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JOHANNES GUTENBERG UNIVERSITÄT MAINZ

ESR #8

Structural investigation of cement hydration mechanism by electron crystallography

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PhD Project

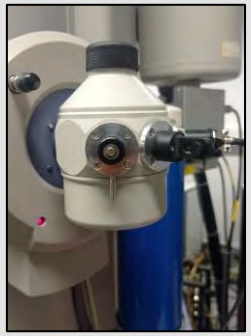
Characterization of metastable hydrate phases of cement

Single Crystal ED | **X-ray diffraction**

CO_2 sensitive / Hydrated

Set-up appropriate sample preparation strategies

Cryo-handling

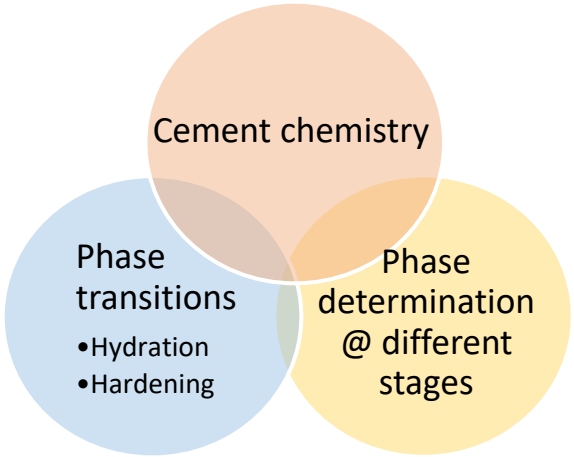


Vitrification

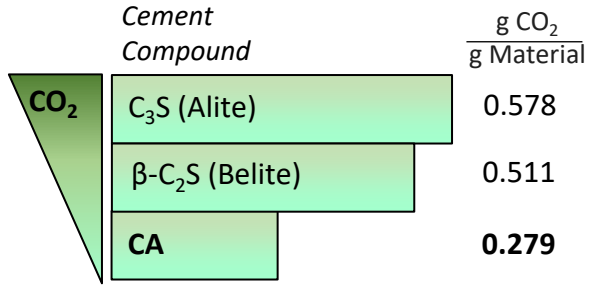
Glovebox

Objective → Gaining understanding of:

in order to



Move away from Portland cement (more energetically demanding and CO_2 producing) to CA cement

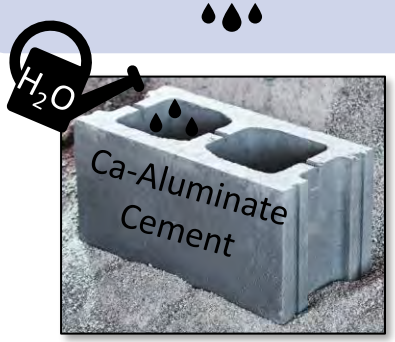


At the moment C_2AH_x phase

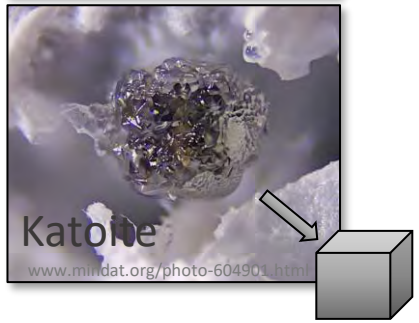
C_2AH_x -> Cement notation | $CaO{\cdot}Al_2O_3{\cdot}XH_2O$ -> Chemical notation

Why this phase?

During hydration of CA-Cem, this pseudo-hexagonal C_2AH_x forms as a metastable intermediate



Depending on storage conditions; converts faster / slower into stable phases Gibbsite (AH_3) and Katoite (C_3AH_6)

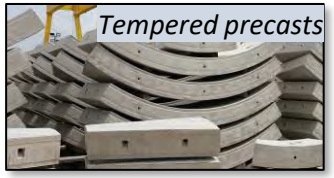


If CO_2 availability -> **Ca-MonoCarboAluminate**

- Decrease in volume
- Increase in porosity
- Decrease in strength
- +Rapid carbonation

Breaking and collapase

At the moment, the difficulty to predict amount of CAH phase formed -> Difficulty in predicting strength development of the cement
-> Narrow use of this low carbon alternative.



to accelerate the conversion process

Knowing the structure allows quantification and enables accurate prediction of cement strength.

More widespread use of CA cement less CO_2 production in construction.

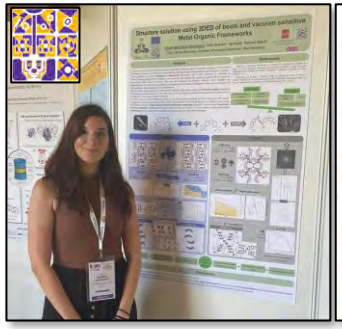
Not the only unsolved cement hydrate phase

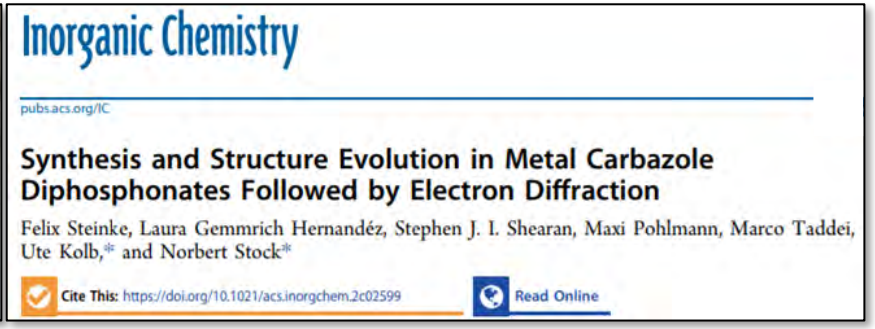
Several CA-cement hydrates (all of them metastable at room temperature) -> with not solved structures. This leads to great difficulties in quantification and prediction of cement behaviour.

A material that has been known for a long time is still riddled with unsolved phases, preventing deeper insight into the microstructural behaviour.

Cement chemist notation (CCN)	Chemical Formula	
$C_2AH_{8.2}$	$2CaO{\cdot}Al_2O_3{\cdot}8.2H_2O$	Mono calcium aluminate 8.2 hydrate
C_2AH_8	$2CaO{\cdot}Al_2O_3{\cdot}8H_2O$	Mono calcium aluminate 8 hydrate
$C_2AH_{7.5}$	$2CaO{\cdot}Al_2O_3{\cdot}7.5H_2O$	Mono calcium aluminate 7.5 hydrate
C_4AH_{19}	$3CaO{\cdot}Al_2O_3{\cdot}Ca(OH)_2{\cdot}18H_2O$	Tetracalcium aluminate 19 hydrate
C_4AH_{13}	$3CaO{\cdot}Al_2O_3{\cdot}Ca(OH)_2{\cdot}12H_2O$	Tetracalcium aluminate 13 hydrate

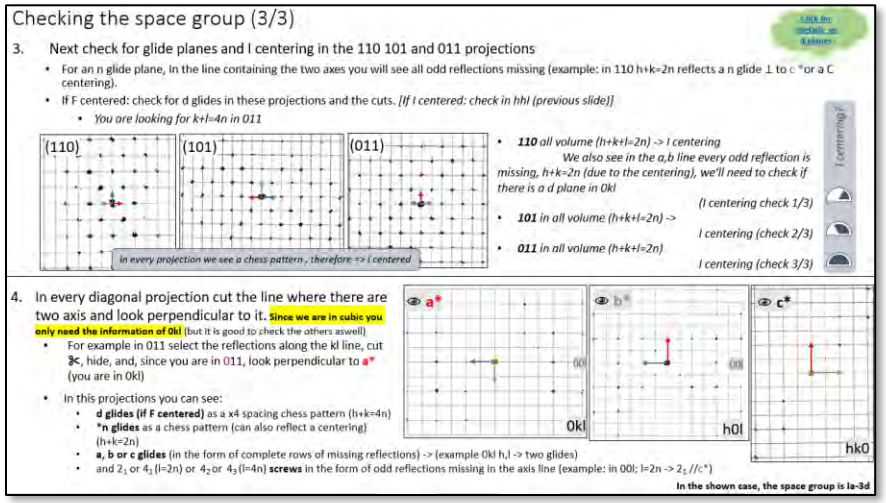
State of the art of the project

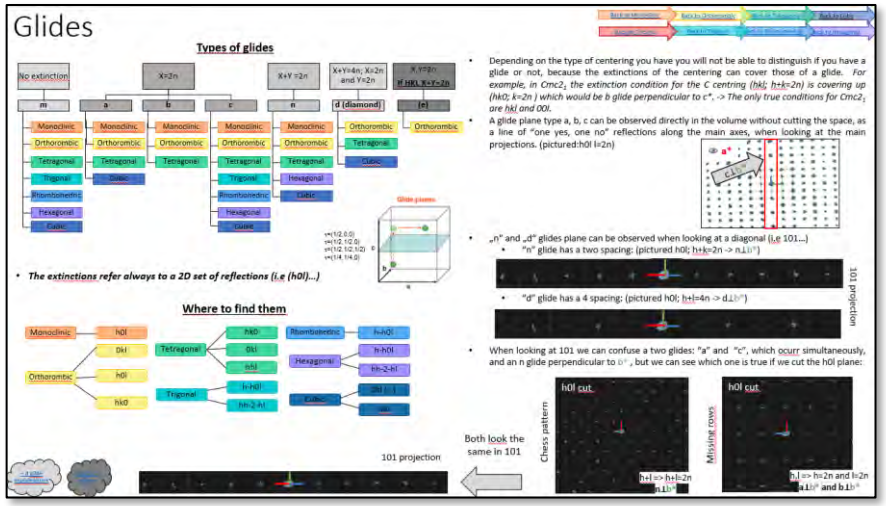




Recent developments

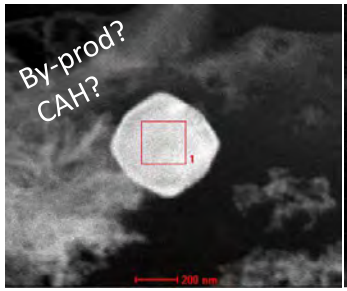
- Poster @ECM33 (beam and vacuum sensitive)
- Paper about solved MOFs -> https://doi.org/10.1021/acs.inorgchem.2c02599
- Visit to BAM (Federal Institute for Materials Research and Testing) to learn cement synthesis + cement research
- Deepening Crystallographic knowledge ("how to" for crystallography and space group identification specifically for ED).
- Python as transversal skill -> Speed up handling of data and structure solution in SIR.

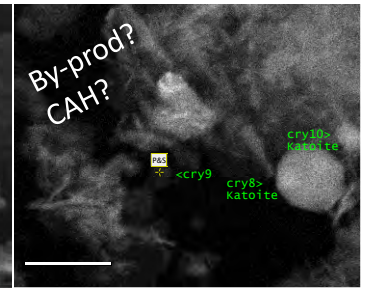




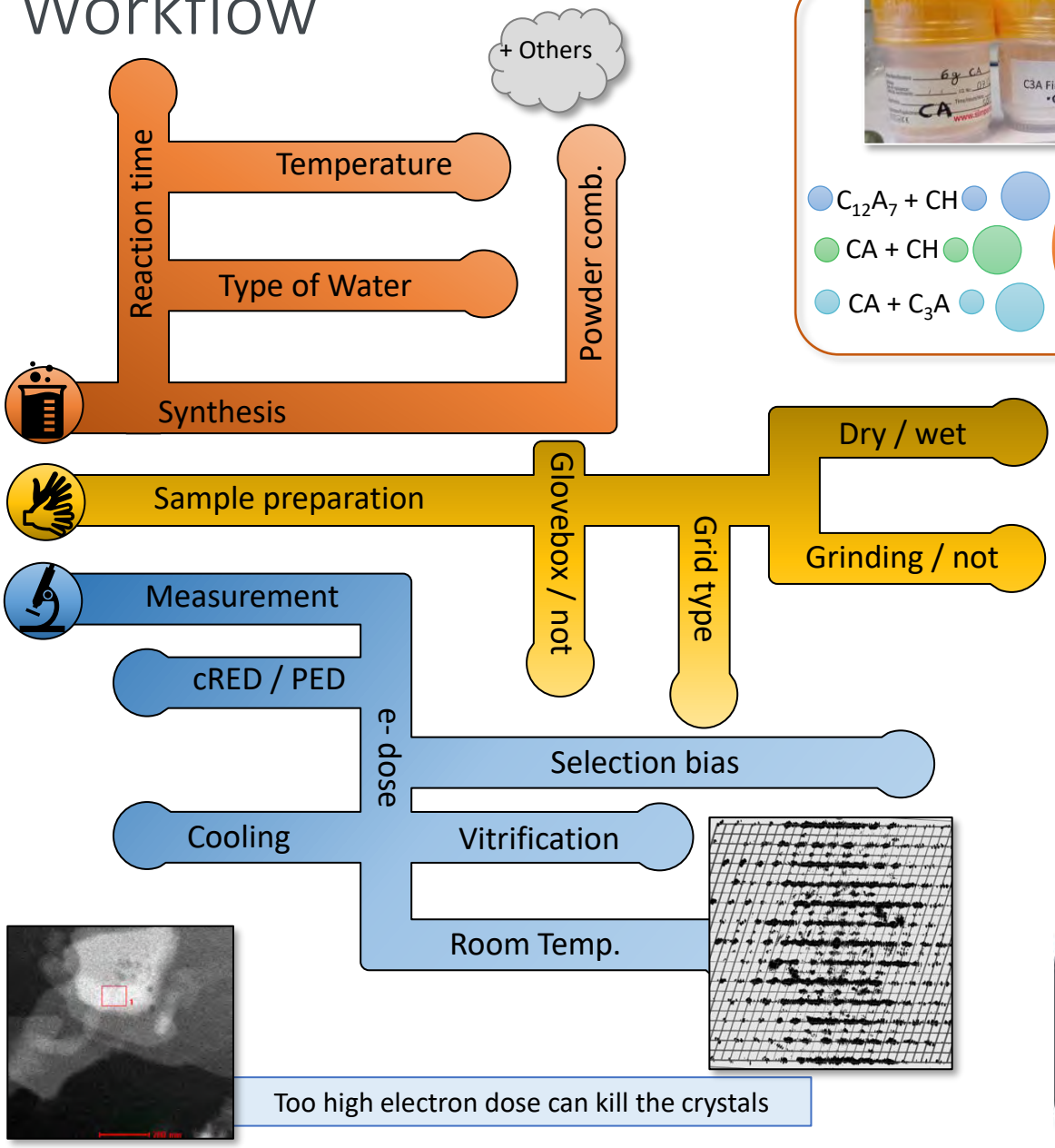
Current challenges

- Optimize synthesis
- Optimizing workflow
- Reducing the by-product formation
- Finding non oriented crystals
- Bypass selection bias (usually what diffracts nicely of looks really crystalline is a by-product).

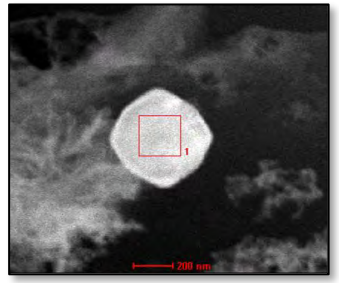


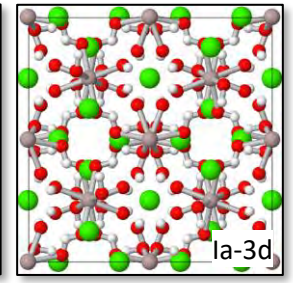


Workflow

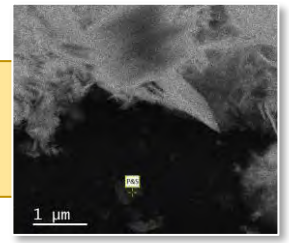


- Too much powder / too high temperature -> Katoite
- If you don't wait enough -> only by-products
- Not enough water purity -> lots of by-products





- If you don't control the gases in the environment -> absorb CO_2
- Wet sample preparation will lead to highly agglomerated grids
- Not grinding leads to too thick and big crystals

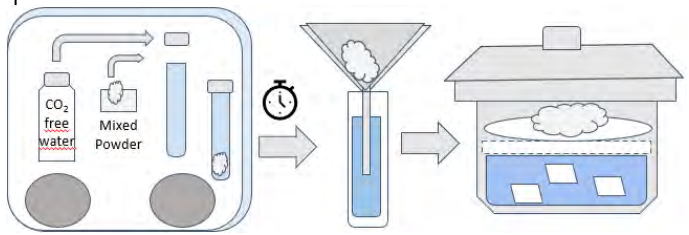


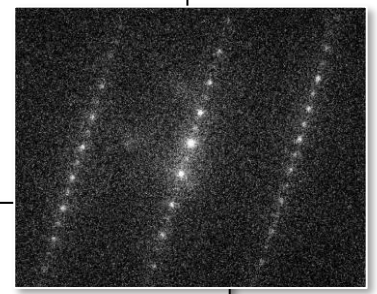
Too high electron dose can kill the crystals

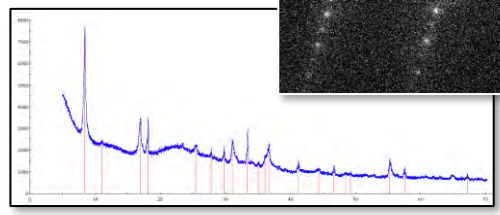
A lot of variables to test and control.

But we have some tools and strategies to make steps forward:

- Simultaneous XRD and TEM measurements
- Working inside a glovebox + CO_2 free water.
- EDX essential to identify (Ca:Al 1:1 correct target)







Byproducts

After bibliographic research I was able to put together a list of known cement by-products, which is helping me identify if what I measured is my phase or not.

Phase	Formula	C.System	s.g.	μ (cm-1)	a [Å]	b [Å]	c [Å]	Alpha (°)	Beta (°)	Gamma (γ)	Vol (Å3)
Portlandite	$Ca(OH)_2$	Trigonal	P-3m	211.4	3.5853	3.5853	4.895	90	90	120	54.49
Gibbsite	$Al(OH)_3$	Monoclin	$P2_1/n$	57.1	8.684	5.078	9.736	90	94.54	90	427.98
Clinotobermorite	$Ca_5(Si_6O_{17})\cdot 5H_2O$	Triclin	C1	168.6	11.274	7.344	11.468	99.18	97.19	90.02	929.78
Tobermorite-14A	$Ca_5Si_6O_{16}(OH)_2\cdot 7H_2O$	Monoclin	Bb	135.6	6.735	7.425	27.987	90	90	123.25	1170.43
Tobermorite-11A	$Ca_4Si_6O_{15}(OH)_2\cdot 5H_2O$	Monoclin	B11m	144.3	6.735	7.385	22.487	90	90	123.25	935.35
Jennite	$Ca_9Si_6O_{18}(OH)_6\cdot 8H_2O$	Triclin	P-1	164.3	10.576	7.265	10.931	101.3	96.98	109.65	759.5
Dicalcium silicate hydrate	$Ca_2(SiO_4)\cdot H_2O$	Orthor	P212121	225.6	9.487	9.179	10.666	90	90	90	928.81
Hydrogamet/C_3AH_6	$Ca_3Al_2(OH)_{12}$	Cubic	Ia-3d	163.7	12.565	12.565	12.565	90	90	90	1983.75
Hydrogamet-Fe /(C4AF?)	$Ca_3(Fe_{0.155}Al_{0.845})_2(SiO_4)_{1.5}(OH)_8$	Cubic	Ia-3d	189.4	12.603	12.603	12.603	90	90	90	2001.88
Katoite	$Ca_3Al_2(OH)_{7.6}(SiO_4)_{1.1}$	Cubic	Ia-3d	187.8	12.27	12.27	12.27	90	90	90	1847.28
Katoite	$Ca_{2.93}Al_2(OH)_{9.44}(SiO_4)_{0.64}$	Cubic	Ia-3d	185.5	12.38	12.38	12.38	90	90	90	1897.41
Hydroandradite	$Ca_3Fe_2(OH)_{8.64}(SiO_4)_{0.84}$	Cubic	Ia-3d	385.5	12.5424	12.5424	12.5424	90	90	90	1973.07
Hydroandradite	$Ca_3Fe_2(OH)_{8.64}(SiO_4)_{1.34}$	Cubic	Ia-3d	406.4	12.4297	12.4297	12.4297	90	90	90	1920.36
"CAH10"	$CaAl_2(OH)_8(H_2O)_2\cdot 1.84H2O$	Hexagonal	$P6_3/m$	58.5	16.387	16.387	8.279	90	90	120	1925
Ettringite	$Ca_6Al_2(OH)_{12}(SO_4)_3\cdot 26H_2O$	Trigonal	$P3_1c$	84.4	11.229	11.229	21.478	90	90	120	2345.34
Ettringite-CO_3	$Ca_6Al_2(OH)_{12}(CO_3)_3\cdot 26H_2O$		No structure	77.6	10.8344		21.25				2160.23
Ettringite-BO_3	$Ca_6Al_2(OH)_{12}[B(OH)_4](OH)_2\cdot 2H_2O$	Trigonal	P3c	71	11.0296	11.0296	10.6992	90	90	120	1127.2
Thaumasite	$Ca_6Si_2(OH)_{12}(CO_3)_2(SO_4)_2\cdot 24H_2O$	Hexagonal	$P6_3$	85.7	11.046	11.046	10.409	90	90	120	1099.9
Kuzelite/C_4ASH_{12}	$Ca_2Al(OH)_6[(SO_4)_{0.5})\cdot 3H_2O]$	Rombohedral	R-3	115.8	5.7586	5.7586	26.7946	90	90	120	769.5
Friedel's salt	$Ca_2Al(OH)_6[Cl\cdot 2H_2O]$	Rombohedral	R-3c	146.7	5.724	5.724	46.689	90	90	120	1324.78
Friedel's salt (Dicalcium aluminium hexahydroxide chloride dihydrate)	$Ca_2Al(OH)_6[Cl\cdot 2H_2O]$	Rombohedral	R-3	141.7	5.7487	5.7487	23.492	90	90	120	672.34
Friedel's salt	$Ca_2Al(OH)_6[Cl\cdot 2H_2O]$	Rombohedral	R-3	259.1	5.873	5.873	23.362	90	90	120	697.85
Kuzel's salt	$Ca_2Al(OH)_6[Cl_{0.5}(SO_4)_{0.25}\cdot 2.5H_2O$	Rombohedral	R-3	126.9	5.7508	5.7508	50.4185	90	90	120	1444.04
Hydrocalumite	$Ca_2Al(OH)_6[Cl_{0.5}(CO_3)_{0.25}]\cdot 2.4H_2O$	Monoclin	C 2/c	130.1	10.02	5.751	16.286	90	104.22	90	909.73
Chloro-carboaluminate	$Ca_2Al(OH)_6[Cl_{0.45}(CO_3)_{0.27}]\cdot 2.27H_2O$	Rombohedral	R-3c	129	5.74	5.74	46.7402	90	90	120	1333.7
Monocarbo-aluminate	$Ca_2Al(OH)_6[(CO_3)_{0.5}\cdot 2.5H_2O]$	Triclin	P1	124.7	5.7747	8.4689	9.923	64.77	82.75	81.43	1453.01
Hemicarbo-aluminate	$Ca_2Al(OH)_6[(CO_3)_{0.25}OH_{0.5}\cdot 2H_2O]$	Rombohedral	R-3c	113.9	5.7757	5.7757	48.812	90	90	120	1410.1
Monocarbo-Ferrite	$Ca_2Fe(OH)_6[(CO_3)_{0.5}\cdot 3.1H_2O]$	Rombohedral	R-3c	222.1	5.9196	5.9196	47.8796	90	90	120	1453.01
Borate-AFm	$Ca_2Al(OH)_6[(HBO_3)_{0.5}\cdot 3.1H_2O]$	Rombohedral	R-3c	106.4	5.7764	5.7764	49.5499	90	90	120	1431.8
Strätlingite/C_2ASH_8	$Ca_2Al(OH)_6[AlSiO_2(OH)_4\cdot 3H_2O]$	Rombohedral	R-3m	98.8	5.745	5.745	37.77	90	90	120	1079.59
Strätlingite/C_2ASH_8	$Ca_2Al(OH)_6[(Al,Si)_2O_2(OH)_6\cdot 2.25H_2O]$	Rombohedral	R-3m	91	5.7536	5.7536	37.732	90	90	120	1081.7
Nitroaluminate	$Ca_2Al(OH)_6[NO_3\cdot 2H_2O]$	Trigonal	P-3c	111.2	5.7445	5.7445	17.235	90	90	120	492.55
Bromoaluminate	$Ca_2Al(OH)_6[Br\cdot 2H_2O]$	Rombohedral	R-3	163.8	5.758	5.758	24.498	90	90	120	703.4
Iodoaluminate	$Ca_2Al(OH)_6[I\cdot 2H_2O]$	Rombohedral	R-3	353.1	5.772	5.772	26.538	90	90	120	765.69
Bromochloroaluminate	$Ca_2Al(OH)_6[Br_{0.478}Cl_{0.522}\cdot 2H_2O]$	Rombohedral	R-3c	153.5	5.7537	5.7537	48.108	90	90	120	1379.25
Calcium cloride dehidrate	$CaCl_2(H_2O)_2$	Orthor	Pbcn		5.893	7.469	12.07	90	90	90	531.26

Minimizing the by-products and learning to find the right crystals is my main focus at the moment.

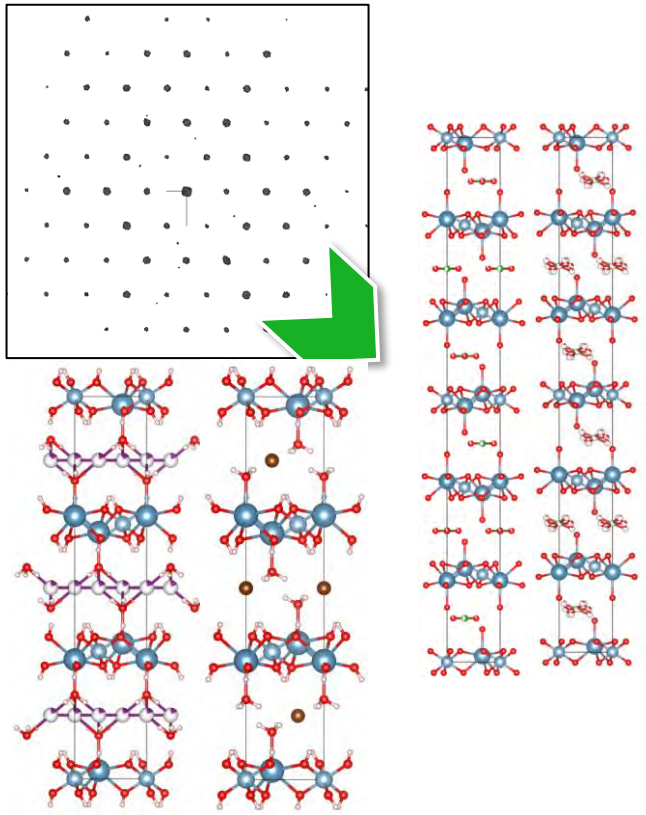
Major issue -> very similar structures

- Barely changing length of c*
- Change small part of the composition

Crystal shape -> oriented on c* (+ if diffuse -> along c*)

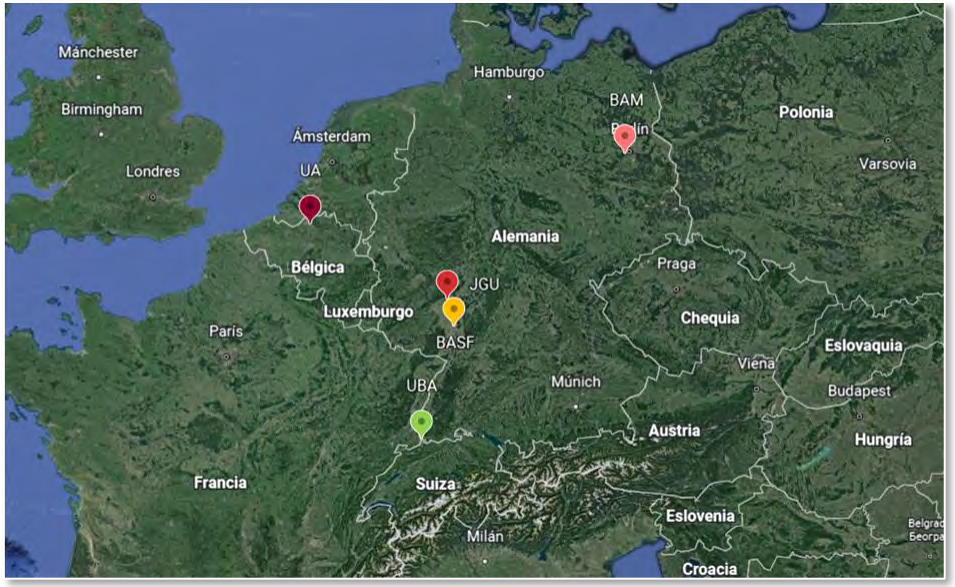
Identifying by-product / Sp.G. becomes tricky.

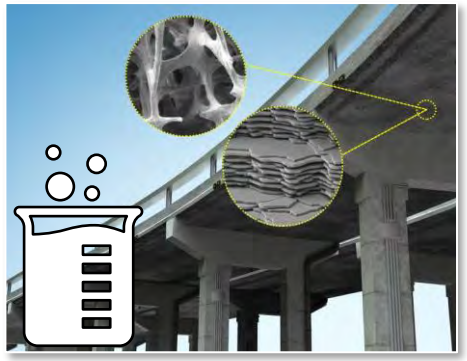
Optimize experiment to be sure that I am measuring what I want.



PhD Secondments

BAM UBA BASF UA





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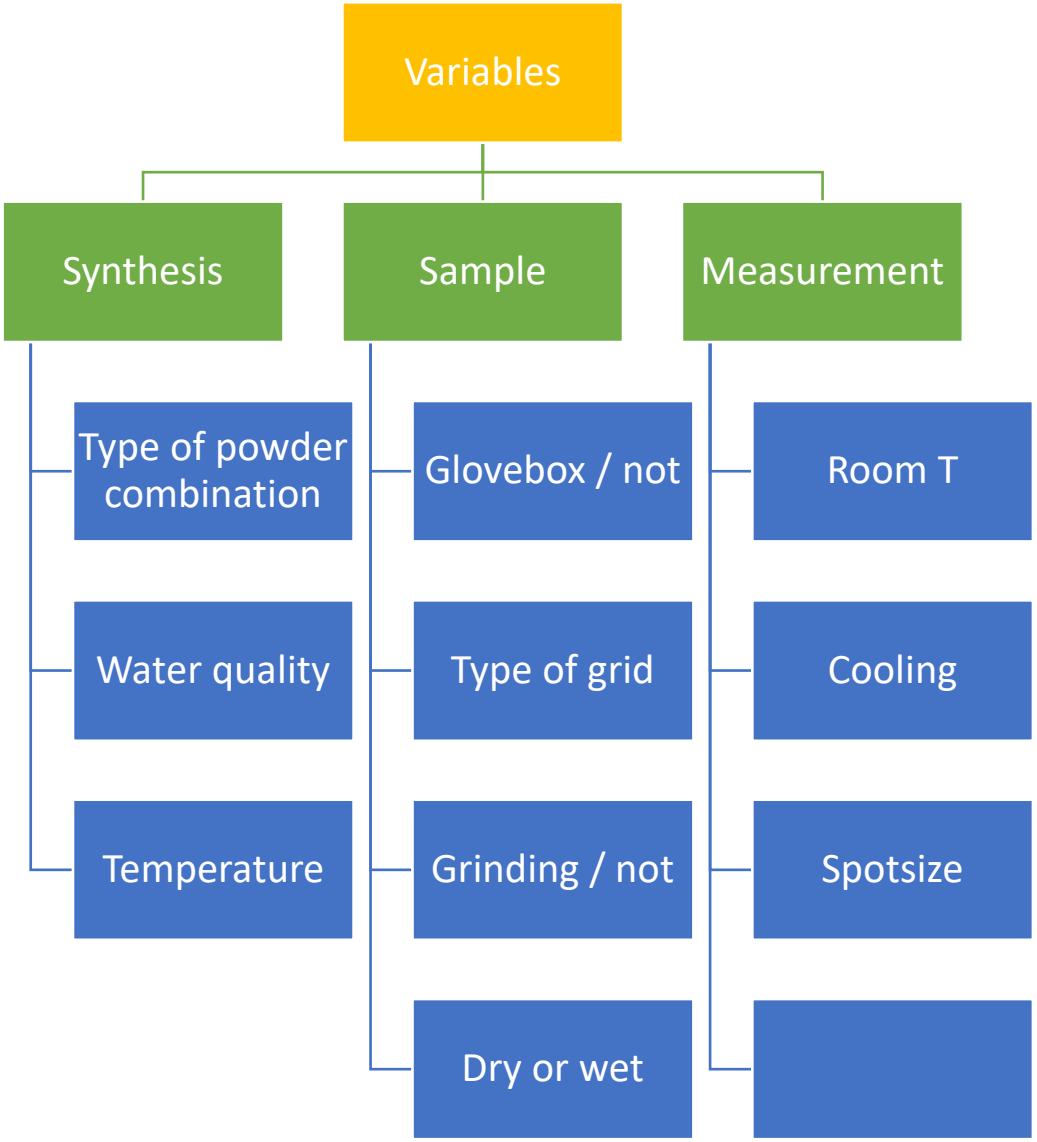
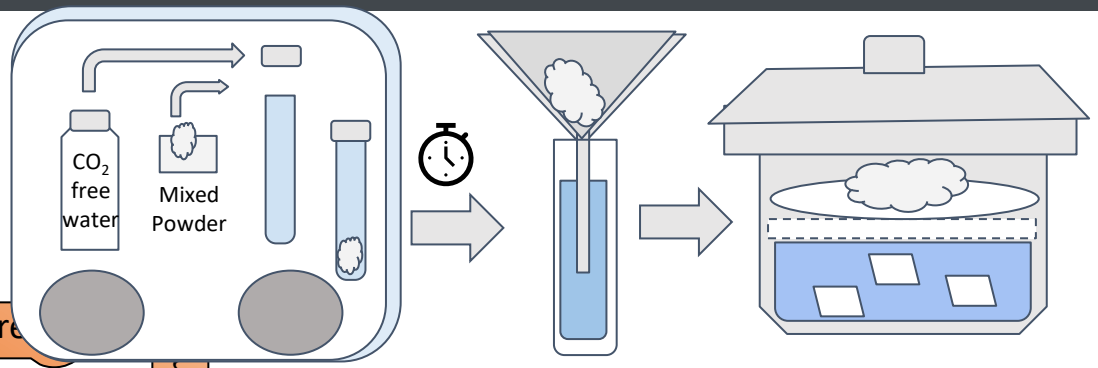

Variables
Synthesis
Sample
Measurement
Type of powder combination
Water quality
Temperature
Glovebox / not
Type of grid
Grinding / not
Dry or wet
Room T
Cooling
Spotsize



Reaction time
Temperature
Type of Water
Powder com
Synthesis

Sample preparation
Glovebox / not
Grid type
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e- dose
cRED / PED
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Vitrification
Room Temp.

Variable

Powder combination
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