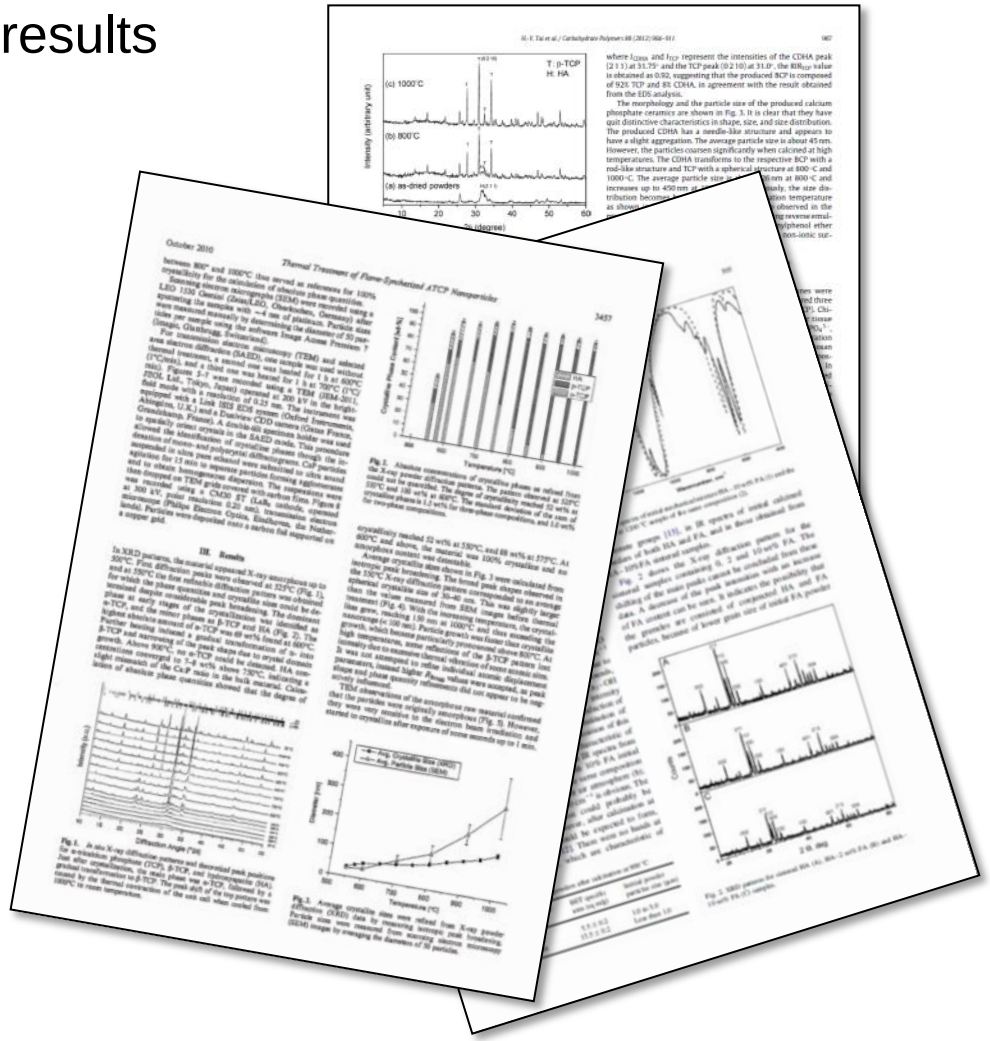
Lesson 9
Publishing XRD Results

Nicola Döbelin('s humble opinions…)
RMS Foundation, Bettlach, Switzerland

…totally irrelevant to the rest of the world

Relevant Topics

- Quality of Rietveld refinement results
- Graphs
- «Experimental» section



RMS
Testing • Research • Consulting

Quality: Accurate + Precise

High Precision, High Accuracy

Low Precision, High Accuracy

High Precision, Low Accuracy

Low Precision, Low Accuracy

https://phidgets.wordpress.com

Quality of Rietveld Refined Data

XRD / Rietveld refinements are very difficult to validate:

- Often no complementary analytical technique available
- Hardly any reference materials available
- Refinement: Highly operator dependent

One option: Participate in round robins

→ Compare your results with other labs

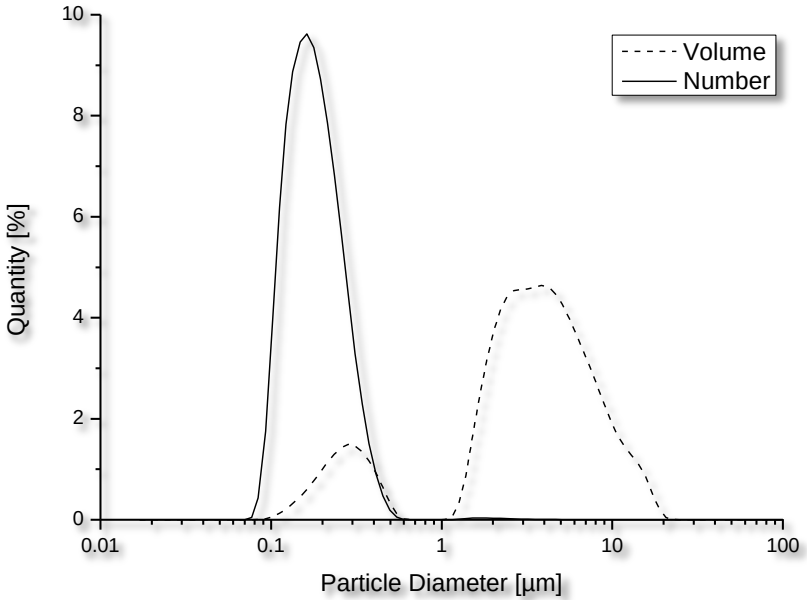
Round robin on CaP phase quantification organized by RMS Foundation / Nicola Döbelin in 2012/2013

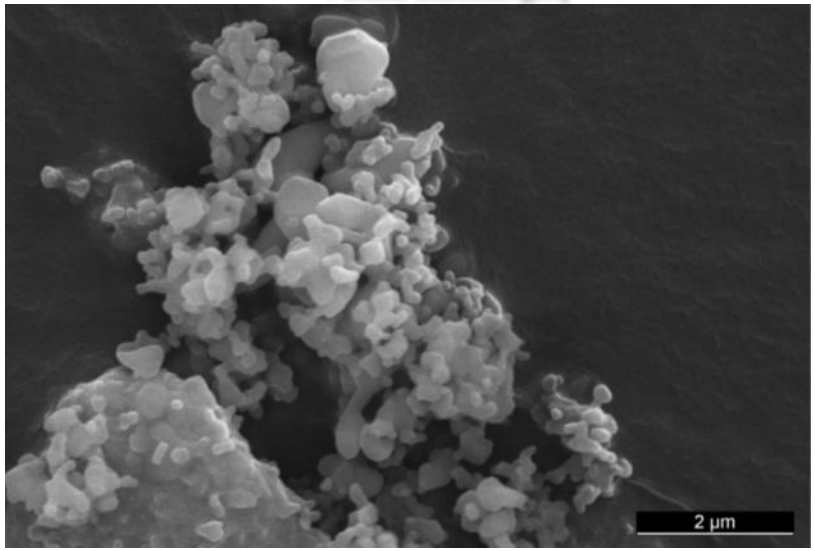
Accuracy of Rietveld Refined Data

Round Robin Reference Sample:

- Simple 2 phase system: HA + β-TCP
- Very homogeneous distribution
- No texture
- No micro-absorption
- Highly crystalline
- Mean cryst size ~200 nm

→ Nearly «Best Case» Scenario





Accuracy of Rietveld Refined Data

Round Robin

12 Labs with 26 different instruments / configurations analyzed the same powder

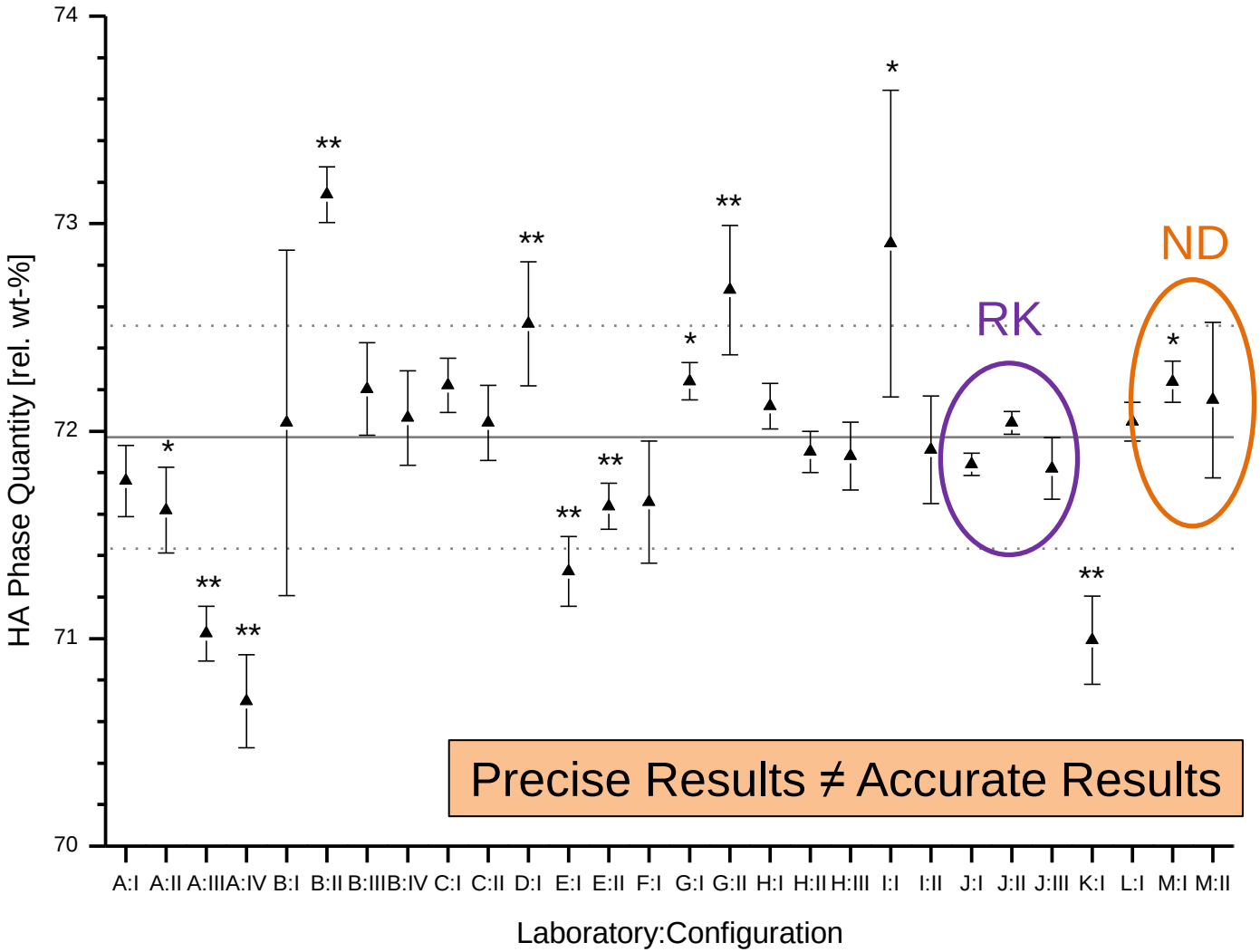
n=5

Results returned from one lab/instrument:

Sample	β-TCP [wt-%]	HA [wt-%]
1	28.01	71.99
2	28.22	71.78
3	28.49	71.51
4	28.29	71.71
5	28.20	71.80
Mean (Std. Dev)	**28.24 (0.17)**	**71.76 (0.17)**

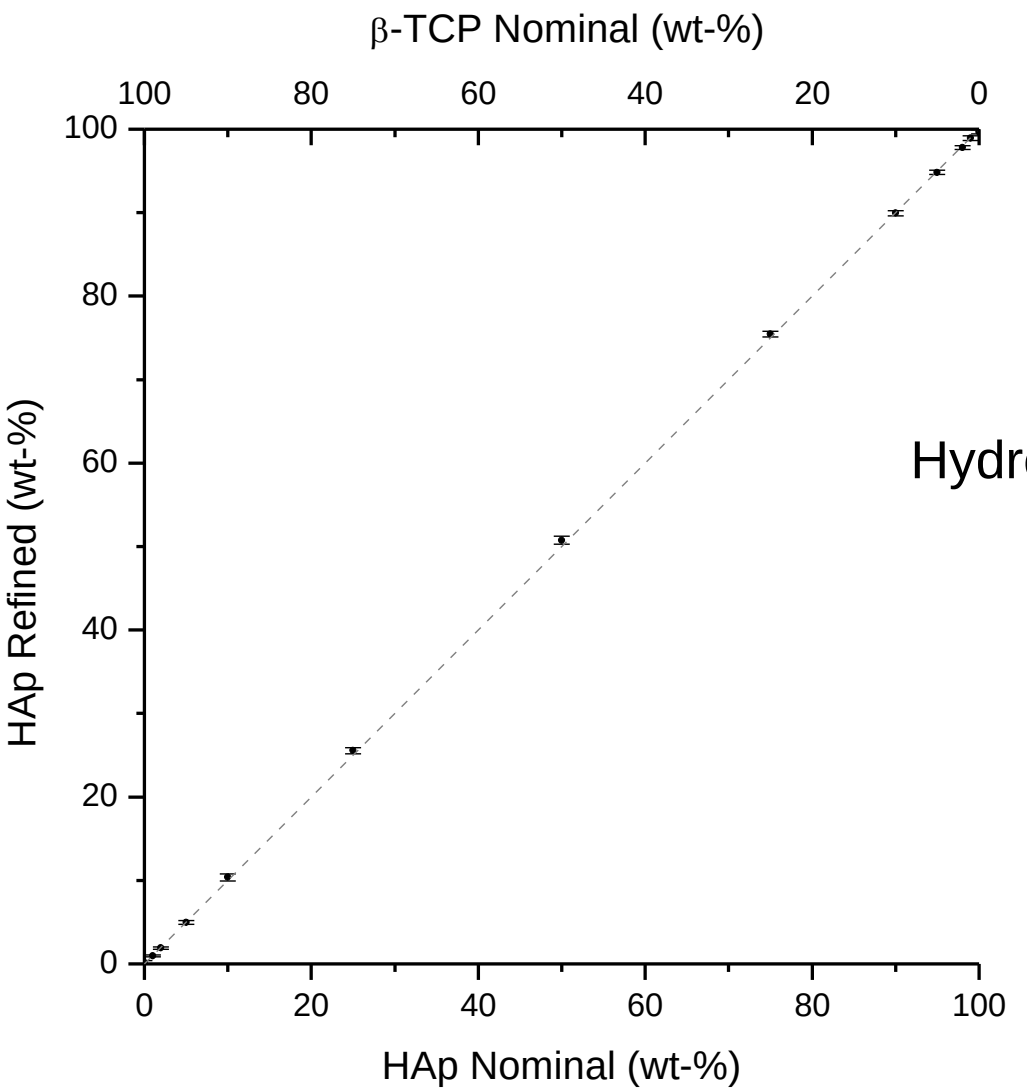
Accuracy of Rietveld Refined Data

* p < 0.05
** p < 0.01



Döbelin, N. "Interlaboratory study on the quantification of calcium phosphate phases by Rietveld refinement." Powder Diffraction, 2015 30(3): 231-241.

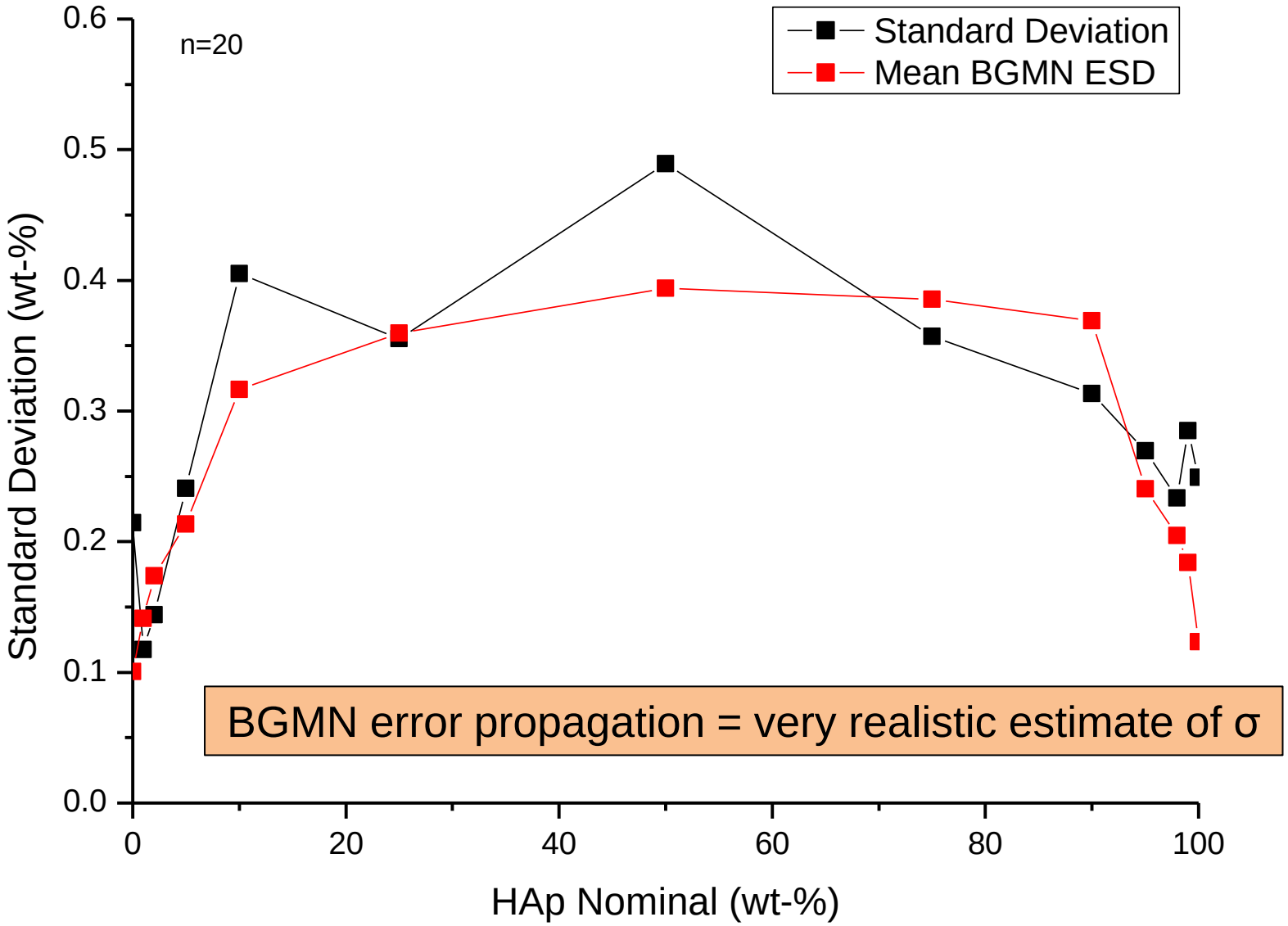
Validation of β-TCP + HAp Quantification at RMS



Reference mixtures
Hydroxyapatite + β-TCP (Whitlockite)

Measured and refined 20x

Quality of Rietveld Refined Data



BGMN error propagation = very realistic estimate of σ

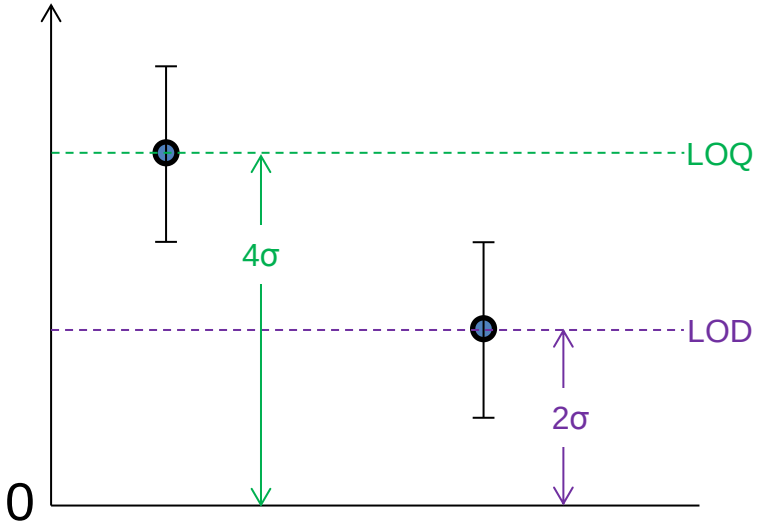
Detection Limits

Possible Definition of Quantification Limit (LOQ):

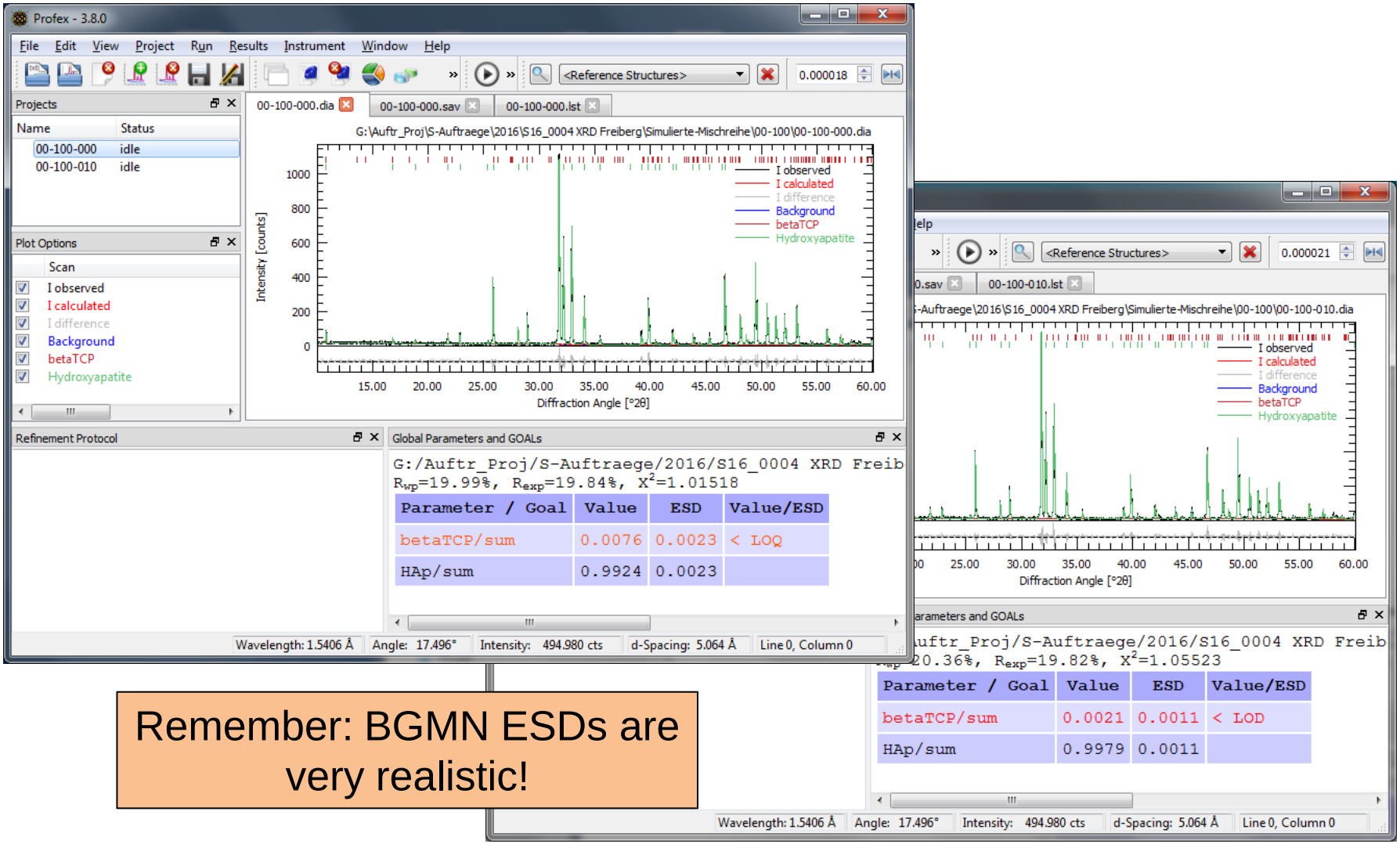
$$Phase\ Quantity < 4 \cdot \sigma$$

Possible Definition of Detection Limit (LOD):

$$Phase\ Quantity < 2 \cdot \sigma$$



LOD / LOQ Warning in Profex



Remember: BGMN ESDs are very realistic!

Guidelines for Reporting Phase Quantities

- For error bars use 3 · ESD or 2.77 · ESD

  3 · ESD = 99.7% repeatability limit, normal distribution
  2.77 · ESD = 95% repeatability limit, t distribution [1]

- Report Values < LOQ as «< 4 · ESD»

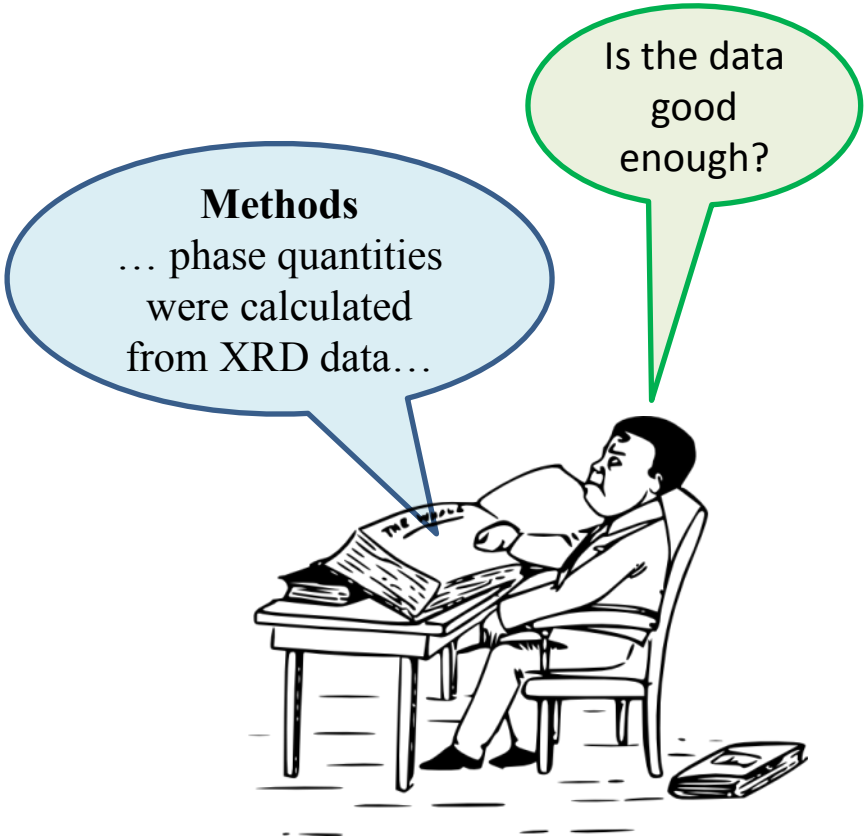
  Report 0.76 ± 0.23 as «< 0.92»

- Report Values < LOD as «not detected»

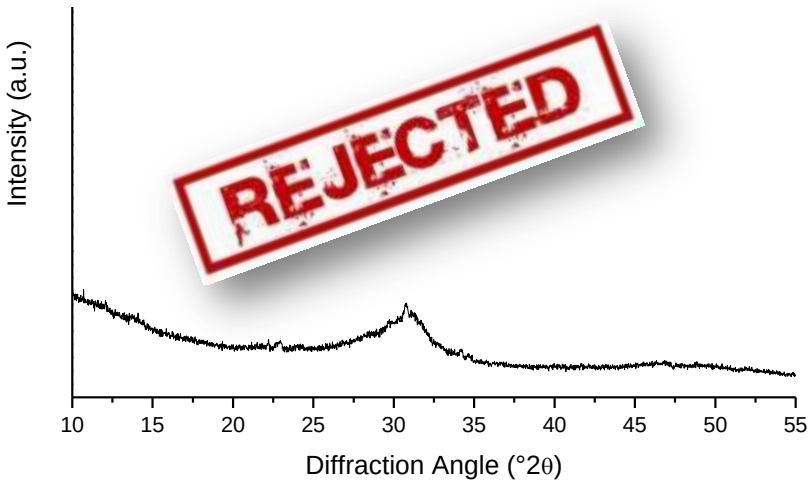
  Report 0.21 ± 0.11 as «not detected»

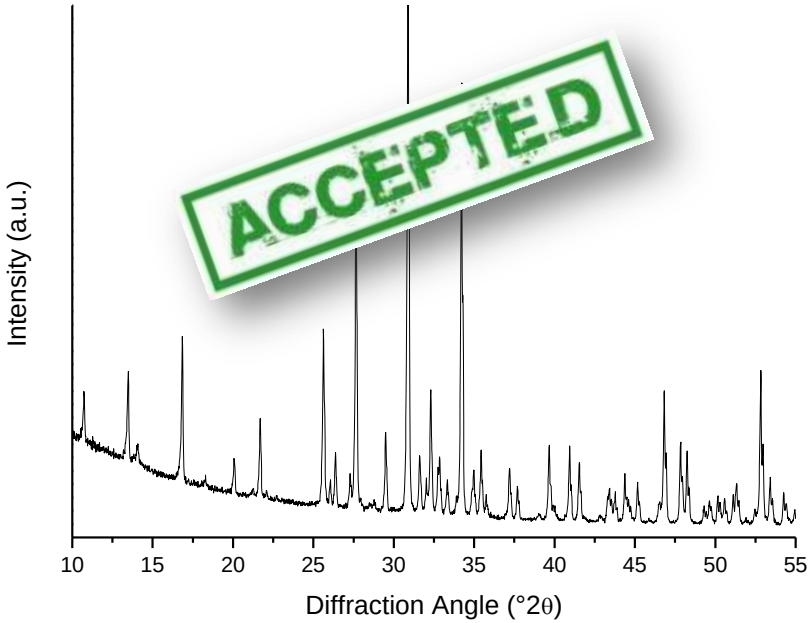
[1] ASTM E177-13: «Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods».

Graphs: XRD / Rietveld are «visual» methods

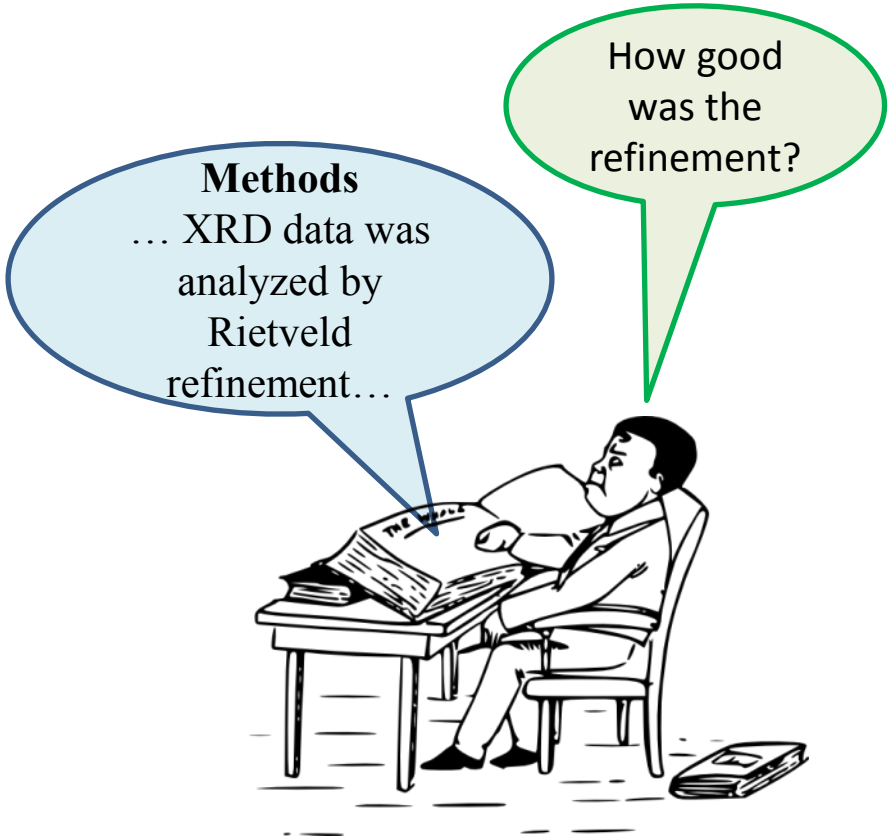


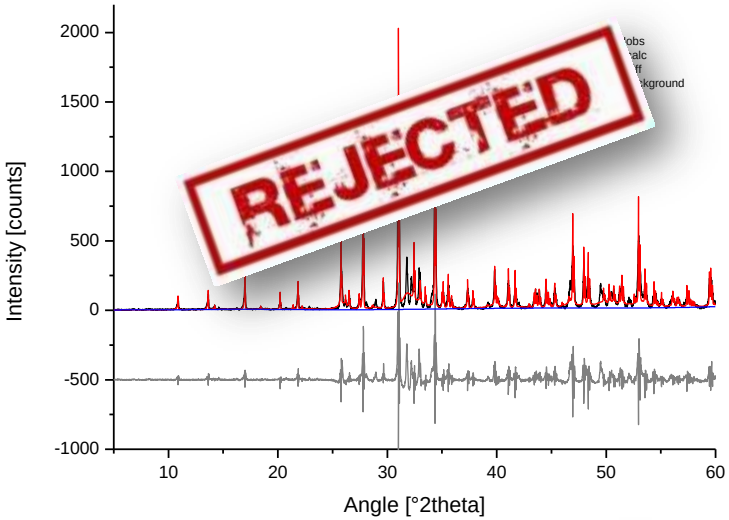
Your friendly reviewer

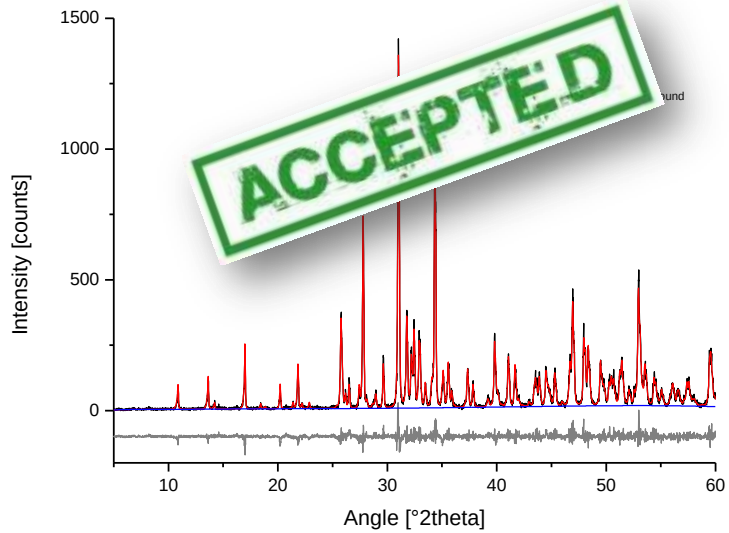




Graphs: XRD / Rietveld are «visual» methods







Graphs: XRD / Rietveld are «visual» methods

Recommendation:

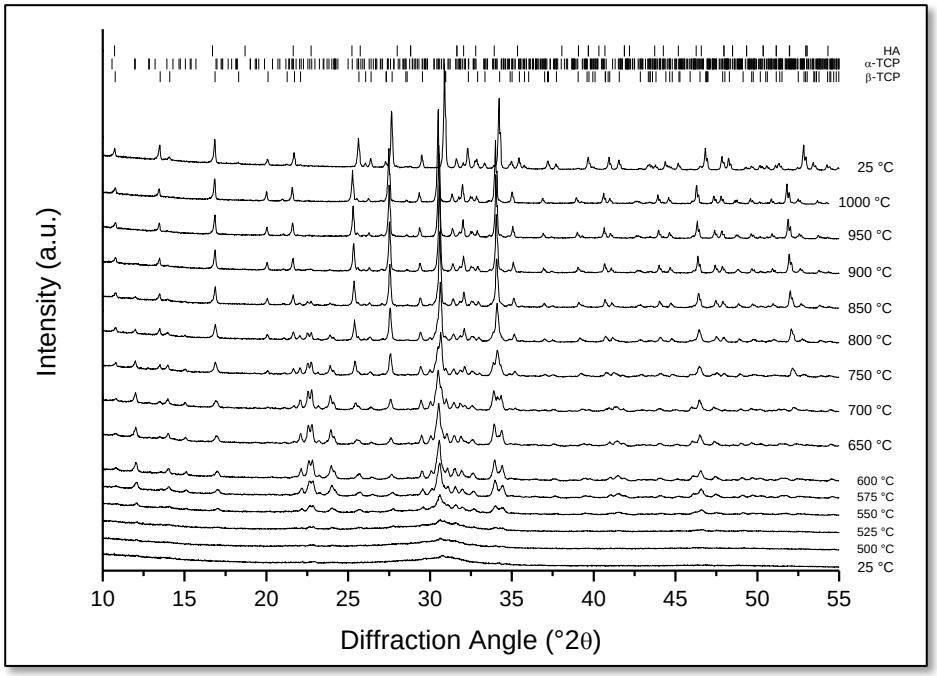
- Show all your raw data (documents your data quality)
- Show 1 full refinement (documents your refinement quality)

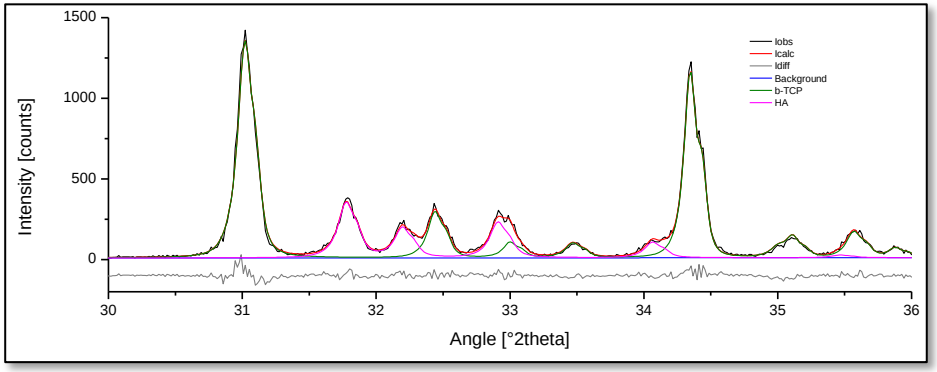
- All the information is in the raw data
- Only additional information in refinement plots (Icalc, Idiff, Bkgr):

  «The refinement was done right»

Graphs: XRD / Rietveld are «visual» methods

Combine your raw patterns





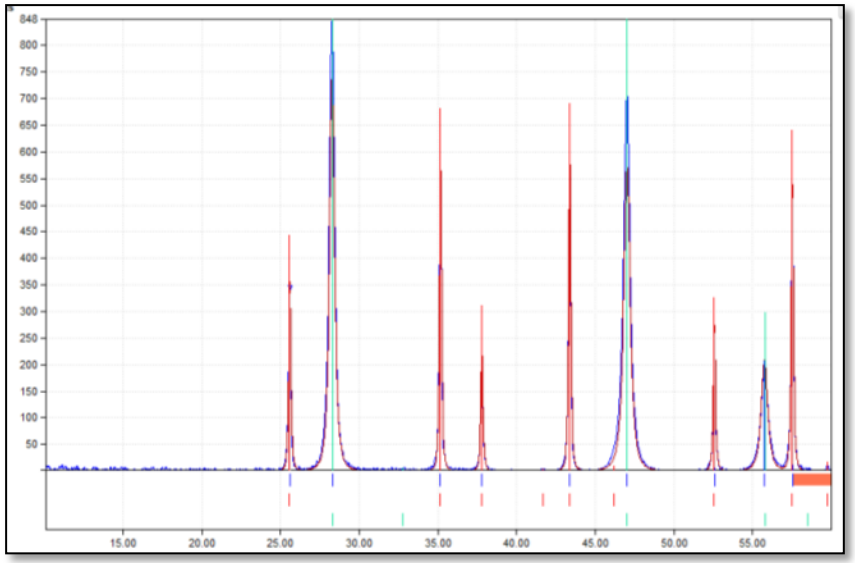
Show more graphs if the manuscript improves

«Materials and Methods» Section

Match the level of detail to the relevance of XRD for the study

Used for phase identification

- Basic intrument parameters:
  - Instrument / Manufacturer
  - Scan range (start, end, step size)
- References to PDF / ICDD / COD phase entries



«Materials and Methods» Section

Materials Science and Engineering C 33 (2013) 527–531

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Influence of water content on hardening and handling of a premixed calcium phosphate cement

Johanna Engstrand *, Jonas Aberg, Håkan Engqvist

2. Method

2.7. X-ray diffraction (XRD)

The resulting phase composition of the cements after setting was analyzed using XRD (diffractometer, Siemens). Diffraction angles (2θ) 20–40 were analyzed at 0.45°/min. The set samples were crushed using a mortar prior to analysis.

3. Results

3.6. XRD

In Fig. 6 the spectra for the composition extremes, 0 and 6.8 wt.% water content, are shown. However, all cement formulations, regardless of water content, formed monetite after setting.

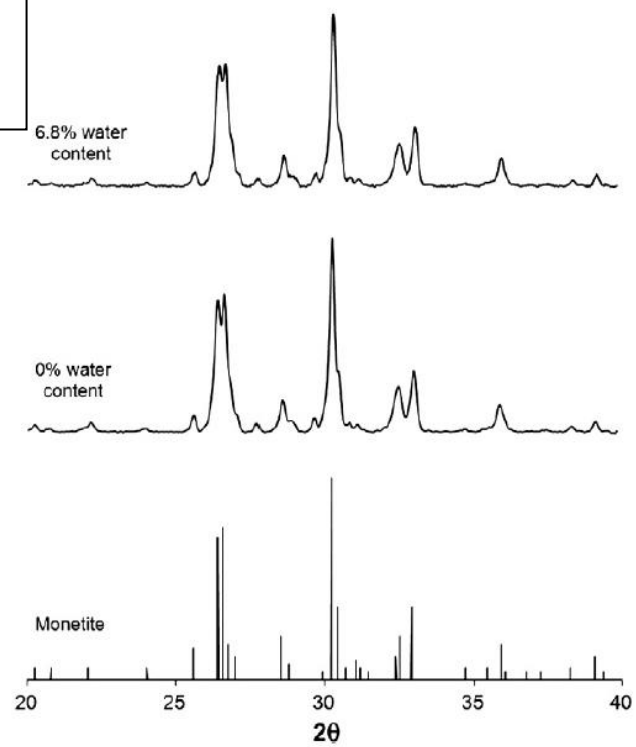
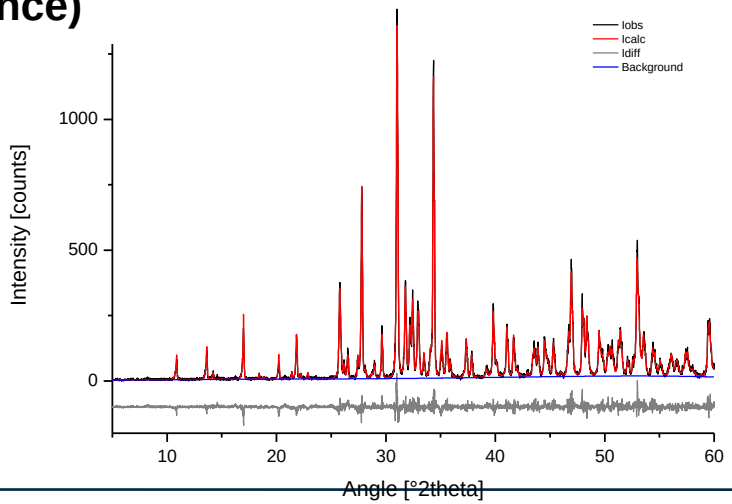


Fig. 6. XRD of cements containing 0 and 6.8 wt.% water after setting. Monetite reference pattern from PDF #00-009-0080.

«Materials and Methods» Section

Used for phase quantification

- Detailed intrument parameters:
  - Instrument / manufacturer
  - Scan range (start, end, step size [°2θ])
  - **Radiation, filter / monochromator, divergence slit**
- References to **sources of crystal structures**
- **Rietveld software (program name, version, reference)**



«Materials and Methods» Section

Acta Biomaterialia 10 (2014) 3922–3930

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Growth kinetics of hexagonal sub-micrometric β-tricalcium phosphate particles in ethylene glycol ☆

Laetitia Galea [a,b], Marc Bohner [a,*], Juerg Thuering [a,c], Nicola Doebelin [a], Terry A. Ring [d], Christos G. Aneziris [b], Thomas Graule [b,e]

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[b] Technical University Bergakademie Freiberg, Institute for Ceramic, Glass- and Construction Materials, Agricolastraße 17, 09596 Freiberg, Germany
[c] ETH Zürich, Department of Materials, Laboratory of Multifunctional Materials, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland
[d] University of Utah, Chemical Engineering, 50 South Central Campus Drive, Salt Lake City, UT 84112-9203, USA
[e] EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, 8600 D

The crystalline composition was analyzed by XRD measurements. For this, a concentrated ethanol suspension was dried on a glass plate, scratched off and spread on a silicon single crystal sample holder to minimize preferred orientation. XRD data were collected in reflective geometry on an X-Pert diffractometer (X'Pert Pro MPD, Panalytical, Almelo, The Netherlands). Ni-filtered Cu K_α radiation and a step size of 0.016° were used to measure from 4.01° to 59.99° 2θ. Due to the limited amount of sample material available, sample transparency, texture and variable irradiated volume limited the quality of the diffraction patterns. Therefore only semi-quantitative phase analyses could be done by Rietveld refinement using the FullProf.2k software (version 5.00) [23] and a previously determined instrument resolution function. Crystalline models for β-TCP, monetite (DCP) and chloroapatite (Cl-HA) were taken from Schroeder et al. [24], Dickens et al. [25] and Hughes et al. [26].

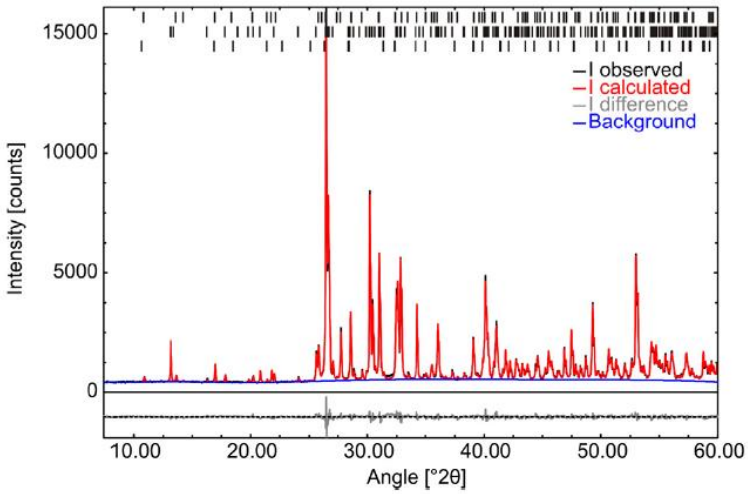

Fig. 3. Representative XRD diffractogram of particles synthesized at 90 °C, 16 mM for 24 h showing the presence of highly crystalline β-TCP and DCP phases. Observed, calculated, differences and background intensities are displayed, as well as the hkl line positions for β-TCP (top), DCP (middle) and Cl-Ap (bottom).

«Materials and Methods» Section

Used for advanced refinements
(structural parameters, amorphous fractions, crystallite size analysis, texture analysis etc.)

- Detailed intrument parameters:
  - Instrument / manufacturer
  - Scan range (start, end, step size [°2θ])
  - Radiation, filter / monochromator, divergence slit
  - **… (detector, masks, ASS, Soller slits, generator settings…)**
- References to sources of crystal structures
- Rietveld software (program name, version, reference)
- **Refinement strategy**
- **Any non-standard calculations, sample preparations, measurement conditions, etc…**

«Materials and Methods» Section

journal

J. Am. Ceram. Soc., **92** [7] 1592–1595 (2009)
DOI: 10.1111/j.1551-2916.2009.03093.x
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Synthesis and Structure Refinement of Zinc-Doped β-Tricalcium Phosphate Powders

Sanjeevi Kannan,[‡] Friedlinde Goetz-Neunhoeffer,[§] Jürgen Neubauer,[§] and Jose M.F. Ferreira[†,‡]

(2) Structure Refinement

For refinement studies, all the powders were heat treated in a Thermolab furnace (Pt30%Rh/Pt6%Rh-thermocouple) with a heating rate of 5°/min to achieve a predetermined temperature of 1000°C, followed by a dwelling time of 2 h, and then cooled to room temperature at the rate of 5°/min. Although low crystalline β-$Ca_3(PO_4)_2$ forms at about 800°C,[21,22] a higher heat treatment temperature of 1000°C was required to obtain the desired well-crystallized phase for Rietveld refinement. Collection of X-ray powder diffraction (XRPD) pattern data was performed with a Siemens D5000 (Karlsruhe, Germany) equipped with a diffracted beam graphite monochromator. The software TOPAS 3 (Bruker AXS, Karlsruhe, Germany) with the fundamental parameters approach was used for Rietveld refinements. All powders were prepared and measured three times independently. Rietveld refinement was performed using the structural model of ICSD card number of # 6191[23] for β-TCP. Refined parameters were scale factor, specimen displacement, background as Chebyshev polynomial of fifth grade, crystallite size, microstrain, lattice parameters, and occupancy factors. As the scattering factor for P^{5+} is not implemented in the TOPAS 3 Rietveld software, the P sites were refined with a combination of Si^{4+} and P for pure β-$Ca_3(PO_4)_2$ phase. This leads to an improved refinement of Ca^{2+} occupancy and of the zinc substitution at Ca^{2+} sites. Zinc content in the heat-treated powders was analyzed by the ICP technique.

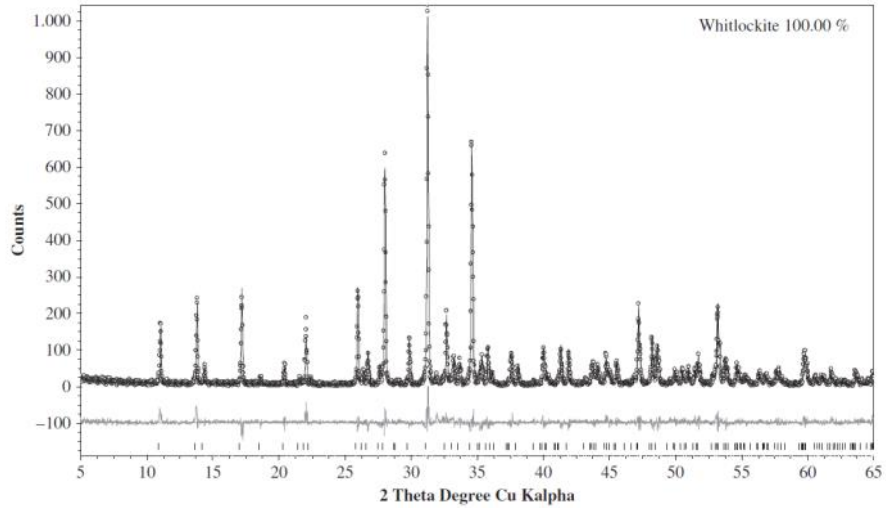

Fig. 1. Rietveld analysis pattern of powder diffraction data of Zn–TCP1 (2.43 mol% zinc). The solid lines are calculated intensities and the marked ones are observed intensities. The difference between the observed and calculated intensities is plotted below the profile.

Refinement strategy

«Materials and Methods» Section

journal

J. Am. Ceram. Soc., 93 [10] 3455–3463 (2010)
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© 2010 The American Ceramic Society

Thermal Treatment of Flame-Synthesized Amorphous Tricalcium Phosphate Nanoparticles

Nicola Döbelin,[†,‡] Tobias J. Brunner,[§,††] Wendelin J. Stark,[§] Martin Fisch,[¶] Egle Conforto,[‖] and Marc Bohner[‡]

In situ XRD data sets were collected using a powder diffractometer (X'Pert Pro MPD, Panalytical, Almelo, the Netherlands) in θ/θ configuration using Ni-filtered Cu*K*α radiation and a fixed divergence slit of 1/8° opening. A heating chamber (HTK-1200, Anton Paar, Ostfildern, Germany) was attached to the goniometer. The samples were prepared in a ceramic sample holder spinning at approximately 1 rps. Data sets were collected from 9°–65° 2θ with a step size of 0.016° 2θ and a counting time of 1 s per step at the following temperatures: 25°, 500°, 525°, 550°, 575°, 600°, 650°, 700°, 750°, 800°, 850°, 900°, 950°, 1000°C, and again at 25°C. The heating rate was set to 1°C/min for all heating sequences, which was slow enough to prevent overshooting within the accuracy of the furnace control unit (±1°C). During data collection, the temperature was held constant, and for the last data acquisition the sample was cooled from 1000° to 25°C at 60°C/min.

XRD patterns were analyzed by Rietveld refinement using the software FullProf.2k.[36] Starting models for the crystal structures were taken from Mathew *et al.*[37] for α-TCP, Dickens *et al.*[38] for β-TCP, and Sudarsanan and Young[39] for hydroxyapatite (HA). No additional crystalline phases were observed in the diffraction patterns. The refinements were performed in three steps, starting with vertical sample displacement, scale factors for all phases, and sampled background points with linear interpolation until convergence was reached. In the second step, the cell parameters of all phases were released for refinement, and in the last step isotropic peak broadening of all phases and one common overall isotropic displacement parameter ($B_{overall}$) were optimized. The instrument resolution function and peak asymmetry were determined with an "NIST SRM 660a—Line Profile LaB_6" standard before the refinements of the sample data sets. Peak shapes were modeled with a pseudo-Voigt function accounting for peak asymmetry due to axial divergence.[40] Average crystallite sizes were calculated from isotropic Gaussian peak broadening using the Scherrer equation.

The most common method to determine X-ray amorphous fractions in a specimen is to add a known quantity of a crystalline internal standard. However, at temperatures up to 1000°C, solid-state reactions of the specimen with the standard powder are to be expected. Relative weight fractions W_P of the crystalline phase P, on the other hand, can be calculated from refined parameters and chemical information of all phases as follows[41]:

$$W_P = \frac{S_P(ZMV)_P}{\sum_i S_i(ZMV)_i} \quad (1)$$

where S is the Rietveld scale factor, Z the number of formula units per unit cell, M the molecular mass of the formula unit, V the unit cell volume, and i iterates over all crystalline phases. The absolute mass m_P of each crystalline component in the specimen is proportional to

$$m_P \propto S_P(ZMV)_P \quad (2)$$

By making the reasonable assumptions that (i) the intensity of the primary beam and the device configuration were identical for all data sets, (ii) the total amount of powder in the specimen remained constant during the experiment, and (iii) all phases involved, including the amorphous powder, have similar particle sizes and absorption coefficients, the dependency of S_P could be reduced to the phase abundance and the overall atomic displacement parameter. The latter, as well as the unit cell volume, are temperature dependent. The value m_P calculated from Eq. (2) for a constant amount of a phase P will thus show a slight linear decrease with the increasing temperature.

In order to determine the amount of X-ray amorphous material in the specimen, a 100% crystalline reference was needed. As the sum of m_P values of all crystalline phases remained constant between 800° and 1000°C, except for a steady decrease caused by the temperature-dependent parameters, it was assumed that all amorphous material was crystallized below 800°C. A linear regression through the sums of m_P values between 800° and 1000°C thus served as references for 100% crystallinity for the calculation of absolute phase quantities.

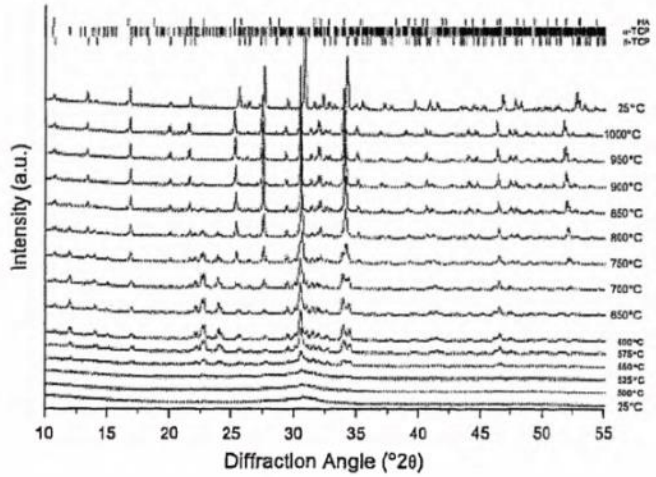

Fig. 1. *In situ* X-ray diffraction patterns and theoretical peak positions for α-tricalcium phosphate (TCP), β-TCP, and hydroxyapatite (HA). Just after crystallization, the main phase was α-TCP, followed by a gradual transformation to β-TCP. The peak shift of the top pattern was caused by the thermal contraction of the unit cell when cooled from 1000°C to room temperature.

Special calculations

Summary: DOs and DON'Ts in Manuscripts

Do:

- Show your raw data (stacked plots)
- Show one full refinement
- Give details according to the relevance of XRD data for the manuscript

Don't:

- Spam the manuscript with refinement plots
- **Publish results from non-standard samples**
- **Publish results from poor refinements!!!**