DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2006/24

CO_2 SINK: WP 3.1 Rock-/Fluid Interactions Laboratory Experiments

Caprock seal capacity characterization of old core material from the Ketzin structure

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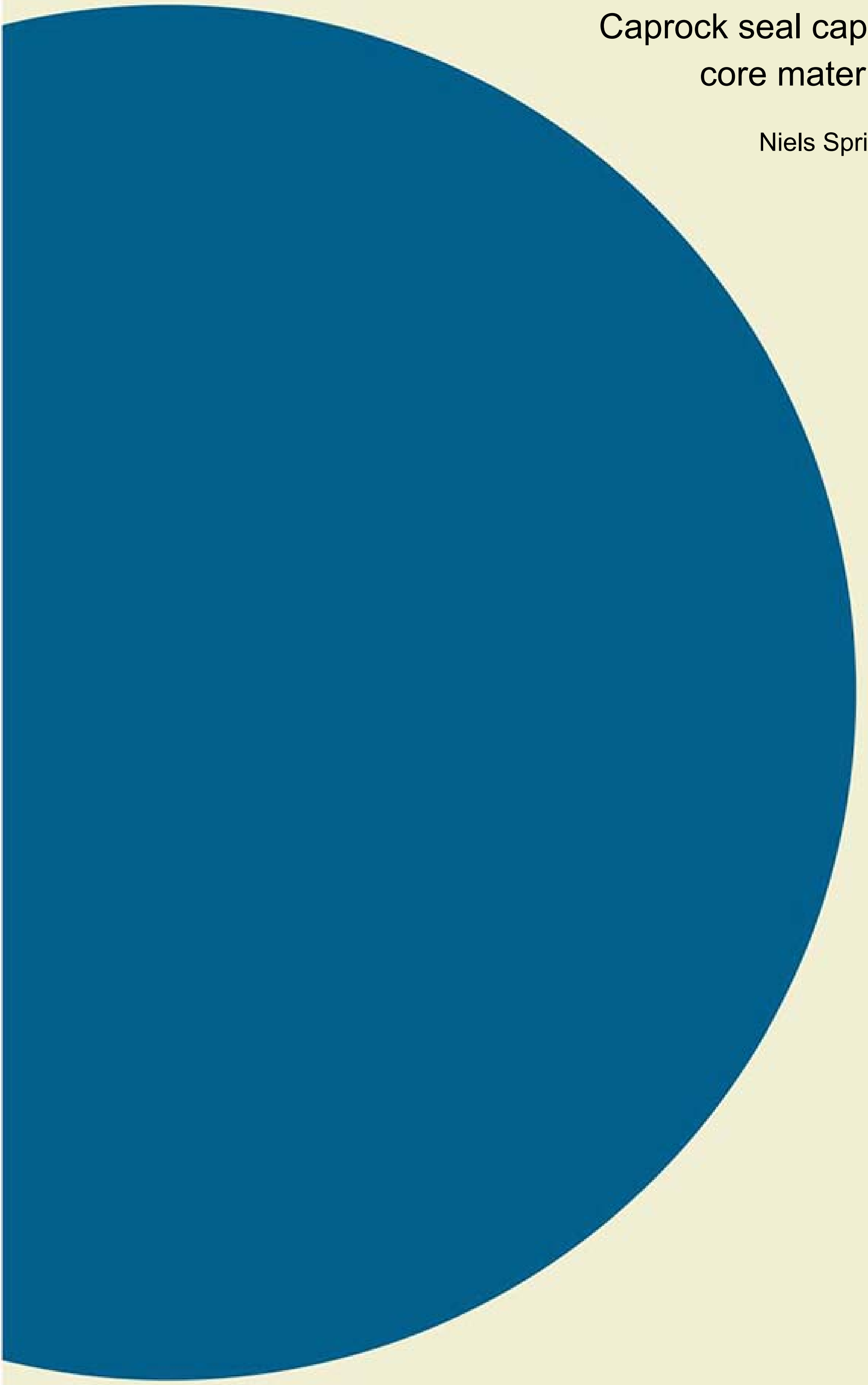

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1. Introduction

As a partner in the EU Project "CO_2 Sink : In-situ R&D Laboratory for Geological Storage of CO_2", GEUS Core Laboratory participates in WP 3.1 "Rock-/ Fluid Interactions – Laboratory Experiments". Our obligation is to evaluate the quality of the caprock sealing the Ketzin structure. Work performed so far on old core material has been directed at characterizing these samples with respect to physical and mineralogical properties and prepare for specific caprock testing (permeability and threshold pressure determination) of 1 or 2 suitable samples.

GEUS Clay Minerals Laboratory carried out bulk mineralogy and clay typing, grain size analysis and specific surface area - important properties when evaluating experimental data from the caprock tests. GEUS Core Laboratory did conventional core analysis to determine porosity and gas permeability of the samples. A progress report on these experiments serving as project Delivery D3.1-6 has been issued earlier. The present report presents the full details of the characterization work performed so far by GEUS on old core material from the Ketzin structure.

2. Sampling

In agreement with GFZ Potsdam GEUS Core Laboratory received samples from 5 intervals in the Ketzin-38 well, representing the caprock to the Ketzin structure.

2.1 Sample description

The sampled interval of the Ketzin-38 well belongs to the Weser Fm (Oberer Gipskeuper) of Triassic age in Brandenburg, Germany. Samples were cylindrical plugs of 38mm diameter and varying length, table 2.1. Sample G1 was fractured and too short for further analysis. The samples can be briefly characterized as a variegated, dolomite cemented mudstone. A short description with photos are contained in figure 2.1. The plug samples had been drilled with compressed air as coolant from old core material that would not stand the effect of water cooling.

Table 2.1. List of plug size samples from the well Ketzin-38. This well was drilled in 1971.

Sample no. GFZ / GEUS	GFZ box no.	Depth interval (MD) [meter]	Description
G1 / -	14	514.30-514.40	3 irregular pieces of fractured core
G2 / G2.1	32	530.90-531.05	4 cylindrical plugs, 2-6 cm in length
G3 / G3.1	41	540.05-540.12	1 cylindrical plug (3 cm), 3 irr. pieces
G4 / G4.1	51	548.10-548.18	3 cylindrical plugs (3-7 cm), 2 irr. pieces
G5 / G5.1	84	579.90-580.00	2 cylindrical plugs, (5-6 cm), 2 irr. pieces

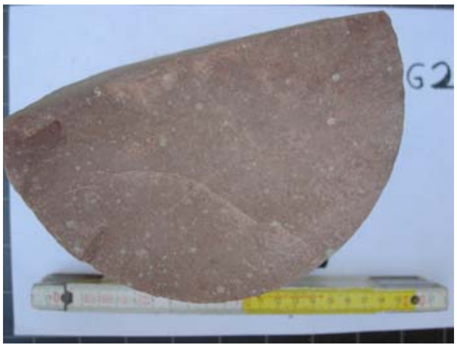
2.2 Sample preparation

Core analysis: Plugs were trimmed to a suitable length for caprock testing, and it was attempted to clean in methanol. However, like water the sample material could not stand treatment with the normal cleaning liquids. It was therefore decided to analyze the plugs just as received.

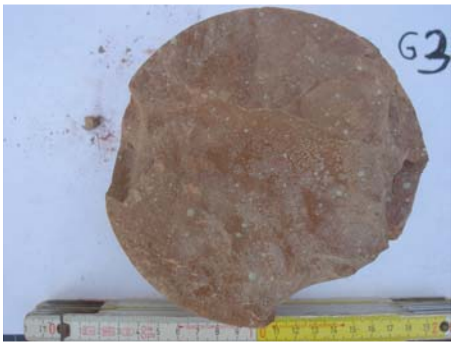
Mineralogy: Plug offtrims or irregular core pieces were used in the mineralogical characterization. Samples were hand-ground to pass a 0.250 mm sieve. The samples were then dispersed by ultrasonic treatment.Chemical pretreatment involved removal of Fe and Al oxides using ~ 50 mg of dithionite per g of sample (Mehra and Jackson, 1960). A microscopic screening of the coarse fraction >63 µm showed that a fair disintegration of the samples had been obtained. Evaluated from morphology and colour, the great majority of grains appeared single, but it could not be ruled out that a few large grains could be composites, figure 2.2.

G1. Massive, black mudstone with vein fillings of dolomite.

G2. Red mudstone with green spots and visible bedding.



G3. Massive red mudstone with small green spots.



G4. Massive red mudstone with filled cracks.

G5. Variegated (red-green) mudstone with flaser bedding texture.

Figure 2.1. Photos (by GFZ) and description of full core caprock samples from the Ketzin-38 well.

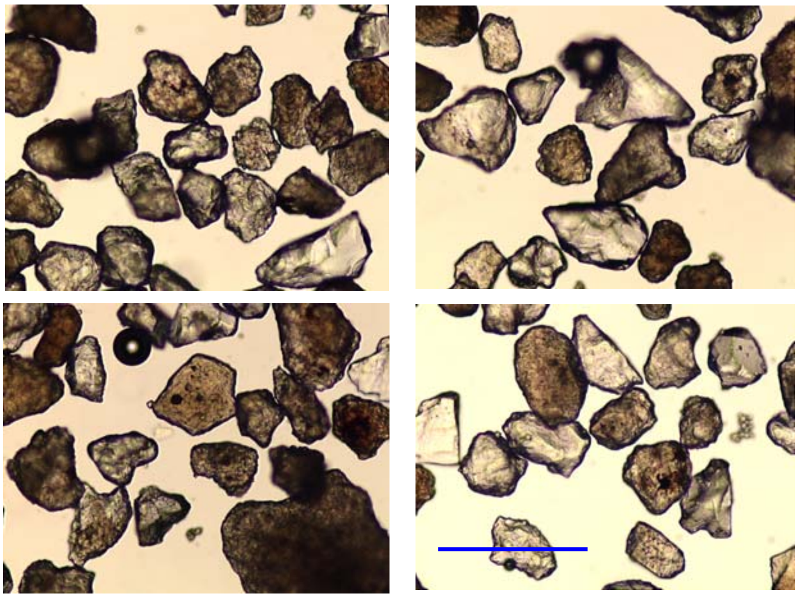


Figure 2.2. Sample G5, grain size fraction >63 µm. Angular to sub-angular single grains show that the cemented mudstone has been successfully disintegrated. Colourless / light grey grains presumably quartz. Normal light micro photo. Length of (blue) scale bar is 300 µm.

3. Core analysis

3.1 Analytical

The samples were analyzed in a dry condition according to API recommended practice for core analysis procedure (API RP 40, 2nd ed. 1998). Porosity and grain density was measured by the Helium injection technique, and gas permeability was measured relative to dry N_2 gas at a confinig stress of 2.7 MPa on the samples.

3.2 Conventional core analysis

The sample material originated from an old, dry core and was observed not to stand any treatment with water or the common cleaning liquids like methanol. We succeeded in trimming 4 plugs of 38 mm diameter for further testing and characterization. The samples were measured for routine core analysis data in a dry condition and after humidity drying that should allow clay minerals to restore to more natural conditions, table 3.1.

Table 3.1. Ketzin 38 conventional core analysis data. Four plug size samples could be measured dry or humidity dried @ 60 ˚C, 40% relative humidity. All samples absorped small amounts of water that caused a decrease in measured porosity (Por) and grain density (GD). Sample G4.1 had a fine fracture network causing gas permeability in the mD (milli Darcy) range; gas permeability for the remaining samples given in nD (nano Darcy). 1 nD ~ 10^{-21} m^2. Sample G5.1 fractured after humidity drying.

Sample	**Depth**	**Drying @ 110 °C**		**Humidity drying**		
ID	**meter**	**Por [%]**	**GD [g/cc]**	**Por [%]**	**GD [g/cc]**	**Gas perm [nD]**
G2.1	530.98	10.7	2.690	9.1	2.650	0.02
G3.1	540.09	12.0	2.656	10.4	2.622	0.03
G4.1	548.14	9.3	2.683	8.6	2.672	0.57 mD
G5.1	579.95	11.3	2.644	10.7	2.633	nd

The caprock samples from Ketzin have porosity values close to 10 % and normal or slightly increased grain densities. The dry grain density for samples G2.1 and 4.1 may indicate cementation with dolomite. Gas permeability for the unfractured samples G2.1 and 3.1 may suggest a very tight caprock.

4. Mineralogy

4.1 Analytical

After sample disintegration the grain size distribution was obtained from a particle size centrifuge (Slater and Cohen, 1962). The coarse and fine clay (size fractions 2-0.2 µm and <0.2 µm respectively) were investigated by X-ray diffraction (XRD) using a Philips 1050 instrument with pulse-height selection and β-filtered Co-K_{α} radiation. Oriented specimens were prepared by the pipette method as follows:

1. Mg-saturated air dry
2. Mg-saturated and glycolated (exposed to glycol vapour for three days at 60°C)
3. Mg-saturated and glycerol treated (glycerol added to the suspension)
4. K-saturated, air-dry and after heating for 1 hour at 300°C

The discrete minerals were identified from peak positions as follows:

Mineral	**Glycol/glycerol**	**Mg-air**	**K-300°C**
Illite	10Å, 5Å	10Å, 5Å	10Å, 5Å
Smectite	17Å/18Å	14Å	10Å
Vermiculite	14Å	14Å	10Å
Chlorite	14Å, 7Å, 4.7Å, 3.5Å	14Å, 7Å, 4.7Å, 3.5Å	14Å, 7Å, 4.7Å, 3.5Å
Kaolinite	7Å, 3.5Å	7Å, 3.5Å	7Å, 3.5Å

No attempt was made to quantify the mineral phases because the degree of similarity between the sample minerals and available standard clay minerals is unknown. The identification of smectite and vermiculite is according to the recommendations of MacEwan and Wilson (1980). Kaolinite is difficult to identify in the presence of chlorite. However, only one peak at 3.5Å corresponding to the chlorite (004) peak is observed in patterns of Mg-saturated air-dry specimens run with high counting and small steps, whereas the kaolinite (002) peak is absent. Accordingly, kaolinite could not be detected. Peaks of ordered mixed-layer minerals were not significant. Less ordered mixed-layer minerals are difficult to identify in the presence of the large amounts of illite and chlorite in the samples. This identification and quantifiction requires that well-crystalline minerals are removed and diffraction patterns are modelled.

Positions of scattering intensities of the less ordered mixed-layer minerals are:

Mineral	**Glycol/glycerol**	**Mg-air**	**K-300°C**
Illite-smectite	5-6Å	10-14Å	10Å
Chlorite-vermiculite	14Å	14Å	10-14Å
Chlorite-smectite	14-18Å	14Å	10-14Å

Specific surface area and pore volume was determined from adsorption isotherms measured on a Coulter SA 3100 gas adsorptometer using liquid N_2.The samples were outgassed at 40° C until stable vacuum. The specific surface area was calculated according to the BET model (Brunauer et al., 1938). Gurvitsch pore volume in cm^3/g dry sample was calculated from the adsorption isotherm by the amount of liquid gas adsorbed at a relative pressure of P/P_0=0,9.

Quantitative determination of carbonates was performed by differential thermal analysis with simultaneous evolved gas analysis. The instrument is a Stanton Redcroft 673-4 DTA with special gas outlet and linked to H_2O and CO_2 non-dispersive infrared detectors (Morgan, 1977). The sample is run in a flow of pure nitrogen at 400ml/min, and the amount of CO_2 evolved during decarbonation determined from the curve for evolved CO_2, using calcite (Merck) as a standard. From the evolved CO_2

and the DTA curve the type of cation is estimated and compared to the carbonates determined by XRD. For the present samples the equivalent amount of dolomite was calculated from the evolved CO_2 assuming an ideal composition of dolomite. Detection limit is approx. 0.1% CO_2.

Atomic force microscopy was carried out using a Rasterscope 4000 instrument. The samples were prepared from intact rock specimens, which were glued onto the sample holder and scanned at room conditions in non-contact mode with a force of 0.1 nN

4.2 Results

The granulometric analysis of the Oberer Gipskeuper caprock show that >50% of the grains are below sand size (63 µm) and silt size grains are between ⅓ and ⅔ by weight, Table 4.1 and Figure 4.1.

Table 4.1. Ketzin 38 grain size and gas absorption data.The fine size fraction ≤ 4 µm is a low 20-30 wt-%, quartz is 15-30 % of the bulk rock. Specific surface area (N_{2BET}) is fairly high ~50 m^2/g presumably due to the high content of illite. G pores is the pore volume confined to pores ≤ 20 nm (Gurvitsch pore volume).

Plug	> 63	63 – 20	20 – 4	4 – 2	2 – 0.2	< 0.2	Σ	Σ Clay	Quartz	N_{2BET}	G pores
ID	µm	µm	µm	µm	µm	µm	wt-%	wt-%	%	m^2/g	cm^3/g
G2.1	31	22	23	5	6	7	94	18	16	43	0.054
G3.1	26	21	24	7	6	12	95	25	18	51	0.056
G4.1	33	21	23	6	6	9	98	21	13	46	0.045
G5.1	26	20	20	8	9	11	92	28	30	54	0.064

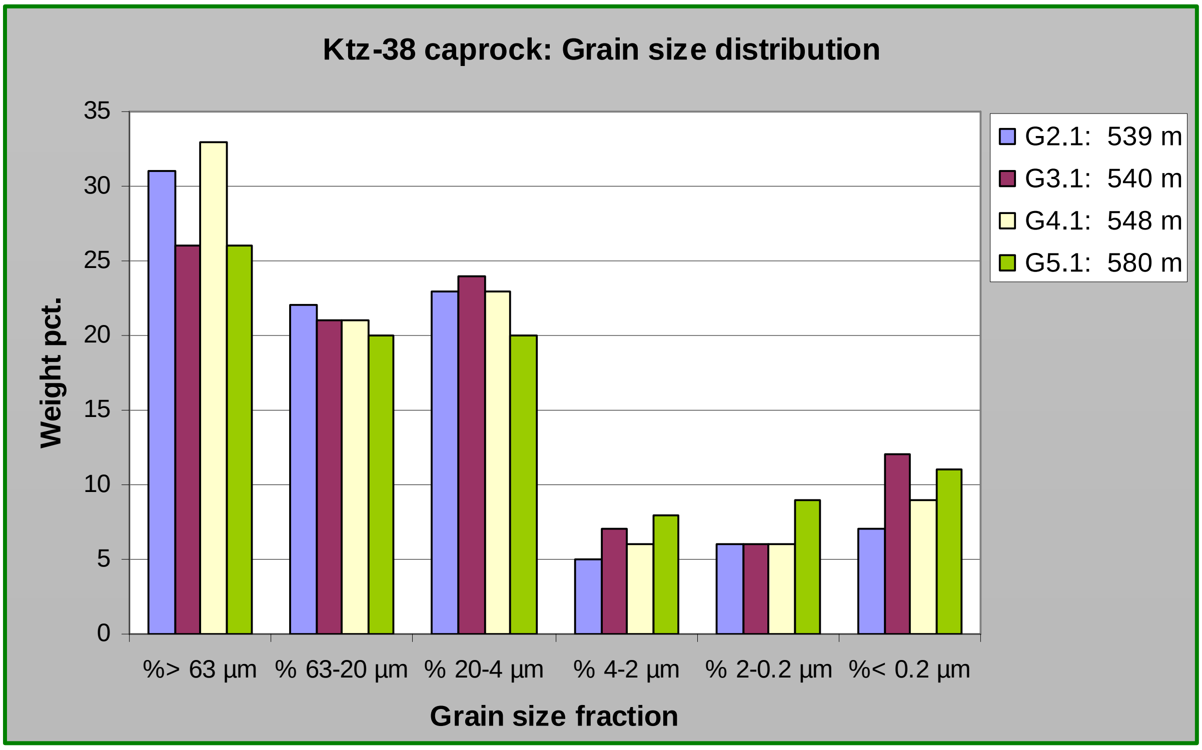


Figure 4.1. Histogram showing grain size distribution as obtained from the centrifuge size fraction analyzer. Observe that samples G2.1 and G4.1 have the highest content of coarse grains.

As the samples are generally non-laminated the Oberer Gipskeuper is identified as a mudstone in the sense of Lundegard & Samuels (1980). Sample G5.1 differs somewhat from the other samples in having the highest quartz content but also the highest clay content and therefore the highest specific surface area, Table 4.1.

Clay mineral typing have been completed for 4 samples; clay XRD-diagrams are shown in Appendix 1.

The clay mineralogical analysis have shown that the coarse clay and fine clay fractions are rather similar for all plugs. The coarse (2-0.2 microns) clay fractions are dominated by illite, but contain minor amounts of chlorite, illite-smectite and chlorite-vermiculite. Trace amounts of quartz is present as well. The fine (<0.2 microns) clay fractions are also dominated by illite, and contain minor amounts of chlorite, illite-smectite, and chlorite-smectite. Kaolinite was not observed in any fraction.

The differential thermal analysis to determine the evolved CO_2 gas content is presented in table 4.2. The equivalent carbonate content is calculated at 0-30% dolomite with sample G3.1 being rather a mixture of magnesite and dolomite.

Table 4.2. Determination of carbonate content by DTA-EGA. Dolomite cementation was not detected in sample G5.1

Sample ID	**CO_2 [%]**	**Eqv. dolomite [%]**
G2.1	15	30
G3.1	8.6	18
G4.1	11	24
G5.1	0	0

Small sample pieces of G4.1 was analyzed by Atomic Force Microscopy (AFM) in an attempt to characterize the pore network in a semi-quantitative manner, fig. 4.2. The transport properties of a caprock is mainly determined by the pore connectivity and dimensions and second by the pore morphology (tortuosity and surface roughness). Examples can be seen from fig. 4.2. Image G402 and G405 demonstrates a poor connectivity between the pores in the upper right corner and the lower left corner. Image G403 and G404 on the contrary shows a very good pore connectivity. The smallest grain size measured from the images appear to be in the range 20 – 50 nm only slightly larger than the dimensions of the pore throats, table 4.3.

Table 4.3. Sample G4.1 pore system. Pore body and pore throat dimensions given as an interval as measured from the 4 images in fig. 4.2.

Image ID	**Body dim. [nm]**	**Throat dim. [nm]**
G402	70 - 200	18 - 36
G403	130 - 340	18 - 20
G404	45 - 470	11 - 21
G405	110 - 270	10 - 18

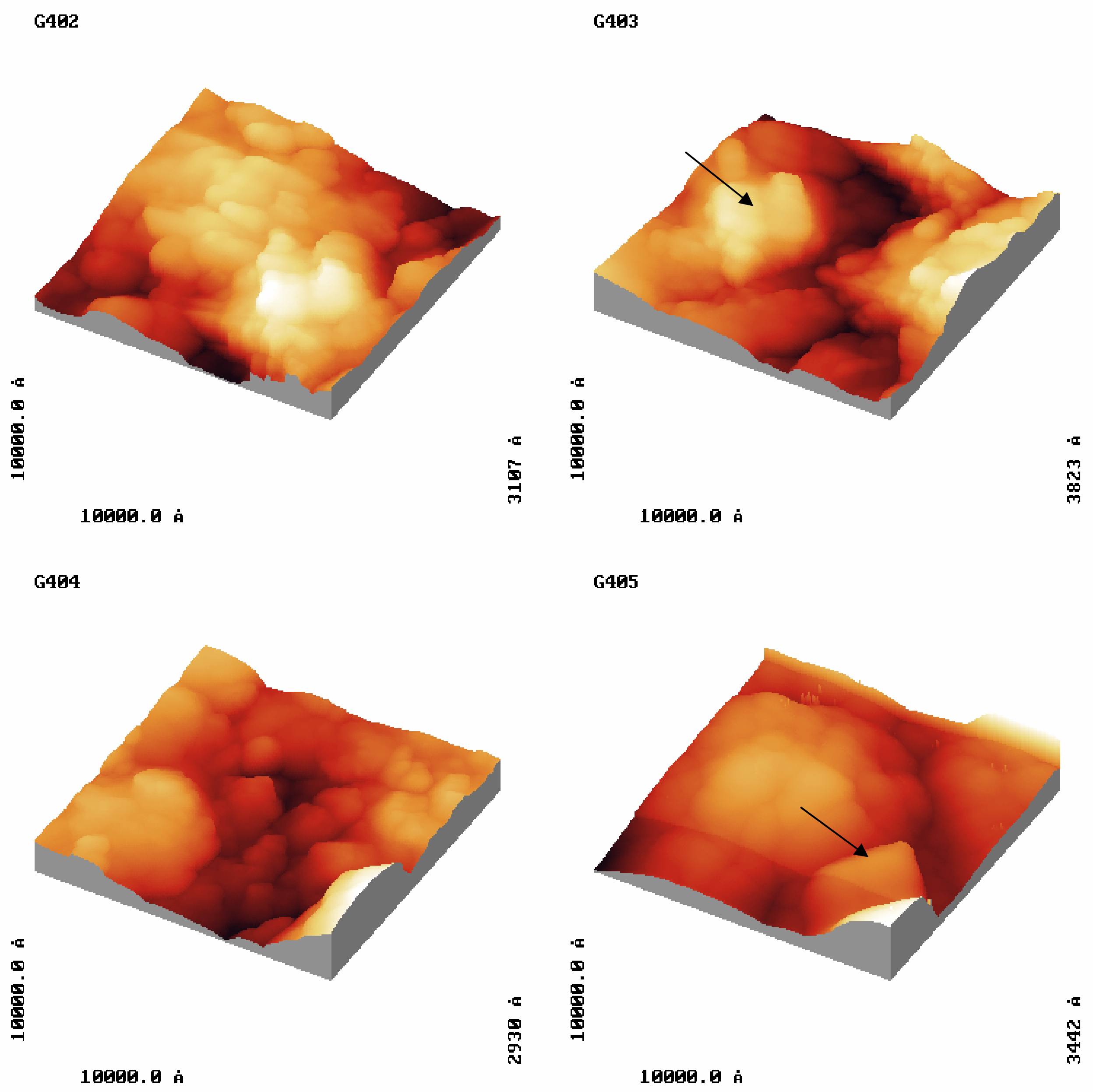


Figure 4.2. Surface morphology of dolomite cemented mudstone G4.1 recorded by AFM. The side length of the 3D images is 1000 nm (10 000 Å). The basal plane is black and the highest "peak" is white in an elevation of 300-380 nm above the basal plane. This gives a 3D impression of the pore system in the mudstone caprock above the Ketzin structure. Arrows show morphologies that may indicate dolomite grains. Details of the pore system are given in table 4.3.

5. Conclusion

Four samples of old, dry core material from the Ketzin-38 well have been characterized with the intention to understand the seal properties of the Weser Fm mudstone, the caprock to the future Ketzin CO_2 repository. Attention has been on a careful sample preparation not to damage delicate clay minerals, and on core analysis to estimate permeability and capillary properties. Details of the bulk and quantitative mineralogy are not given here but can be looked up elsewhere (Luckert and Thieke, 2005).

The old core was found not to tolerate normal cleaning liquids or water (brine) without breaking which limited the validity of some of the measured data. Most samples are cemented with dolomite in various proportion, and intact samples have very good caprock properties with permeability in the nano Darcy range or below, ie. $\leq 10^{-21}$ m^2, and porosity of ~ 10% ref. table 3.1.

Acid treatment was not applied to the dolomite cemented samples which means that the grain size analysis may be slightly biased towards larger grain sizes. This could be the case for samples G2.1 and G4.1 that have the highest content of dolomite vs. sample G5.1 that is not dolomite cemented, cf. figure 4.1 and table 4.2. Considering the relatively small clay size fraction (≤ 20 wt-%), the specific surface area is surprisingly high presumably due to the presense of illite and mixed-layer minerals. The fine clay size fraction dominates over the coarse clay size fraction, figure 4.1.

Bulk quartz content determined by XRD was in the range 15-30 %, table 4.1. According to a correlation by Krushin (1997) this predicts a displacement pore throat size of approx. 2-21 nm, but this must be considered an upper limit due to the cementation with dolomite. Analysis of AFM-images from one sample yielded throat sizes in the range 10-20 nm, table 4.3, but smaller throats may well be present but is difficult to measure correctly. Mercury injection porosimetry/pore size distribution has previously been carried out by GFZ on one sample of the Weser Fm. from the Ketzin-38 well. It was observed that the mean pore size was below 20 nm – close to 10 nm would seem a fair estimate from the published diagram (Spangenberg and Kulenkampff, 2005).

The capillary entry pressure 'P_{ce} ' for an idealized waterwet system (contact angle $\theta = 0^\circ$) can be estimated from the well known Purcell equation (Purcell, 1949):

$$P_{ce} = \frac{2\sigma}{r} \quad \text{[Pa]}$$

'r' is the pore throat radius, thus 2r = pore throat size. Assuming an injection depth of c. 700 m in the Ketzin reservoir, pore pressure is estimated to be ~ 7.5 MPa (Förster et al., 2006), ie. the interfacial tension 'σ' for super critical CO_2 ($scCO_2$) will be close to 36 mN/m @ 35 ˚C (Chun and Wilkinson, 1995).

The capillary entry pressure is then calculated at 7.2 – 72 MPa for pore throats '2r' = 20 – 2 nm. It is therefore expected that the Ketzin caprock will hold a $scCO_2$ column of ~ 1470 - 14700 m. In this calculation it is assumed that the density contrast between formation water and $scCO_2$ is 500 kg/m^3. The critical properties of $scCO_2$ (density and interfacial tension) are very sensitive to temperature and pressure in the P-T regime found for the Ketzin reservoir, and a more accurate evaluation of the seal capacity must await better pressure and temperature data for the reservoir.

6. References

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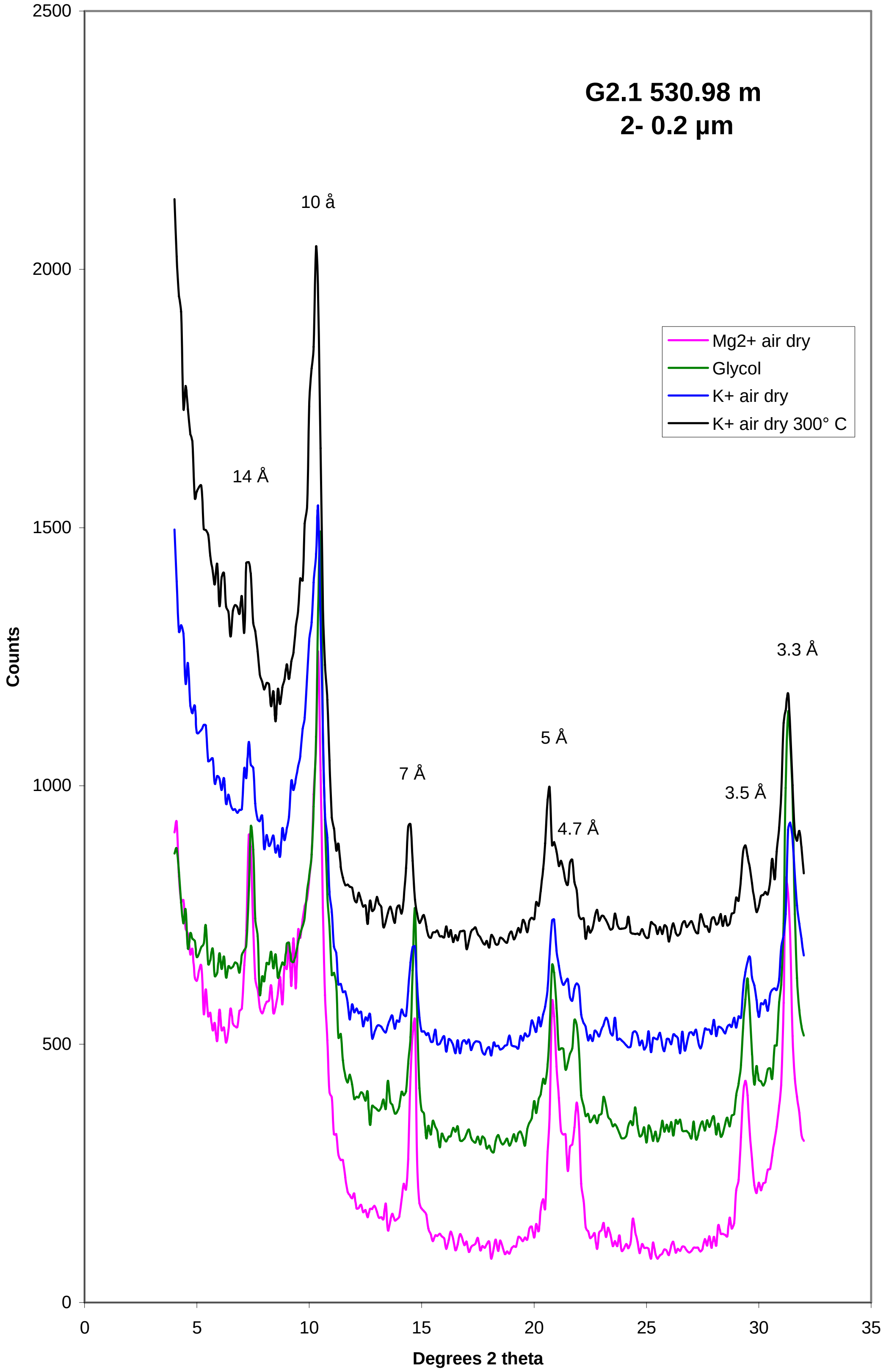
7. Appendix

X-ray diffractograms (XRD) recorded for the clay size fraction of mudstones of the Weser Fm. sampled from the Ketzin-38 well. Indexing of reflection peaks are given in scetion 4. A very good agreement with XRD spectra published by Luckert and Thieke (2005) is observed.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2- 0.2 µm
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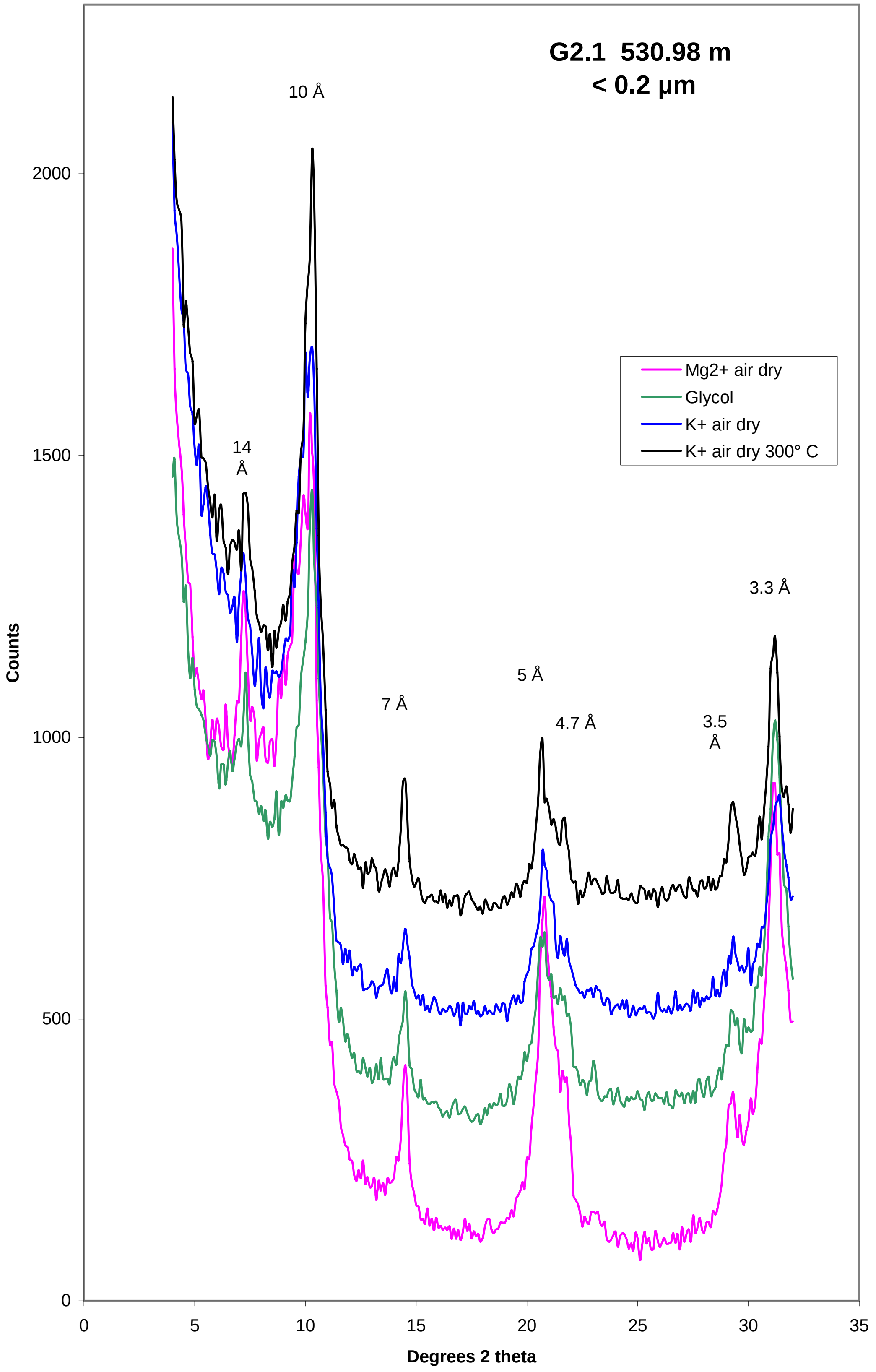
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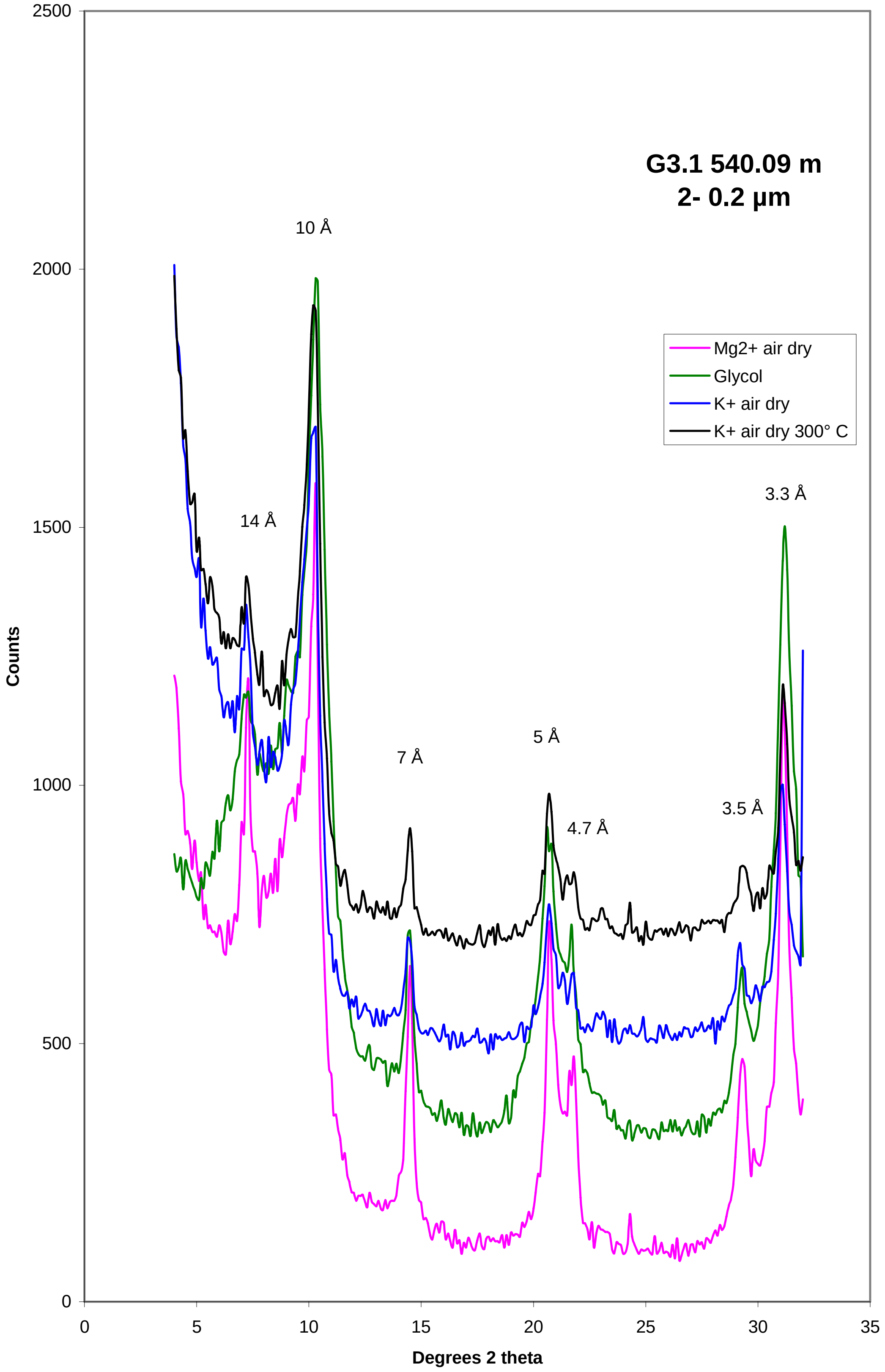
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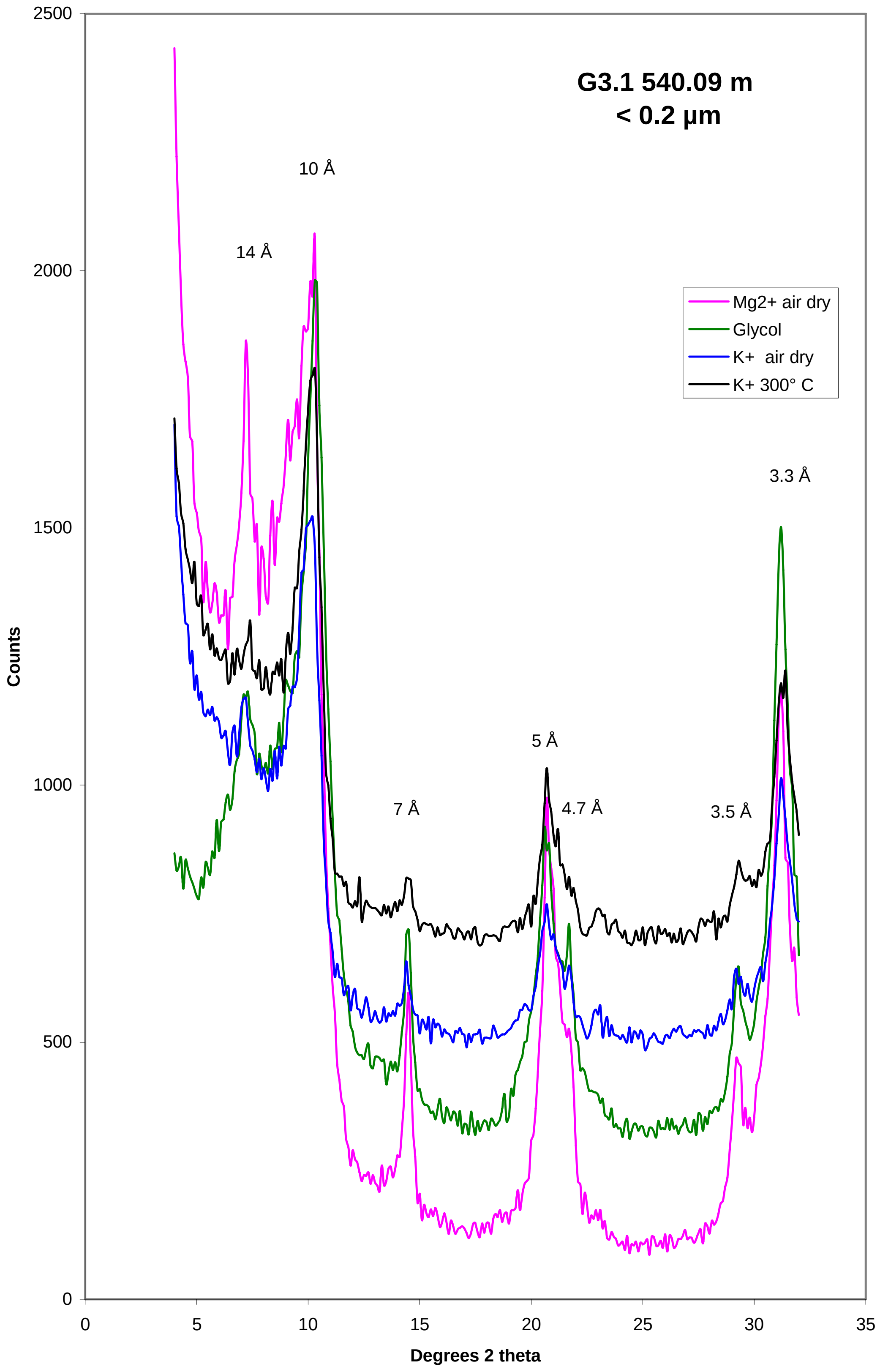
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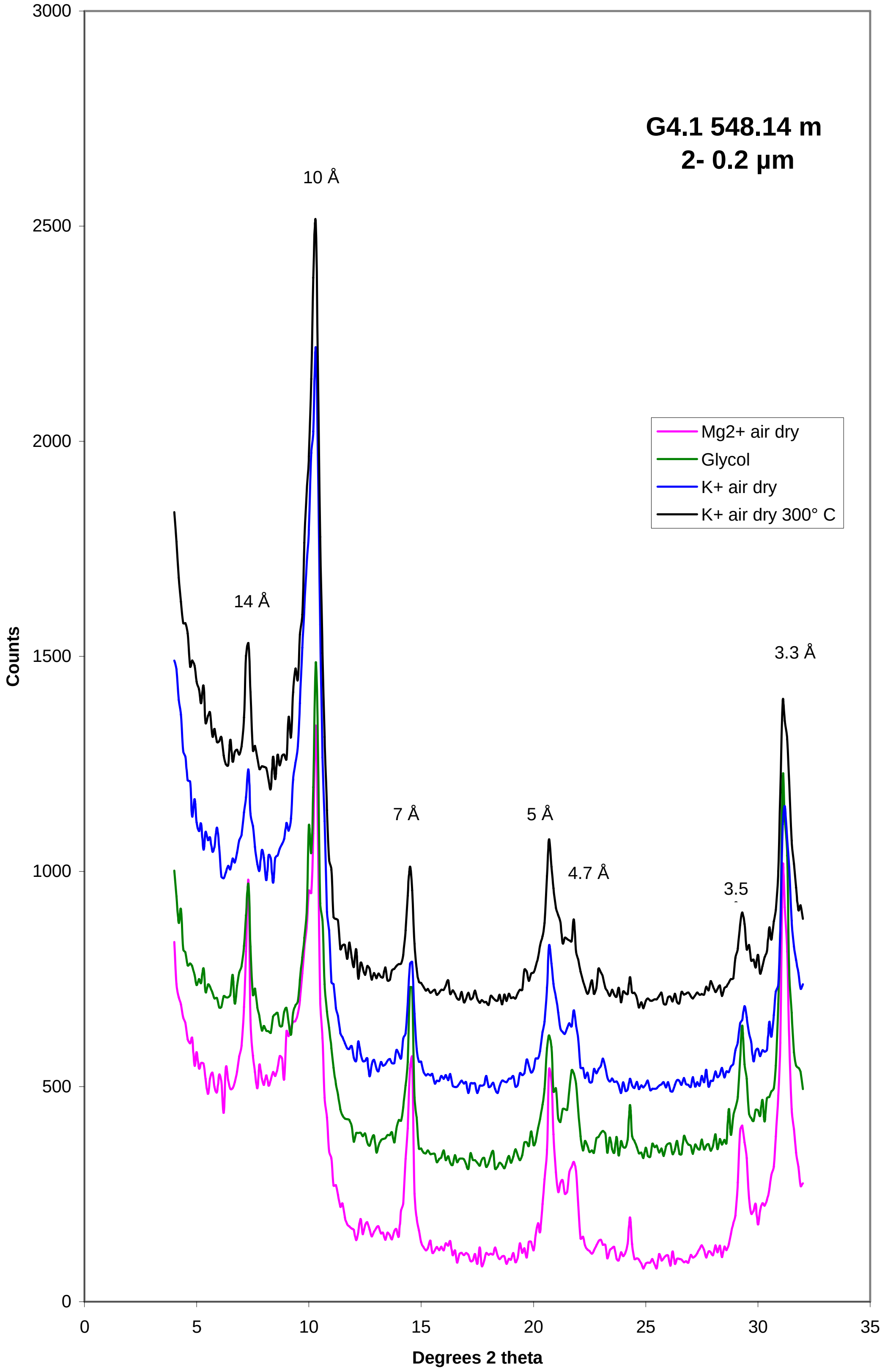
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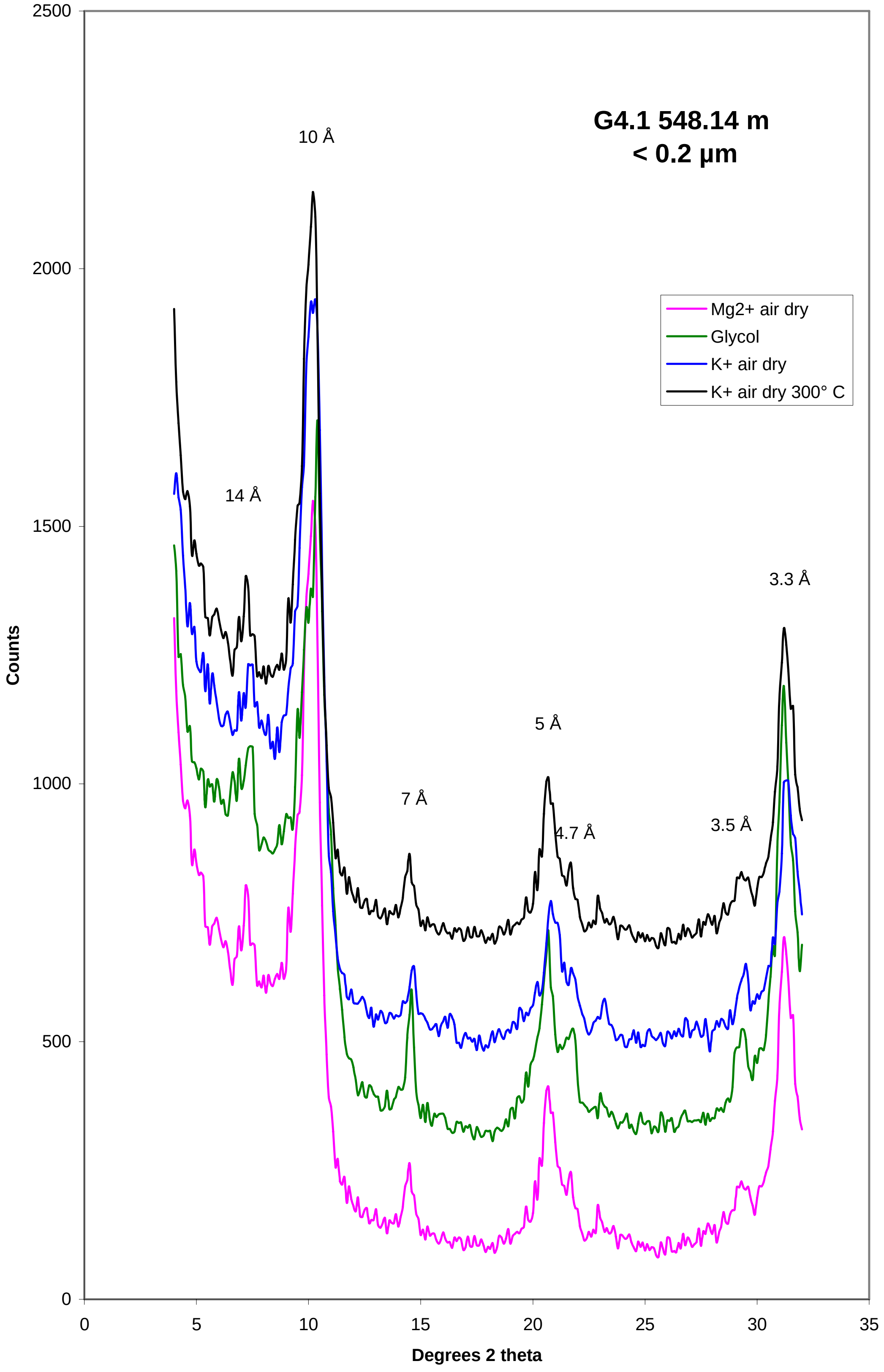
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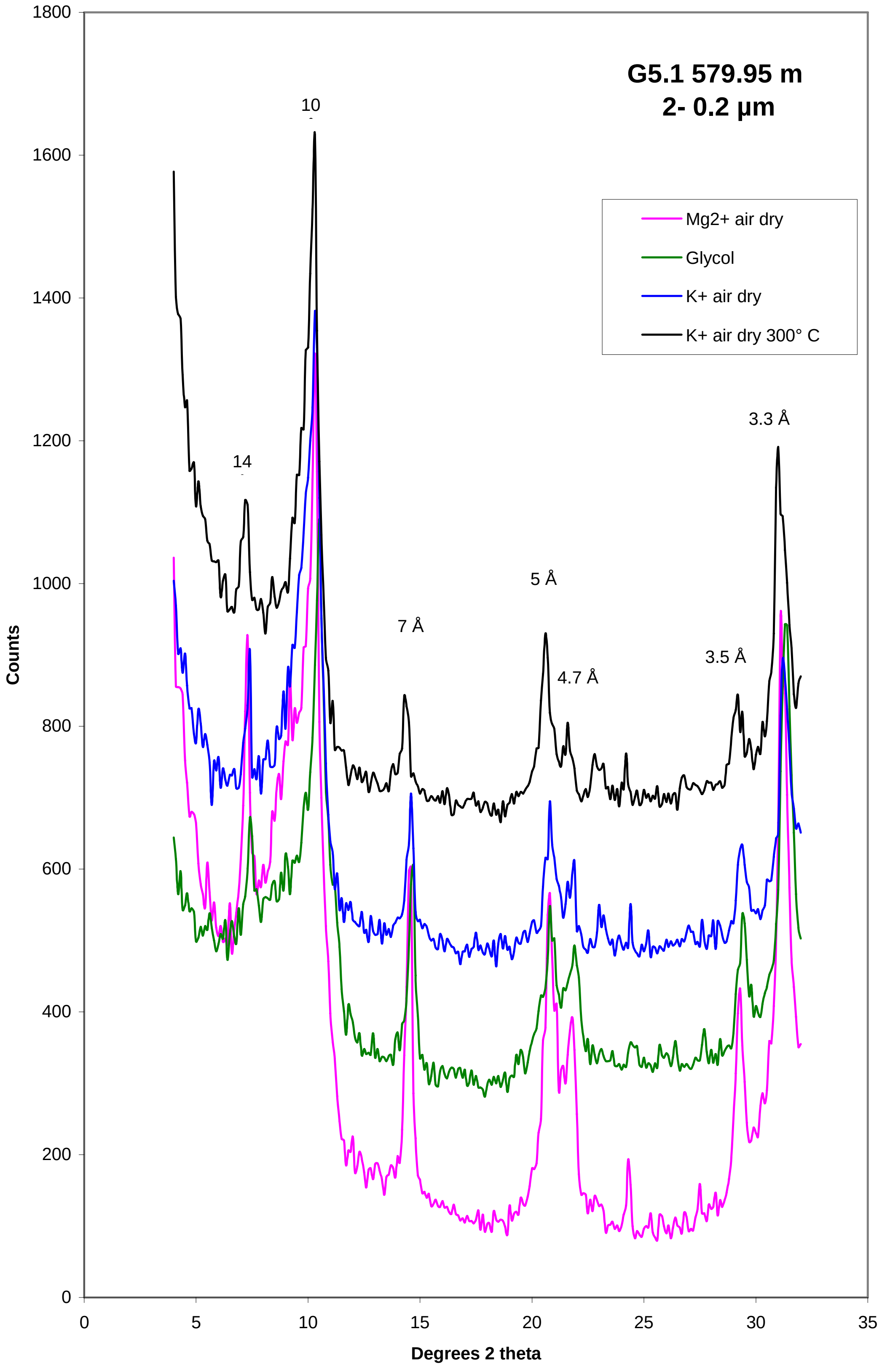
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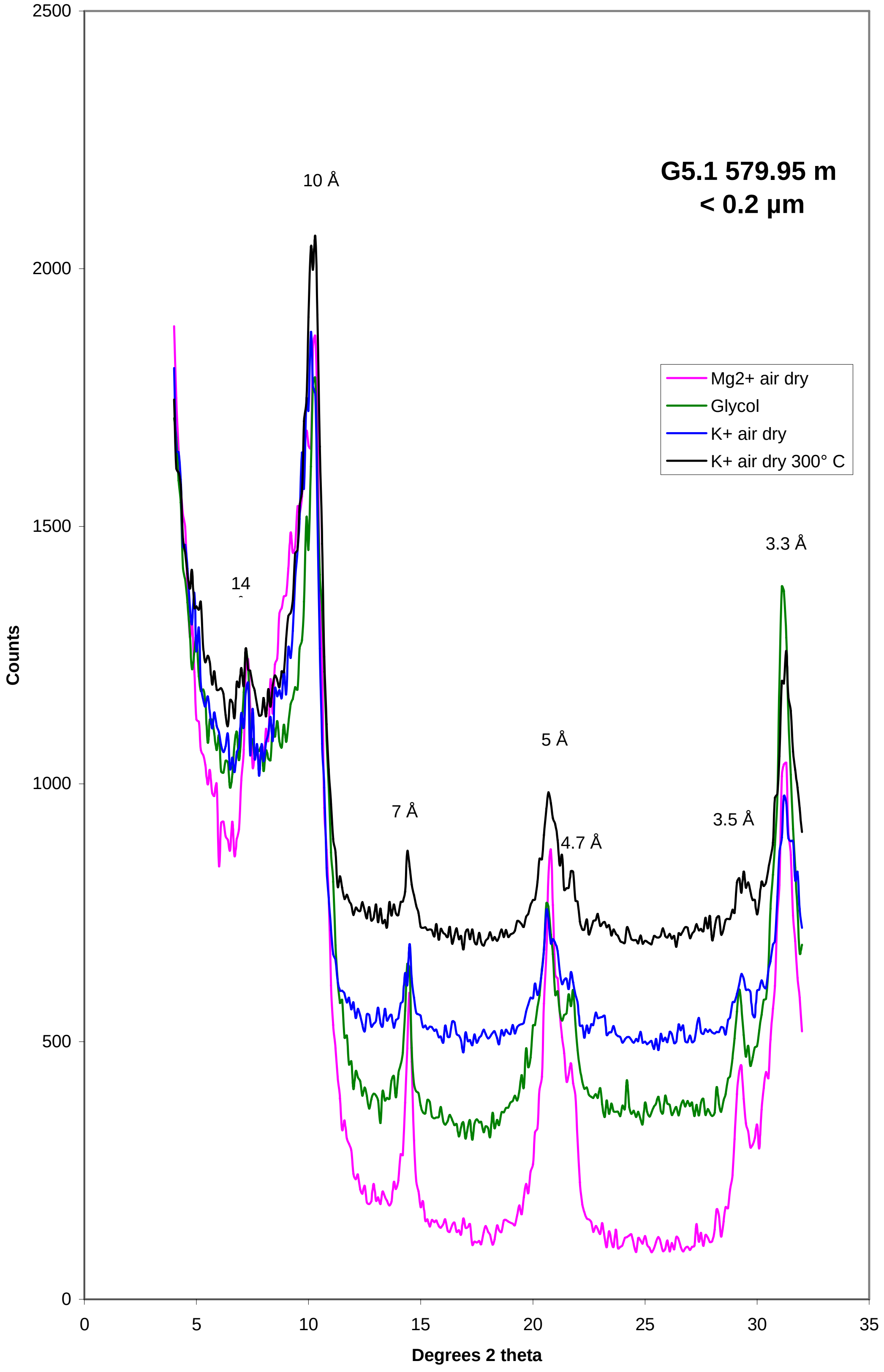
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