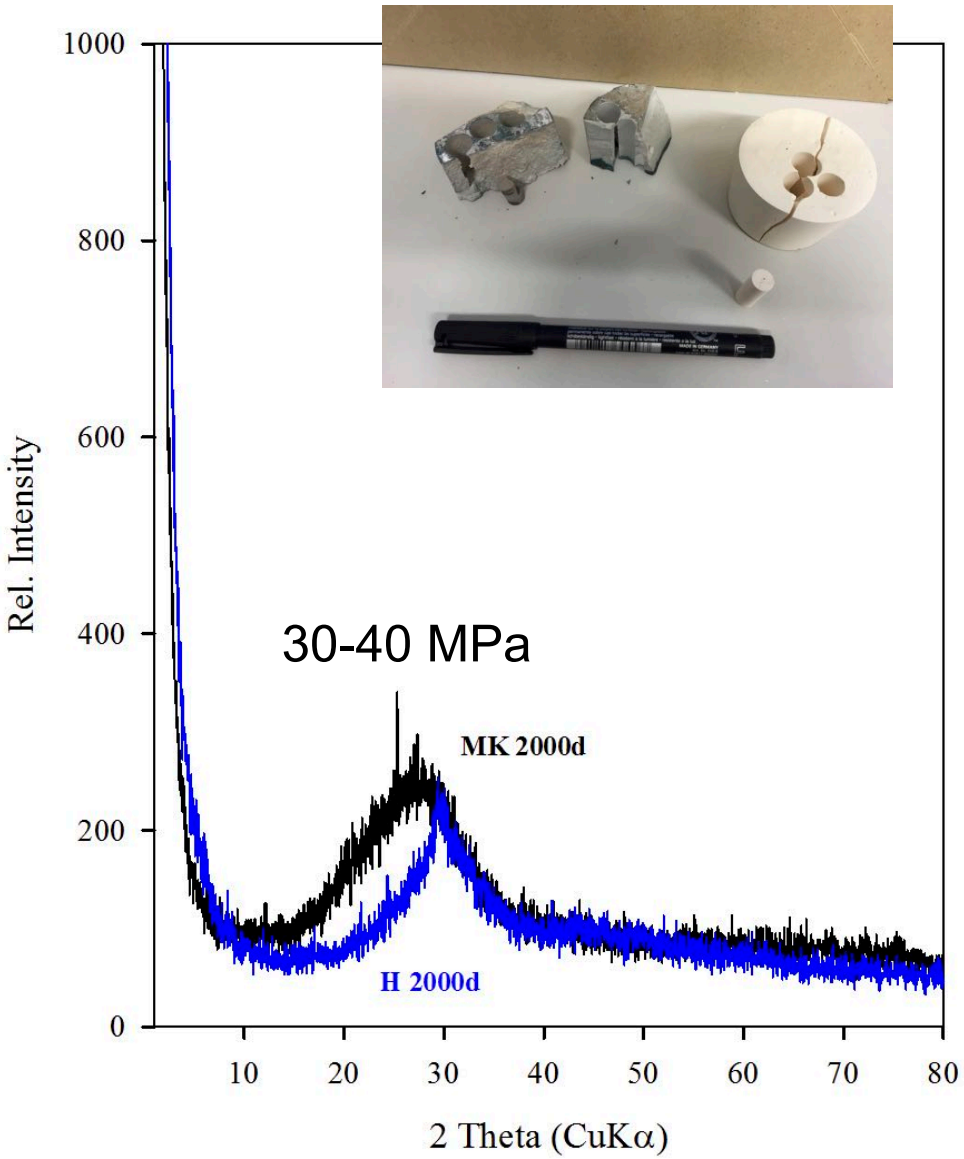


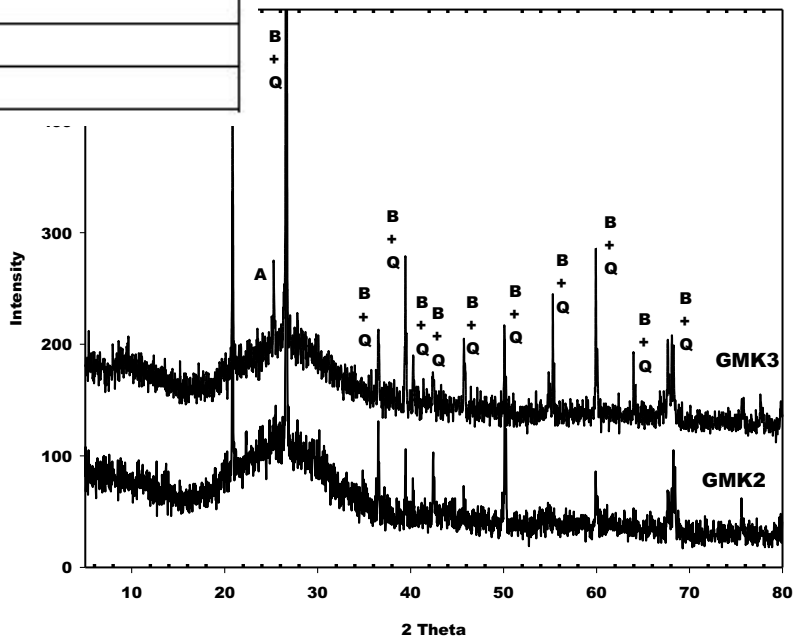
OPC + H_2O => CSH-binder!

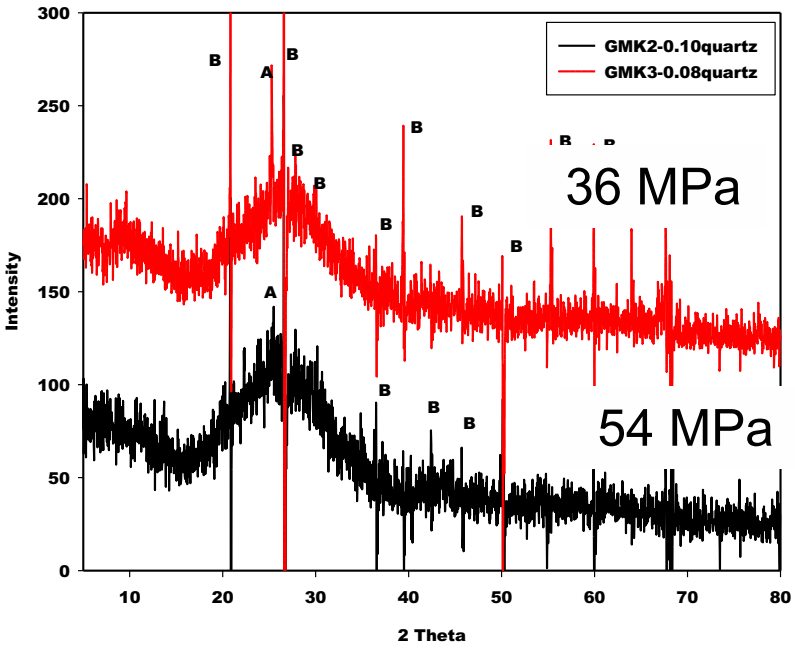


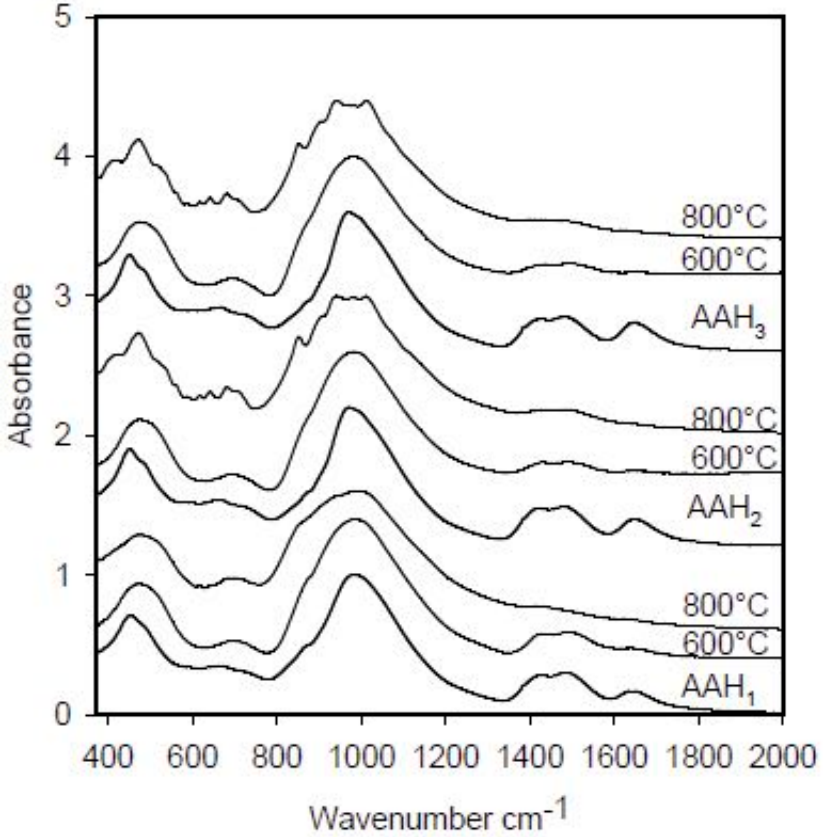
Tab.1 Compressive strength of samples AAMK and AAH

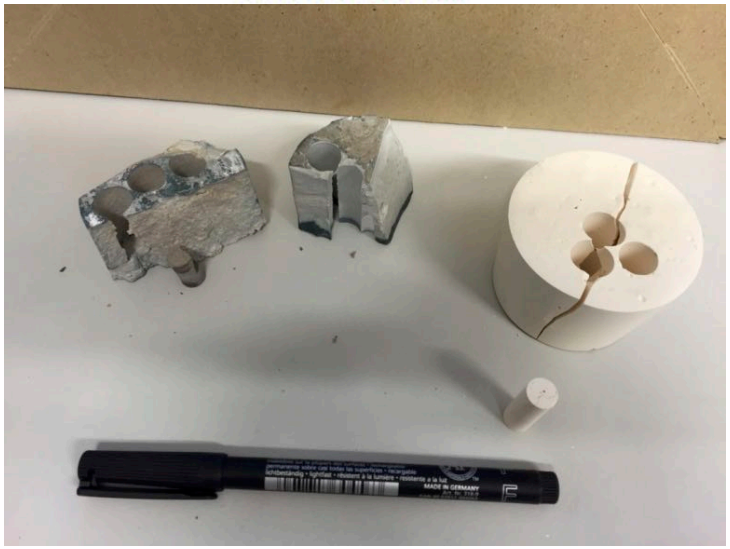
Sample	unheated	800°C heated
AAMK	35MPa	31 MPa
AAH_1	100 MPa	55 MPa
AAH_2	63 MPa	11 MPa

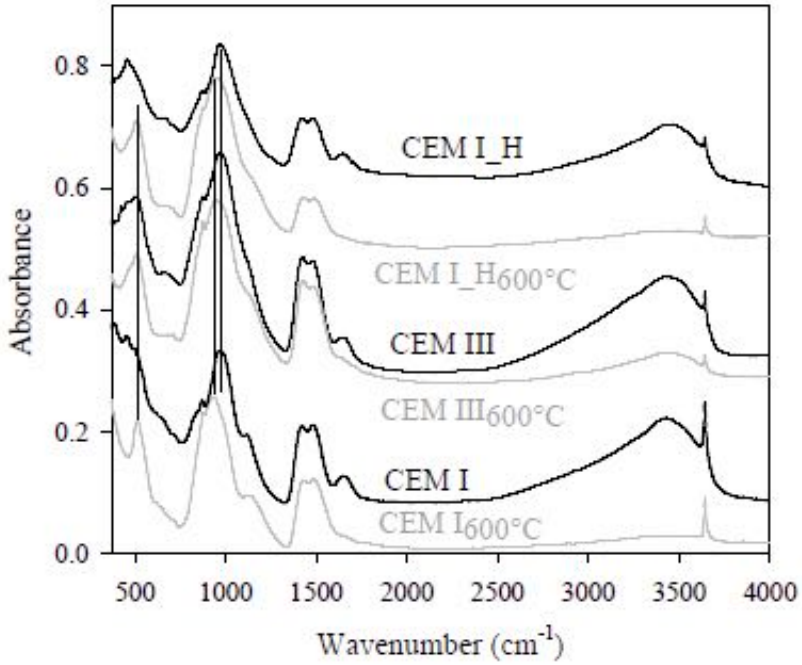


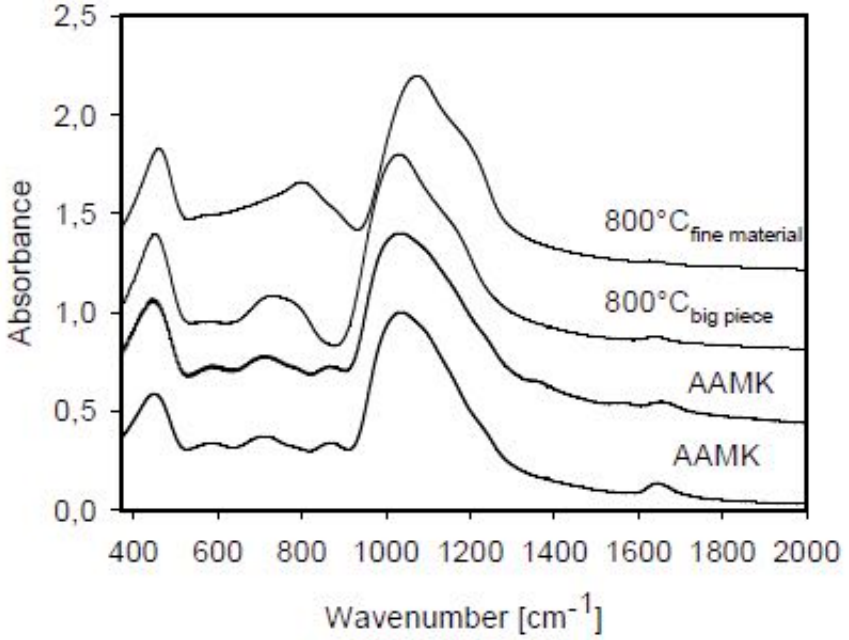


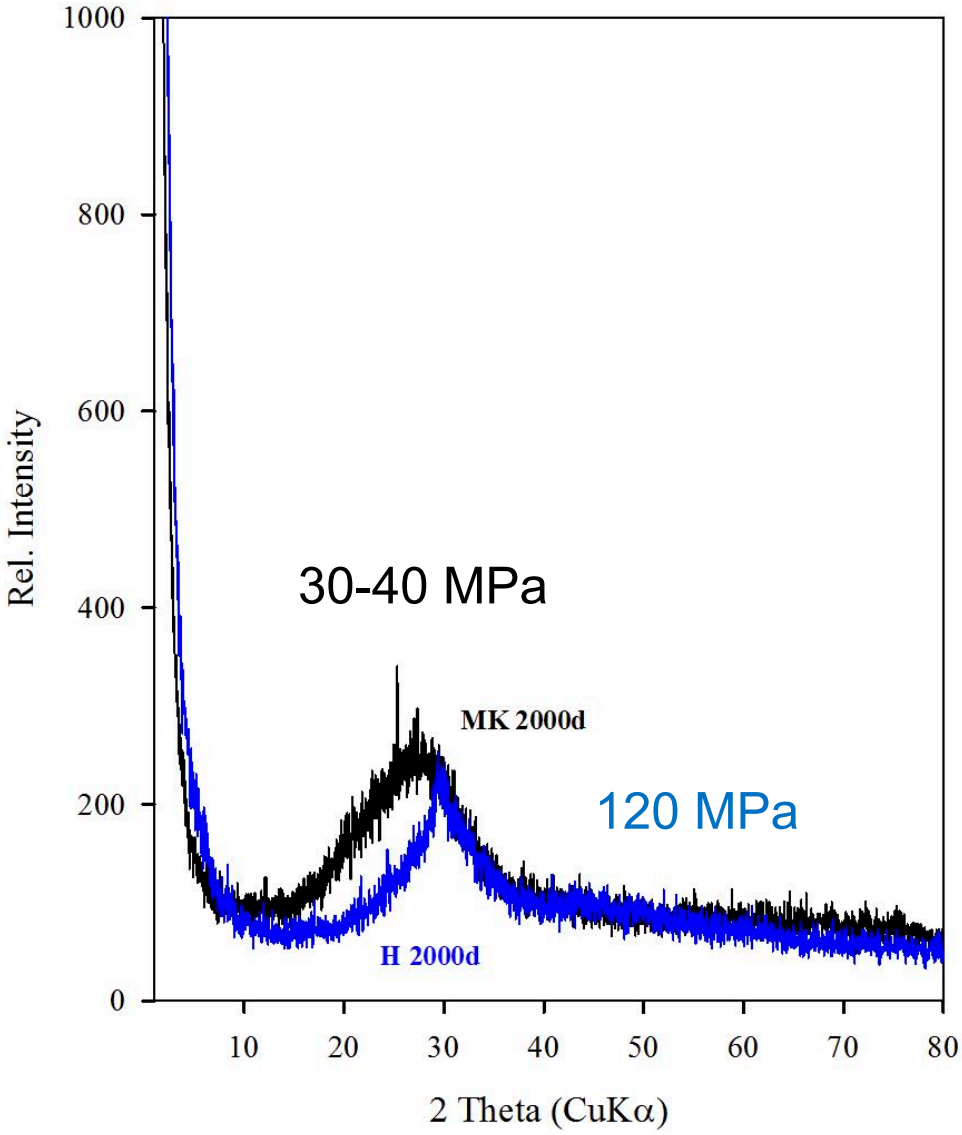


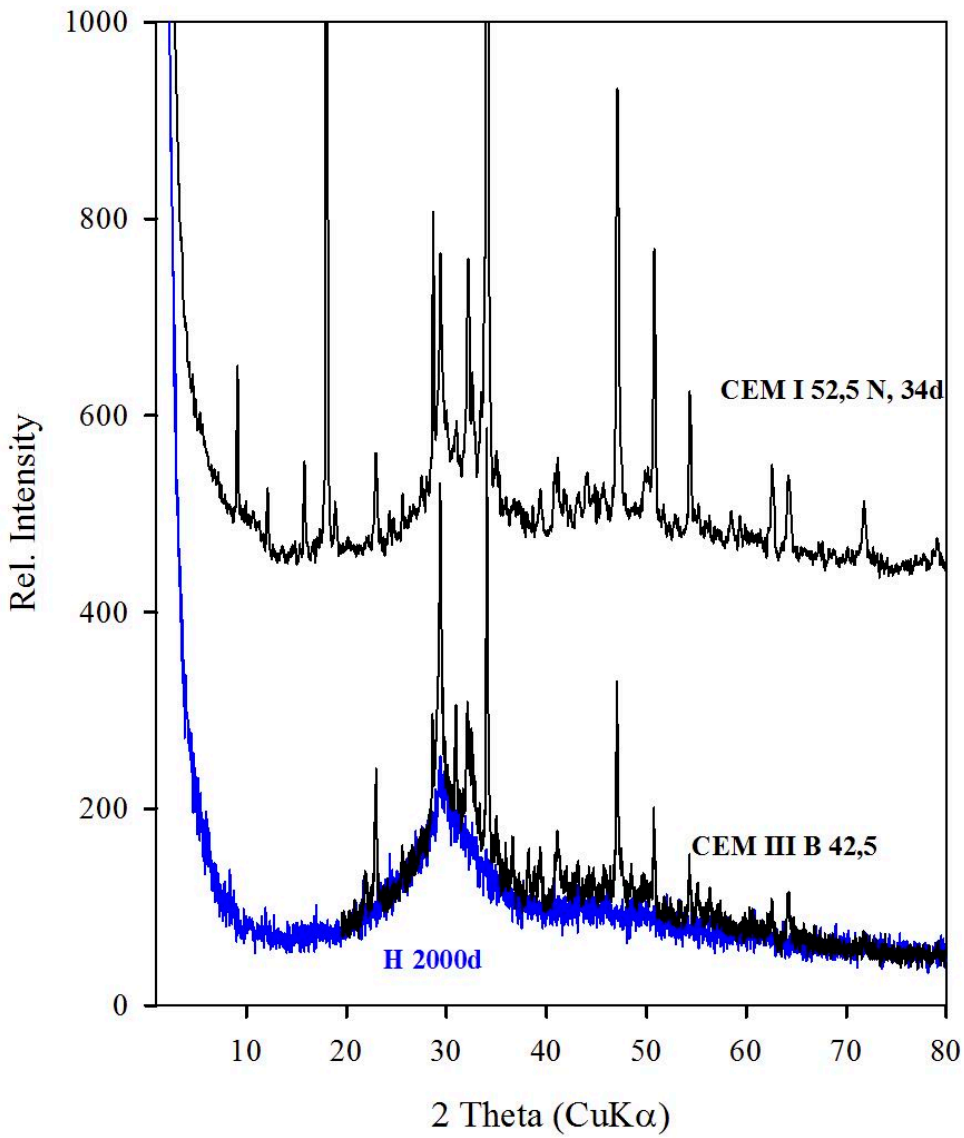

Absorbance
Wavenumber cm-1
800°C
600°C
AAH3
800°C
600°C
AAH2
800°C
600°C
AAH1




Absorbance
Wavenumber (cm-1)
CEM I_H
CEM I_H600°C
CEM III
CEM III600°C
CEM I
CEM I600°C


Absorbance
Wavenumber [cm-1]
800°Cfine material
800°Cbig piece
AAMK
AAMK


1000
800
600
400
200
0
Rel. Intensity
30-40 MPa
MK 2000d
120 MPa
H 2000d
10
20
30
40
50
60
70
80
2 Theta (CuKα)


1000
800
600
400
200
0
Rel. Intensity
CEM I 52,5 N, 34d
CEM III B 42,5
H 2000d
10
20
30
40
50
60
70
80
2 Theta (CuKα)

Thanks